Artists´ Pigments

A Handbook of Their History and Characteristics

VOLUME 3

ELISABETH WEST FITZHUGH, Editor

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Elisabeth West FitzHugh, Editor

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Note to the Reader

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Publisher's Note

As a result of demand, this volume of *Artists' Pigments* is reissued without modification in the form first published in 1997. For later developments and research in the field, the reader is advised to consult the newer literature on the subject.

Editor's Note

Perhaps the most notable changes in pigment research in recent years have been in the analytical methods used. Today, for example, surface-enhanced Raman spectroscopy can be effectively applied to an extremely small sample of an organic pigment. Pigments can now be characterized in situ on a painting by such methods as fiber optics reflectance spectroscopy.

Considerable additional research has been carried out on some of the pigments in this book and on their dates of use. Significant work has identified many more synthetic arsenic sulfide minerals than were mentioned in the original chapter. In addition, many pigments have been newly identified. For a comprehensive source, which also supplies well-illustrated information on polarized light microscopy of the significant pigments, see:

Nicholas Easthaugh, Valentine Walsh, Tracey Chaplin, and Ruth Siddall, *Pigment Compendium: A Dictionary of Historical Pigments* (Taylor and Francis, 2008).

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Preface

The National Gallery of Art is delighted to present the third volume in the series *Artists' Pigments: A Handbook of Their History and Characteristics*. This project originated with the late Rutherford J. Gettens, formerly of the Freer Gallery of Art, who envisioned the compilation of a comprehensive, scholarly guide to artists' pigments and related materials more than thirty-five years ago. The series now comprises volume 1, edited by Robert L. Feller, and volume 2, edited by Ashok Roy, as well as this latest installment expertly edited by Elisabeth West FitzHugh, research associate in the Department of Conservation and Scientific Research at the Freer Gallery of Art and Arthur M. Sackler Gallery of Art, and Gettens' colleague for many years. The project continues under the guidance of the National Gallery of Art's chief of conservation, Ross M. Merrill, who, with Barbara Berrie, senior conservation scientist, is currently overseeing production of a fourth volume.

Volume 3 includes ten additional pigments from some of the earliest, such as Egyptian blue and gamboge, to later, man-made colorants such as Prussian blue and the present century's titanium dioxide whites. With these latest additions, the series now covers forty "traditional" pigments; the two remaining will be included in volume 4. Also offered for the reader's benefit are more than 200 images including works of art that were created with the pigments described, as well as x-ray diffraction patterns, scanning electron micrographs, and thin-layer chromatographs. The present volume, like its predecessors, marks the culmination of considerable research and analysis by conservators and conservation scientists, and represents the Gallery's commitment to sharing knowledge assembled by these researchers from all over the world. I wish to express my grati-

tude for their labors and the efforts of the Gallery's Conservation Division.

Our thanks also to the Andrew W. Mellon Foundation and the Publications Fund of the National Gallery of Art for their continuing support of this series.

EARL A. POWELL III
Director

Foreword

The origin of this series of books on artists' pigments can be traced to the 1942 publication *Painting Materials: A Short Encyclopaedia* by Rutherford J. Gettens and George L. Stout. At that time, Gettens and Stout envisioned a series of books addressing the various components of paintings: film-forming media, pigments, solvents, supports, and tools.

In 1958, Gettens presented a paper, "The Identification of Pigments and Inerts in Paintings and Other Museum Objects," at a seminar on the *Application of Science for the Examination of Works of Art* at the Museum of Fine Arts in Boston. In that paper, he outlined a proposal for a handbook on the identification of materials for chemists, conservators, curators, and collectors.

At the 1961 Rome conference of the International Institute for Conservation of Historic and Artistic Works (IIC), Gettens presented a formalized "Proposal for a Handbook on Analysis of Materials of Paintings," which was published in 1963 in the conference proceedings, *Recent Advances in Conservation*. At that time, Gettens established the format for data comprising each chapter that is now used in the *Artists' Pigments* series. In the Rome presentation, citing his 1958 paper, he said, "In making this proposal it was fully realized that the creation of such a handbook would be a large undertaking; much too large for any single person to embark upon unless he had a lifetime ahead of him or a corps of assistants to help with the job." He went on to suggest that the preparation of the handbook should be a cooperative venture among several laboratories. He noted that his proposal met with strong support in America. Gettens also related that Norman Brommelle, then secretary general of the IIC, suggested that the handbook be sponsored by the IIC and "Miss Joyce Plesters of the National Gallery expressed interest and she

was gradually drawn into the project as a collaborator." The first nine monographs on pigments appeared from 1966 to 1974 in the IIC journal *Studies in Conservation* and later were republished in a revised and updated form in volume 2 of *Artists' Pigments*, edited by Ashok Roy of the National Gallery, London.

Following the publication of the monograph series in *Studies*, Gettens asked the National Gallery of Art to aid in the effort to publish his proposed *Handbook*, and, as a result, the ten chapters in volume 1 of *Artists' Pigments*, edited by Robert L. Feller, who served as the scientific advisor to the National Gallery of Art, was released in 1986. Plans are underway to reprint volumes 1 and 2.

In keeping with Gettens' vision, this *Artists' Pigments* handbook series has become an important resource for information used for identifying pigments and placing them in their historical context and use.

Volumes 1 through 3 of *Artists' Pigments* include all of the major "traditional" pigments, with the exception of the iron oxide and carbon black pigments, which will be discussed in volume 4. The twenty-nine chapters in the first three volumes cover more than 40 pigments and span the history of art from one of the earliest known pigments—Egyptian blue—to the modern titanium dioxide whites. Research and writing for volume 4 is underway and a volume editor and authors have been engaged for organic brown, the earth pigments, cobalt and cerulean blue, Hansa yellow, and carbon-based black pigments.

No undertaking as ambitious as this series would be possible without the editors and authors who applied their expertise, patience, and energy to making this book a reality. Sincere gratitude goes to each author for their patience and cooperation. To them, our field owes a large debt of appreciation. The editor of this volume, Elisabeth West FitzHugh, research associate at the Department of Conservation and Scientific Research, Freer Gallery of Art and Arthur M. Sackler Gallery of Art, worked with Gettens for more than 18 years. Her astute oversight and quiet efficiency have been critical to the evolution of this volume.

This publication is the result of a myriad of components, assembled through the assistance of many people, and, although the list is too extensive to give individual names, I would like to express my thanks to those who provided information to the conservators and scientists whose research is found here. Our knowledge of artists' pigments is ever-changing and it is not possible to cover every aspect of the pigments discussed here, although every possible effort has been made to be thorough.

Upon Gettens' appeal, J. Carter Brown, director emeritus, National Gallery of Art, initiated the Gallery's participation in this project by providing the resources to pursue Gettens' vision. Brown's successor, Earl A. Powell III, recognizing the significance to the field, has made the continuation of this endeavor possible through his enthusiasm and support. Two of the Gallery's staff have been critical to this series, Frances Smyth, editor-in-chief and Janice Gruver, editor for the Conservation Division. Mrs. Gruver has patiently overseen the many details necessary to produce a cohesive publication.

This volume has been made possible by support from the Andrew W. Mellon Foundation and the Publication Fund of the National Gallery of Art.

ROSS M. MERRILL
Chief of Conservation
National Gallery of Art

Introduction

The purpose of this volume is to continue the discussion of important artists' pigments that began with volumes 1 and 2, and to provide basic known information about ten pigments. Every chapter is intended to be self-contained and is essentially a review article; in some cases important new material has been introduced. The chapters are arranged to be accessible to readers with diverse backgrounds; some readers will find certain sections of each chapter of more interest than others. For example, the art historian or museum curator will be drawn to the sections on terminology and history of use, while the scientist may be more interested in the analytical methods that can be or have been used to study or identify a particular pigment. The artist is likely to be most concerned with the information about pigment properties and compatibility. The conservator or conservation scientist can find facts of use or significance throughout each chapter. It is my hope, however, that readers will be drawn into sections with which they are not readily familiar and will be able to not only learn more about other aspects of the colorant in question but gain an understanding of other approaches to pigment investigation.

For the editor it was a difficult task to decide what to omit, what to expand, and what to condense in order to satisfy a wide variety in the potential readership. Therefore my intention was to make the information presented here appropriately balanced. In this respect, if the specialist finds insufficient detail on a particular topic, references can be found in each chapter that will lead to further sources. Gaps still exist in our knowledge about all of these pigments and these chapters should offer a solid basis for further research. For example, the information presently known about the pigment Scheele's green is summarized here, but much remains to be learned.

In our attempt to reach readers with varied backgrounds we have tried to create bridges between the humanist and the scientist. One example is our presentation of x-ray diffraction information that includes photographs of x-ray diffraction powder patterns. A crystallographer or mineralogist would commonly publish a table of intensities and *d*-spacings, rather than a picture of the pattern. Both are included here to allow the nonscientist to visualize the difference between the data from analysis of different materials. Appropriately, Rutherford J. Gettens, who initiated this series and pioneered in the application of x-ray diffraction to the fields of conservation and the history of technology, was the first to use this method of illustrating x-ray diffraction data in the conservation literature.

The lists of occurrences that accompany some of these chapters require a word of explanation. When the first pigment article appeared in 1966 in *Studies in Conservation* there were relatively few published pigment identifications; therefore the lists in volumes 1 and 2 were given the heading "Notable Occurrences." Since then, the number of known occurrences has burgeoned. Most occurrences noted here are drawn from published sources and some were supplied to authors by particular laboratories. Many other unpublished analyses of pigments undertaken in museum laboratories worldwide are not included here as it was beyond the scope of this project to carry out such an extensive survey; to do so may prove to be a worthwhile investigation for another venue. Because our listings are not exhaustive it seems more reasonable to cite them simply as "Occurrences," rather than venturing to make judgments on their importance. The reader will find few identifications here of the organic colorants indigo, madder, and gamboge because until relatively recently the analytical methods for organic materials such as these were not easily applicable to tiny samples. Few occurrences are noted for Vandyke brown because of the uncertain identity of the pigment; the clarification here of the nature of this complex mixture of organic substances should make future identification easier for the analyst.

Another difference in terminology from the first two volumes is in the section previously called "Criteria for Positive Identification" or "Certain Identification." This section is now titled "Criteria for Identification." Here the authors note the ideal identification method or combination of methods and also explain limitations of other procedures. Any researcher who has worked with the small pigment samples usually available from works of artistic and cultural importance will be aware that the use of the ideal method is often simply not possible and that any limitations

must be noted when the results are reported. It is hoped that the possible choices have been clearly established for the reader.

The pigments are discussed in approximate chronological order, based on the date they were first used, beginning in the fourth millennium B.C. when Egyptian blue was recorded as the first synthetic inorganic pigment. The naturally occurring yellow mineral orpiment was also used early and then later was introduced in its synthetic form. Indigo and madder, organic colorants that are also important dyestuffs, were first known in ancient Egypt as dyes from plants and are still in use today as both dyes and pigments in their synthetic forms. Gamboge, an organic colorant from tree resin, originated in east Asia in the eighth century and is also still in use. Vandyke brown was first employed in the late sixteenth century and remains an artist's pigment. Man-made colorants include Prussian blue, which was discovered in the early eighteenth century, and emerald green and the chromium green oxides, which were first made in the nineteenth century. The final chapter discusses the twentieth-century synthetic titanium dioxide whites.

The information in this book reflects the striking variety of sources of coloring materials used throughout history and serves as a testimony to the ingenuity and imagination of the artists, craftspeople, and scientists who discovered, developed, and refined these pigments.

Acknowledgments

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1
Egyptian Blue

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1.0 Introduction

1.1 Pigment Definition

Egyptian blue is a calcium copper silicate that is made by heating together to approximately 850°C a calcium compound (such as powdered limestone), a copper compound (such as malachite), and silica (usually in the form of quartz sand). It is listed in the *Colour Index* (1971) as Pigment Blue 31, no. 77437. It was the first synthetic pigment. In antiquity Egyptian blue was the most extensively used blue pigment from the early dynasties in Egypt until the end of the Roman period in Europe. It was used on materials such as stone, plaster, pottery, wood, papyrus, on canvas, and on wall paintings. Figure 1 shows its use on an Egyptian wall painting. With a few exceptions, Egyptian blue is used mostly as a pigment, but it is also used to form objects (fig. 2). It is sometimes confused with Egyptian faience, a special type of surface glaze, which is quite a different material. (For example, see Wulff et al., 1968; Vandiver, 1982; Lavenex Vergès, 1992.)

1.2 Current Terminology

English: Egyptian blue
French: bleu Egyptien
German: Ägyptisch Blau
Italian: blu egiziano

2.0 History

2.1 Archaic and Historical Names

Other names for Egyptian blue include blue frit, copper frit, Pompeian blue, Vestorian blue, Alexandrian blue, Pozzuoli blue, *bleu fritte*, *bleu d'Alexandrie*, *bleu de Pompéi*, *bleu de Pouzzoles*, *azzuro egiziano*, and *Frittenblau*. The Latin word *caeruleum* could mean Egyptian blue, but it could sometimes refer only to a blue pigment. The same is true of the Greek word *kyanos*.

2.2 History of Use

2.2.1 ***Ancient Egypt and West Asia.*** The invention of the manufacturing process of Egyptian blue during the first dynasties of ancient Egypt, beginning about 3100 B.C., was a consequence of other known technical processes used since pre-dynastic periods in Egypt and West Asia.

Egyptian blue is manufactured by fusing sand and other materials together with copper compounds used as coloring agents. A similar process also occurs naturally when copper ores are melted and bluish materials are formed as slag, or intentionally when blue glazes are prepared to decorate objects of stone or pottery. Forbes (1955) suggested that this blue frit was first used as a glaze and later in powdered form as a pigment. Thus, blue siliceous materials were familiar to early cultures long before the pigment Egyptian blue was intentionally manufactured.

The earliest examples of the use of Egyptian blue are from the Fourth Dynasty (c. 2613–2494 B.C.). The pigment occurs on a sarcophagus in the Egyptian Museum, Cairo, and on painted limestone sculptures (see Occurrences). The best-known examples are the sculptures of Rahotep in the Egyptian Museum, Cairo, and the *Beer Brewing Wife* in the Museo Archeologico, Florence.

Beginning in the Fifth Dynasty (c. 2494–2345 B.C.) there are numerous objects painted with Egyptian blue; thereafter this pigment was the blue paint used almost exclusively on both inor-

Fig. 1 Wall painting with Egyptian blue, probably from tomb of Nebamun, Eighteenth Dynasty (c. 1567–1320 B.C.), Thebes, 97 x 83 cm, *Hunting Birds in a Papyrus Thicket*, British Museum no. 37977.

ganic and organic materials. Early examples of use in the Fifth Dynasty include the deeply etched hieroglyphs on the reliefs in the pyramid of Unas at Saqqara, which are filled with solid masses of Egyptian blue, indicating that in this period there must already have been extensive manufacture of the pigment. Other examples of this are numerous reliefs as well as limestone sculptures decorated with Egyptian blue in the tombs of Saqqara.

An extension of Egyptian blue's use during the Middle Kingdom (c. 2133–1786 B.C.) can be observed especially in the decoration of tombs in wall paintings executed in enormous dimensions and furnishings of painted wooden objects and statuettes.

Egyptian blue was rarely used on pottery; it was found, however, on pottery vases from the Saff el-Dawaba tomb of the Eleventh Dynasty at el-Târif in western Thebes (Arnold, 1972). The vases are painted with bright colors on a white ground after firing. This technique is quite different from the vases of the Eighteenth Dynasty that were painted with cobalt blue, which was applied as a mixture of a clay and a cobalt compound before firing (Riederer, 1974). Egyptian blue has been identified on a Twelfth Dynasty (c. 1991–1786 B.C.) alabaster jar (Miller, 1986).

Egyptian blue's wide use on painted objects continued during the New Kingdom (c. 1567–1085 B.C.) when large necropolises were built and extensively decorated; these include the Valley of the Kings, the Valley of the Queens, and the tombs of Deir el-Bahri, all close to Thebes in Middle Egypt. The pigment was identified on a wooden coffin (Young & Whitmore, 1968), on the thirteenth-century B.C. wall paintings in the tomb of Nefertari (Stulik et al., 1993), and on the fourteenth-century B.C. bust of Nefertiti from Tell el-Amarna (Wiedemann & Bayer, 1982).

This extensive production of painted objects continued through the Late Dynastic Period (c. 1085–343 B.C.); many painted sarcophagi and

masks of mummies have been preserved in addition to wall paintings and painted architectural decoration.

During the Greek (332–30 B.C.) and Roman (30 B.C.–A.D. 395) periods in Egypt, the extensive production of decorative objects decreased, but when a blue pigment was used, that pigment was Egyptian blue.

Despite the abundance of written documents on papyrus preserved from ancient Egypt, there is no written information from Egyptian sources on the manufacture, trade, or use of Egyptian blue.

Even less is known from written sources about Egyptian blue's use in ancient Mesopotamia and Persia, compared to Egypt, although we know from many excavation reports that this pigment was used extensively in West Asia.

Granger (1933) published an analysis of an Egyptian blue sample from the Assyrian palace at Til Barsip, the late-Assyrian (1000–612 B.C.) city. Matson (1957) studied pigment samples and objects made of Egyptian blue from Persepolis, the Achaemenid Persian city, which flourished from 520 to 330 B.C. He described the microscopic properties in detail and discussed the possible technique of manufacture, referring to Assyrian formulas on glassmaking preserved on cuneiform tablets. Chase (1971) carried out research on Egyptian blue when he analyzed two ninth-century B.C. objects from Hasanlu, Iran, made of this material. Dayton (1978) mentioned that many beads and small objects found in the Near East were made of Egyptian blue, including an object in the shape of an oxhide ingot from the Assyrian city of Nimrud in Iraq. Copper ingots in the stylized shape of an ox skin, used in the Bronze Age by Syrian traders, were found in underwater shipwrecks and shown in fourteenth- to thirteenth-century B.C. Egyptian tomb paintings.

Stodulski et al. (1984) studied pigments from the Persian sites of Persepolis and Pasargadae (sixth–fifth centuries B.C.). Nineteen samples of a blue pigment from reliefs and pottery bowls found in different areas of the Persepolis terrace proved to be Egyptian blue. In two cases azurite was found.

2.2.2 ***India, Central and East Asia.*** In India and central Asia, where the earliest wall paintings date from the first centuries B.C., Egyptian blue has not been found in the pigments analyzed from these historical sites. Only natural ultramarine, azurite, and indigo were identified, suggesting that these pigments were available in sufficient quantities to make it unnecessary to produce or import Egyptian blue (Riederer, 1977a).

Fig. 2 Object made of Egyptian blue, New Kingdom (c. 1567–1085 B.C.), height 8 cm, vessel for ointment in the shape of Bes, Ägyptisches Museum, Berlin, inv. no. 17882.

Egyptian blue has never been reported from East Asia. FitzHugh and Zycherman (1983, 1992) describe a purple barium copper silicate, Han purple ($BaCuSi_2O_6$), and a blue barium copper silicate, Han blue ($BaCuSi_4O_{10}$), from China. Han blue is an analogue of Egyptian blue with similar microscopic appearance. These pigments occur as paint on ceramic and metal objects from the Han dynasty (208 B.C.–A.D. 220) and as a component in octagonal sticks from the Warring States period (475–221 B.C.) or the Han dynasty.

2.2.3 ***Greece.*** There was extensive use of Egyptian blue in ancient Greece. The applications in Crete are dated so early that it must be assumed, following its invention, that it was immediately introduced from Egypt to Crete and other Greek islands. It has been identified in numerous locations on wall paintings and facades.

A very early occurrence on the island of Keros was mentioned by Filippakis et al. (1976). The

sample they analyzed (dated to 2500 B.C.) was provided by the Archaeological Museum of Naxos. At Knossos there is evidence that Egyptian blue was in use before 2100 B.C. (Evans, 1910; Heaton, 1910; Eibner, 1926). At this early period Egyptian blue was used for wall paintings at Knossos either alone or mixed with the minerals glaucophane (a gray-to-blue sodium magnesium aluminum silicate) or riebeckite (a dark blue-to-black iron-containing variety of glaucophane) (Filippakis et al., 1976; Cameron et al., 1977). At Thera (ancient Santorini) the same mixture was used earlier than 1500 B.C. (Filippakis et al., 1976; Profi et al., 1977).

From the Mycenaean period (dating from the thirteenth century B.C.) Egyptian blue is found in the House of Idols and the Temple of Mycenae (Profi et al., 1974). Samples of unused Egyptian blue from Mycenae from Heinrich Schliemann's excavations in 1876 are stored in the Greek National Archaeological Museum. Egyptian blue from Tiryns is mentioned by Eibner (1926); Duell and Gettens (1942) also identified Egyptian blue from Tiryns, as well as from Phaistos and Mycenae. It was found on wall paintings from the period between 1400 and 1100 B.C. at the Palace of Nestor at Pylos (Filippakis et al., 1976).

At Pella, Macedonia, Egyptian blue was used on wall paintings in a house of the first Pompeian style (Calamiotou et al., 1983). The paintings are dated 400 to 168 B.C., when Pella was the capital of Macedonia.

Egyptian blue was identified on the facades of the earlier temple of Aphaia at Aegina (sixth century B.C.) where it was used for larger areas; the small details of the facades were painted with azurite (Riederer, 1985).

In Greece, Egyptian blue was used mostly for wall paintings and facades; there are only a few occurrences on pottery. For the decoration of the Tanagra figurines of ancient Greece, Egyptian blue was used together with a variety of other pigments. Noll et al. (1974, 1975b) mentioned it on Attic *lekythoi* and the author found it on Greek painted vases from Centuripe, Sicily, dating from the second century B.C. (Riederer, 1976). Higgins (1970) noted its use on Greek terra-cotta figurines in the British Museum from the period between 540 B.C. and the third century B.C. and Caley (1946) identified it on classical period (no precise date given) terra-cotta objects from the Agora in Athens.

Preusser et al. (1981) analyzed the pigments from Greek gravestones from Demetrias, close to Volos in central Greece, dating from the third and the first century B.C. Egyptian blue was the only blue pigment used on the gravestones.

From these examples, it is known that Egyptian blue was an important blue pigment in Greece used from the first half of the third millennium B.C. until the Roman period.

In ancient Greek literature, only Theophrastus (371–287 B.C.) mentioned a blue pigment, which could be Egyptian blue (Caley & Richards, 1956). In *De lapidibus* he wrote of trade of an artificial blue pigment from Egypt. This may indicate that Egyptian blue was produced until this relatively late period in Egypt and brought by trade to Greece. Theophrastus used the word *kyanos* to refer to this blue and also to other blues from Cyprus and Scythia, which were probably azurite and lapis lazuli, respectively.

2.2.4 ***Roman sites and Italy.*** Egyptian blue was used in Italy by the Etruscans, whose civilization reached its height in the sixth century B.C. There are many occurrences in wall paintings found in tombs (Duell & Gettens, 1940).

There is extensive information on Egyptian blue used during the Roman period based on finds of unused pigment, wall paintings, and detailed descriptions in Roman literature.

Scientific investigations have been aided by the finding of many samples of unused Egyptian blue at Roman sites. Augusti (1967a, b) reported large quantities found in color shops at Pompeii, which was destroyed in A.D. 79. In addition, there are numerous finds of unused Egyptian blue in Roman tombs of painters. The best-known examples are the tombs of St. Médard-des-Prés in France, from which Chevreul (1850) analyzed the pigments, and of Herne-St. Hubert in Belgium, from which samples were analyzed and published in Huybrigts' report (1902). At St. Médard-des-Prés approximately eighty samples of pigments were found in bronze and wooden boxes together with various painting tools. At Herne-St. Hubert, more than one hundred cubes and some larger cakes of pigments were recovered, again with various tools. Comparable finds of a smaller extent were also published (Bachmann & Czysz, 1977; Bachmann & Von Pfeffer, 1979/1980). Balls of the pigment were found in excavations in Hungary at a villa at Baláca in the Roman province of Pannonia (Járó & Kriston, 1987). At the second-century A.D. site of Carnuntum/Petronell in lower Austria it was also found as dry material as well

as on wall paintings (Nauer & Kny, 1978). It is evident that Egyptian blue was a common pigment in the Roman painter's palette.

There have also been numerous examinations of wall paintings from all parts of the Roman Empire that reveal the wide use of this pigment (Giovanoli, 1966/1967, 1968a, b, 1969; Lazzarini, 1978; Biek, 1981). Many Roman wall paintings in Germany have been systematically studied at the Rathgen-Forschungslabor, Berlin; no blue pigment other than Egyptian blue has been found.

An unusual occurrence of Egyptian blue in a painting on canvas from the third/fourth century A.D. is given in Sack et al. (1981). Although the painting was purchased in Cairo, it was originally from Akhmim. Egyptian blue was used extensively for decorations in the painting's background, indigo was identified in minor quantities, and a few particles of ultramarine were found.

There is extensive information on Egyptian blue in Roman literature. Vitruvius, in the first century B.C., gave the most detailed information about its production although he neglected to mention lime, or any source of calcium, an essential ingredient (Morgan, 1926):

> Methods of making blue were first discovered in Alexandria, and afterwards Vestorius set up the making of it at Puzzuoli. The method of obtaining it from the substances of which it has been found to consist, is strange enough. Sand and the flowers of natron are brayed together so finely that the product is like meal, and copper is grated by means of coarse files over the mixture, like sawdust, to form a conglomerate. Then it is made into balls by rolling it in the hands and thus bound together for drying. The dry balls are put in an earthen jar, and the jars in an oven. As soon as the copper and the sand grow hot and unite under the intensity of the fire, they mutually receive each other's sweat, relinquishing their peculiar qualities, and having lost their properties through the intensity of the fire, they are reduced to a blue color.

No additional information was contributed by Pliny the Elder and Strabo, the Greek geographer.

2.3 **Dates of Use**

Egyptian blue was used in Egypt, Mesopotamia, and Greece from the third millennium B.C. to the Roman period and it was used in Italy and central Europe until the Middle Ages as the almost exclusively used blue pigment. Azurite, ultramarine, indigo, or rare pigments such as cobalt blue in Egypt or glaucophane on the Greek islands were less frequently used.

After the Roman period, Egyptian blue was used rarely. Isidore of Sevilla (A.D. 636) was the last writer to mention it, as *Venetum caeruleum* (Spurrell, 1895). There are a few occurrences of Egyptian blue on wall paintings from the early Middle Ages; one is mentioned by Raehlmann (1913/1914), who had investigated it on Egyptian and Roman objects. He wrote, "The latest place, where I found the old blue frit, when examining the blue and green areas of the walls, was the chorus of the old Basilica Santa Maria antiqua on the Forum Romanum, dating from the fifth and sixth century A.D. and dedicated to the Greek religion."

Lazzarini (1982) found Egyptian blue on a fresco in the lower church of San Clemente, Rome, which dates to the ninth century A.D.; the fresco was probably made during the time of Pope Leo IV (847–855). Somewhat earlier in the ninth century A.D. there is an occurrence on the Carolingian wall paintings in a convent in Müstair, Switzerland (Mairinger & Schreiner, 1986).

Orna et al. (1980), in a study of the early technical literature of the Middle Ages from the ninth to the sixteenth century, found no written evidence that Egyptian blue was produced after the Roman period.

3.0 **General Pigment Properties**

3.1 **Color**

The color of Egyptian blue varies considerably, depending on its composition, process of manufacture, and grain size (fig. 3). All intensities,

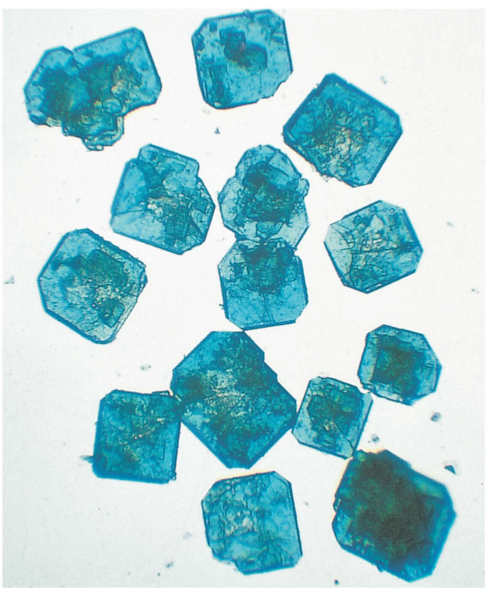

Fig. 3 Sample of synthetic Egyptian blue. From Bayer and Wiedemann (1976b). 1,870x.

from a dark blue to a whitish blue, can be observed, with a lighter color resulting when the grain size is reduced by grinding. Temperatures above 850°C up to 1,000°C during manufacture produce greenish to grayish varieties.

The visible absorption spectrum of Egyptian blue was reported (Ludi & Giovanoli, 1967), and the effect of substituting nickel or germanium for copper or silicon, respectively, on the structure and color of Egyptian blue was investigated (Hassanein, 1969).

Spurrell (1895) wrote that Egyptian blue with a violet tone can be produced and Forbes (1955) noted that the Assyrians prepared a purple frit; this information has never been followed up by analytical studies, however.

A green pigment containing wollastonite ($CaSiO_3$) occurred with Eighteenth-Dynasty Egyptian blue, possibly as an accidental byproduct of the synthesis of the blue (Noll & Hangst, 1975b; Noll, 1981). This same wollastonite-containing pigment, called "green frit" by the authors, who suggested that its production may have been intentional, was found at several Fifth–Sixth Dynasty sites (Jaksch et al., 1983). This green was also found in the tomb of Nefertari and was termed "Egyptian green" (Stulik et al., 1993).

3.2 Permanence

Egyptian blue is completely stable in all media. No change of color has been observed when it is applied with organic media to stone, wood, or paper nor when used for wall paintings on alkaline mortars. The same is true of its exposure to strong light, which also does not influence its color. Egyptian blue that has been exposed for thousands of years to sun and heat on monuments in Egypt has retained its blue color.

3.3 Chemical Properties

As a very stable silicate, Egyptian blue can be dissolved only in hydrofluoric acid. Other cold or hot acids do not dissolve this pigment. When heated to temperatures above 1,050°C, Egyptian blue decomposes to form a mixture of cupric and cuprous oxides. Egyptian blue is also decomposed in a soda flux and can then be dissolved in nitric acid.

3.4 Compatibility

Egyptian blue occurs with lime or gypsum priming on sculptures and wall paintings and shows no reaction with these materials. As a pigment, it was mixed with glaucophane and green earth and no change of Egyptian blue or the other pigments was observed; because of its composition, any reaction with other pigments is improbable.

Some possible fading and darkening of Egyptian blue has been noted, but there is no analytical evidence to support these observations (Lucas & Harris, 1962).

4.0 Composition

4.1 Chemical Composition

Egyptian blue is an artificial calcium copper silicate. Because of the coincidence of x-ray diffraction data of Egyptian blue with the mineral cuprorivaite, the accepted formula for this pigment ($CaCuSi_4O_{10}$) is that of cuprorivaite. Chemical analysis of samples from antiquity vary considerably in composition and differ from the composition of pure cuprorivaite. The difference between theoretical composition and the analytical results from paint samples is due to the presence of a certain amount of quartz and other phases of silicon dioxide, such as tridymite, in the pigment that did not react with the copper compounds during the manufacturing process. Wollastonite ($CaSiO_3$) can be present as a result of the use of excess lime in the starting materials, and copper oxides such as cuprite (Cu_2O) or tenorite (CuO) can form if excess sources of copper are used (Jaksch et al., 1983).

Numerous authors in the early nineteenth century expressed an interest in Egyptian blue (see Select Bibliography).

The first qualitative analyses of the pigment were by Chaptal (1809) and Davy (1815). Chaptal studied seven samples of pigments from shops in Pompeii and defined the blue pigment as a blue frit containing oxides of copper, calcium, and aluminum. Chaptal wrote that M. Descotiles had observed on hieroglyphs of Egyptian paintings a blue, vitreous pigment, whose color was due to copper. Davy collected a number of pigment samples from Roman and Pompeian wall paintings and the contents of terra-cotta vases and identified them as the same blue pigment described as *caeruleum* by ancient authors.

The first quantitative analysis of Egyptian blue was by Vauquelin (1826), who found: 70.2% silicon dioxide (SiO_2), 8.3% calcium oxide (CaO), 2.8% sodium oxide (Na_2O), 2.3% alumina (Al_2O_3) and iron(III) oxide (Fe_2O_3), and 16.4% copper(I) oxide (Cu_2O). In 1872, Rammelsberg obtained

similar data, which are published in the treatise of Lepsius on metals in ancient Egypt: 70.5% silicon dioxide, 8.5% lime, 3.7% iron(III) oxide, 4.2% magnesium oxide (MgO), and 13.0% copper(II) oxide (CuO) (Lucas & Harris, 1962).

De Fontenoy (1874) received two samples of Egyptian blue from a Roman painter's shop in Autun, France, and from the Gallic town of Bibracte (Mont-Beuvray). The results of his quantitative analysis are virtually the same as those published by Vauquelin fifty years earlier: 70.25% silicon dioxide, 16.44% copper(II) oxide, 2.36% iron(III) oxide and alumina, 8.35% calcium oxide, and 2.83% sodium oxide. De Fontenoy fused a mixture of seventy parts of white sand, 15% copper oxide, 25% chalk, and 6% sodium carbonate to get Egyptian blue.

Fouqué (1889) found the following composition: 63.7% silicon dioxide, 14.3% calcium oxide, 21.3% copper(II) oxide, and 0.6% iron(III) oxide. He proposed "CaO, CuO, $4SiO_2$" as the formula for Egyptian blue, the equivalent of the currently accepted formula. Since he found no alkalies, he indicated that Egyptian blue could be produced without any addition of salts of sodium or potassium.

Russell (1894) analyzed Egyptian blue from painted walls at Tell el-Amarna and found the following: 88.7% silicon dioxide, 7.9% calcium carbonate ($CaCO_3$), 2.1% copper(II) oxide, 0.8% sodium oxide, and 0.6% iron(II) oxide (FeO).

In 1903 J. K. Crow obtained the following analysis (Lucas & Harris, 1962): 70.0% silicon dioxide; 9.4% lime, 18.3% copper(II) oxide, 2.0% sodium oxide and potassium oxide (K_2O), and 0.3% iron(II) oxide and alumina.

Le Chatelier (1907) published analyses of three samples of a dark Egyptian blue given below by percent:

	Sample 1	*Sample 2*	*Sample 3*
Silicon dioxide (SiO_2)	75.6	67.1	71.4
Calcium oxide (CaO)	11.2	16.8	15.4
Copper(II) oxide (CuO)	11.7	13.8	10.3
Sodium oxide (Na_2O)	1.5	2.3	2.8
Magnesium oxide (MgO)	1–2	1–2	—
Iron(II) oxide and alumina (Fe_2O_3+Al_2O_3)	trace	trace	—

Eibner (1926) received a sample of Egyptian blue from F. W. von Bissing, who had collected it in Nubia. The following composition was found: 74.3% silicon dioxide, 10.5% calcium oxide, 9.7% copper(II) oxide, 1.8% magnesium oxide, 2% iron(II) oxide and alumina.

Table 1 **Analysis by Emission Spectroscopy of an Object Fragment (PT15) Made of Egyptian Blue Found at Persepolis**[a]

Compound	*Percent*
Silicon dioxide (SiO_2)	major
Alumina (Al_2O_3)	0.76
Iron(III) oxide (Fe_2O_3)	2.1
Calcium oxide (CaO)	11.4
Magnesium oxide (MgO)	0.89
Copper(II) oxide (CuO)	10.1
Titanium dioxide (TiO_2)	0.51
Lead oxide (PbO)	0.009
Cobalt(III) oxide (Co_2O_3)	0.008
Nickel oxide (NiO)	0.006
Antimony oxide (Sb_2O_3)	0.005
Tin(IV) oxide (SnO_2)	0.004
Chromium oxide (Cr_2O_3)	0.004
Silver oxide (Ag_2O)	0.003
Sought for, but not found: barium, gallium, manganese, potassium, sodium, strontium	

a. From Matson (1957).

Granger (1933) gave a more detailed analysis of a sample from an Assyrian palace at Til Barsip: 74.27% silicon dioxide, 10.37% copper(II) oxide, 2.98% alumina, 0.50% iron(III) oxide, 0.17% manganese oxide (MnO), 9.19% calcium oxide, 0.84% magnesium oxide, 0.85% potassium oxide, and 0.29% sodium oxide.

Matson (1957) published an analysis of a solid object made from Egyptian blue at Persepolis (table 1).

An analysis of a sample from the Nineteenth Dynasty was given by Lucas and Harris (1962); they found it was extremely poor in silica and relatively rich in alkalies. They reported 57.2% silicon dioxide, 13.8% calcium oxide, 18.5% copper oxide, 7.6% sodium and potassium oxides, 0.5% magnesium oxide, and 0.8% iron oxide and alumina.

Saleh et al. (1974) published an analysis of a sample from one of the large cakes of unused Egyptian blue found at Thebes in 1958 in the courtyard of the tomb of Keruf (table 2).

Bayer and Wiedemann (1976a) reported an analysis of a sample of Egyptian blue that contained 70.0% silicon dioxide, 18.3% copper(II) oxide, 9.4% calcium oxide, 0.3% alumina and iron(III) oxide, and 2.0% alkali oxides.

Dayton (1978; Dayton et al., 1980) published a

Table 2 **Analysis by Wet Chemistry and X-ray Fluorescence of a Sample of Egyptian Blue Found at Thebes**[a]

Compound	*Percent*
Silicon dioxide (SiO_2)	60.59
Aluminum oxide with some iron oxide (Al_2O_3+)	7.05
Calcium oxide (CaO)	16.12
Copper(II) oxide (CuO)	12.33
Tin(IV) oxide (SnO_2)	1.79
Magnesium oxide (MgO)	†
Sulfur trioxide (SO_3)	†
Sodium oxide (Na_2O)	1.62
Potassium oxide (K_2O)	†
Ignition loss	0.50

†=Trace

a. From Saleh et al. (1974).

Table 3 **Analysis by Atomic Absorption Spectrometry of Samples of Egyptian Blue Found in Egypt and Mesopotamia**[a]

	In Weight Percent			
Compound	*Sample from Mesopotamia*	*Samples from Egypt*		
Silicon dioxide (SiO_2)	74.2	78.6	70.9	67.3
Calcium oxide (CaO)	6.8	7.1	8.0	7.0
Copper(II) oxide (CuO)	11.0	10.0	13.3	11.4
Sodium oxide (Na_2O)	2.3	1.1	2.2	1.6
Potassium oxide (K_2O)	0.4	0.5	0.6	0.4
Alumina (Al_2O_3)	1.5	1.4	1.2	1.0
Magnesium oxide (MgO)	0.4	0.4	0.7	0.4
Iron(II) oxide (FeO)	2.4	0.5	0.4	0.8

a. From Tite et al. (1980).

series of semiquantitative x-ray fluorescence analyses of samples from Tell el-Amarna, Deir el-Medina, Nimrud, Mycenae, and Knossos and quantitative analyses of two of these samples.

Tite et al. (1980) published analyses of four samples of Egyptian blue, one from Mesopotamia, and three from Egypt (table 3). Tite et al. (1984) extended their studies to the chemical analysis of a series of forty-six samples of Egyptian blue from Egypt, Mesopotamia (Nimrud and Nineveh), and the Roman period in western Europe. The extensive data they obtained are reported in their publication.

By comparing the analytical data of samples of different origin, Tite et al. (1984) showed that samples from Egypt are characterized by an excess of calcium oxide and relatively high amounts of alkalies. The Roman Egyptian blue is not very different from the material from Egypt. The samples from Nimrud show an excess of copper(II) oxide and very low concentrations of potassium oxide and sodium oxide. The samples from Nineveh are also poor in alkali oxide, and have an excess of either calcium or copper. Assuming a composition of cuprorivaite ($CaCuSi_4O_{10}$), all analyzed samples contained excesses of silicon dioxide.

Among the trace elements, Tite et al. (1984) found higher amounts of cobalt in samples from Nineveh and Nimrud. In Egyptian and Roman samples, higher amounts of tin, arsenic, and lead were found, supporting the theory that bronze scrap metal was used to make the pigment.

Tite et al. (1984) published a ternary plot of silicon dioxide, calcium oxide, and copper(II) oxide (fig. 4) and a diagram of potassium oxide versus sodium oxide to show the variation of compositions of Egyptian blue (fig. 5). For comparison, a ternary plot of the earlier published analyses is shown in figure 6.

The results of the above chemical analyses show considerable variation. Silicon dioxide ranges from 58.5% to 78.6% in recent analyses and to as high as 88.7% in the early analysis by Russell (1894).

The amount of calcium oxide also varies considerably. The highest amounts were found by Saleh et al. (1974) who determined 16.12% in an unused pigment sample from Thebes. Tite et al. (1980) determined the lowest value in a sample from an Egyptian figure.

Copper(II) oxide was found in a concentration range of between 2.1% and 21.4% Cu. The lower value was published by Russell (1894), but Dayton (1978) also mentioned samples with only 3.26% and 4.38%. The high copper value was determined by Tite et al. (1984) in a sample from Nineveh, where high concentrations of copper(II) oxide are normal.

Among the alkali oxides, sodium oxide was found in amounts between zero and 3.85%. The observation of Tite et al. (1984) that Roman and Egyptian samples usually contain more sodium oxide than samples from Nimrud and Nineveh is confirmed by earlier analyses. Potassium oxide varies between zero and 1.95%. Again, the higher

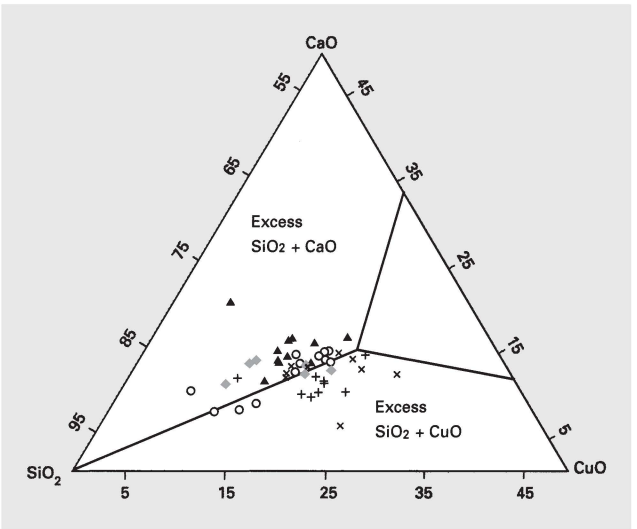

Fig. 4 Ternary plot of silica, calcium oxide, and copper oxide concentrations for ancient Egyptian blue (after normalization to 100%). The point toward the center right of the ternary plot from which the three lines radiate toward the pure component positions represents the composition of the stoichiometric Egyptian blue mineral. *Key*: ○=Egypt, ▲=Tell el-Amarna, +=Nimrud, x=Nineveh, ◆=Roman. From Tite (1984).

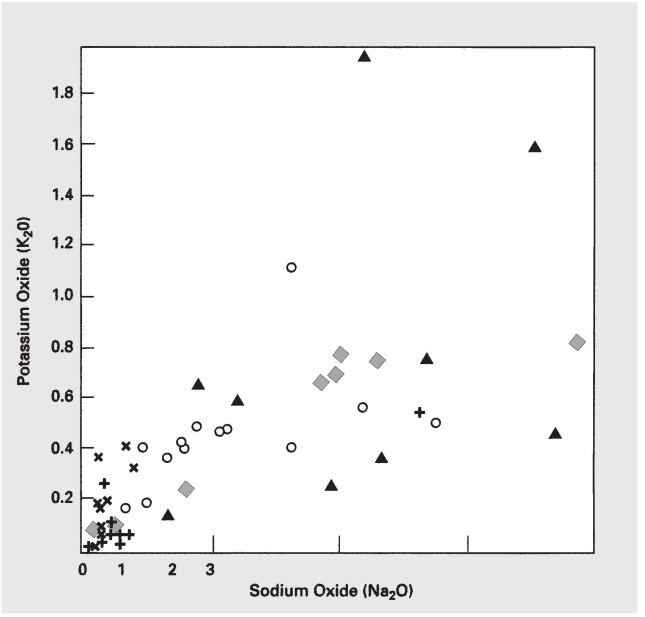

Fig. 5 Potassium oxide versus sodium oxide concentrations from samples of ancient Egyptian blue. *Key*: ○=Egypt, ▲=Tell el-Amarna, +=Nimrud, x=Nineveh, ◆=Roman. From Tite (1984).

concentrations occur in Egyptian and Roman-period samples.

The concentration ranges of all elements found in Egyptian blue are given in table 4.

The trace elements of Egyptian blue in a series of samples from the Eighteenth Dynasty, found at Tell el-Amarna (table 5), were analyzed by neutron activation analysis at the Rathgen-

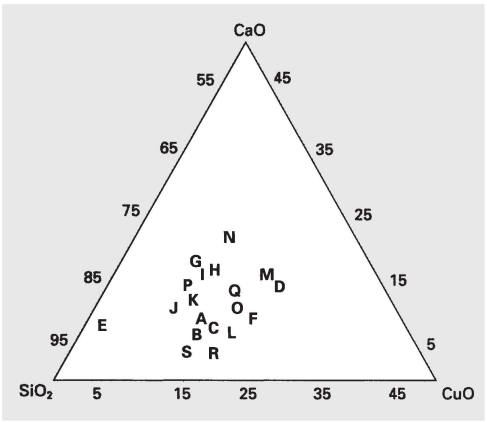

Fig. 6 Ternary plot of silica, calcium oxide, and copper concentrations for early analyses of Egyptian blue.

A. Vauquelin (1826)
B. Rammelsberg (1872 [in Lucas & Harris, 1962])
C. De Fontenoy (1874)
D. Fouqué (1889)
E. Russell (1894)
F. Crow (1903 [in Lucas & Harris, 1962])
G., H., I. Le Chatelier (1907)
J. Eibner (1926)
K. Granger (1993)
L. Matson (1957)
M. Lucas and Harris (1962)
N. Saleh et al. (1974)
O. Bayer and Wiedemann (1976a)
P., Q., R., S. Dayton (1978)

Table 4 **Concentration Ranges of All Elements Found in Egyptian Blue**

Compound	*Percent*
Silicon dioxide (SiO_2)	50.5–88.7
Calcium oxide (CaO)	4.9–16.8
Copper(II) oxide (CuO)	2.1–21.4
Sodium oxide (Na_2O)	0–6.01
Potassium oxide (K_2O)	0–1.95
Magnesium oxide (MgO)	0.1–4.2
Alumina (Al_2O_3)	0–3.4
Iron(III) oxide (Fe_2O_3)	0.2–2.7
Tin(IV) oxide (SnO_2)	0–1.79

Forschungslabor. Among these trace elements, the relatively high amounts of gold and tin are of interest, indicating that bronze, and not always a pure copper or copper minerals, was used for the production of Egyptian blue. The high amount of tin in Egyptian blue mentioned by other authors (Saleh et al., 1974, Tite et al., 1984) also suggests the use of bronze as a raw material. Jaksch et al. (1983) note that the presence of tin is especially common beginning at the New Kingdom period.

4.2 **Sources**

The pigment Egyptian blue certainly was always a manufactured product. Cuprorivaite, the mineral corresponding in its chemical and mineralogical properties, is so scarce in nature that it could not be collected in large enough quantities to be used as a pigment. Cuprorivaite was described first by Minguzzi (1938), who determined its formula to be $CuO.2SiO_2.(CaO,Na_2O).2SiO_2$, the equivalent of $CuCaSi_4O_{10} + Na_2O$. With the advent of the technique of x-ray diffraction, Egyptian blue was definitely confirmed to be the natural analogue of cuprorivaite, $CuCaSi_4O_{10}$ (Pabst, 1959; Mazzi & Pabst, 1962).

4.3 **Preparation**

After the nature of Egyptian blue was established in the early nineteenth century, attempts to synthesize it were carried out by three groups: (1) scientists interested in trying to reproduce the ancient pigment for historical purposes; (2) technicians who wanted to reintroduce Egyptian blue as a modern pigment; and (3) mineralogists who experimented with the synthesis of cuprorivaite to understand its crystallographic properties. As a result, there are many publications about this topic and only those will be mentioned that are of interest for the history of Egyptian blue.

The first attempts to prepare Egyptian blue with the aim of discovering the ancient technique of pigment production were by Davy (1815) who succeeded in producing it in experiments. A short time later Darcet tried to manufacture Egyptian blue as a pigment for the paper industry, keeping his process a secret. In 1893, Egyptian blue (or Vestorian blue) was announced at the Chicago World's Fair as a product manufactured on an industrial scale by MM. Deschamps that would attract the attention of visitors (Adrian, 1893). Bock (1916) described the industrial manufacture of Egyptian blue.

Fouqué (1889) and Russell (1892) both carried out experiments in the preparation of Egyptian blue. Laurie et al. (1914), basing their work on that of these earlier researchers, were the first to carry out an extensive series of experiments under varying conditions to investigate how Egyptian blue was formed. They fused quartz sand, calcium carbonate, and copper carbonate at 850°C, using various fluxes, including one that approximated

Table 5 **Egyptian Blue Samples from Tell el-Amarna Analyzed by Neutron Activation Analysis**

Nuclide	*Line*	*1*	*2*	*3*	*4*	*5*	*6*	*7*
Ag-110	659	3.5	2.7	5.8	2.0	0.5	5.1	0.5
Au-198	412	143.0	148.0	18138.0	1480.0	176.0	5213.0	902.0
Ce-141	145	1.6	1.5	4.3	5.6	12.0	4.9	—
Co-60	1333	2.7	3.1	12.2	9.8	11.0	9.8	27.0
Cr-151	320	2.4	0.9	19.1	12.3	9.0	21.0	15.8
Eu-152	779	38.0	35.0	95.0	122.0	141.0	120.0	110.0
Hf-181	482	0.5	1.1	0.2	0.6	1.4	0.2	0.2
Lu-177	208	0.7	0.7	—	0.1	—	0.3	—
Co-58	811	2.5	1.9	1.3	1.0	5.8	1.9	1.2
Sb-124	1691	9.7	8.2	28.0	25.7	32.8	36.0	33.0
Sc-46	1120	0.3	0.1	0.2	0.1	0.3	0.8	1.0
Sn-113	392	2.5	1.6	223.0	439.0	271.0	404.0	214.0
Ta-182	1221	51.0	47.0	39.0	71.0	89.0	47.0	63.0
Zn-65	1115	3.1	2.5	1.0	0.8	1.0	1.0	1.0
Yb-169	197	38.0	32.0	73.0	89.0	139.0	78.0	102.0

the soda occurring naturally in the Egyptian desert. Hodgson (1936) conducted similar experiments with some variation in the fluxes.

Schippa and Torraca (1957a, b) also studied the preparation of Egyptian blue in a series of tests under varying conditions. They used twenty-one different mixtures of quartz, copper carbonate, and calcium carbonate with potassium carbonate as a flux. The different mixtures were heated to temperatures of 830°C to 900°C over a period of 96 to 312 hours. The reaction products were studied optically and by x-ray diffraction techniques. From most of the mixtures, reasonable qualities of Egyptian blue were obtained. Schippa and Torraca found that the formation of Egyptian blue is determined by (1) the reaction time (2) the ratio of silicon dioxide, calcium oxide, and copper(II) oxide, and (3) the particle characteristics of the materials used for the reaction when temperatures of 850°C to 900°C are used.

Chase (1971) also did extensive experimental work on the synthesis of Egyptian blue, studying the influence of time and temperature of reaction and of the reaction atmosphere. Chase used four different mixtures of sand, synthetic natron, malachite, and calcium carbonate, which he heated in oxidizing and reducing atmospheres up to 1,150°C, studying the reaction products in increments of 50°C to 100°C between 830°C and 1,150°C.

Bayer and Wiedemann (1975) reconfirmed in extensive laboratory tests the observations of Schippa and Torraca, as well as Chase. Without any flux, it was necessary to heat the components to 1,000°C and to slowly cool the product to 800°C. When a flux was added at a temperature of 850°C to 900°C, a product of an intense blue color was obtained. When gypsum or calcium hydroxide instead of calcium carbonate, malachite instead of copper(II) oxide, and silica gel instead of quartz powder were used with no flux, the required reaction temperature was lowered to between 900°C and 950°C. At temperatures between 1,150°C and 1,300°C, homogeneous blue glasses were formed, from which no Egyptian blue can be obtained since calcium silicates and tridymite (a form of quartz) crystallize out after a thermal treatment.

Tite et al. (1984) produced Egyptian blue from a mixture of a coarse-grained and a fine-grained quartz, calcium carbonate, malachite, and anhydrous sodium carbonate. The components were mixed in ratios so that quartz was added in excess to achieve low- and high-alkali types of Egyptian blue. The mixed components were treated for up to twenty-seven hours at temperatures of 900°C to 1,000°C using either a single- or two-stage firing cycle. In this way, fourteen different conditions for preparing Egyptian blue could be selected. Microstructure, hardness, and color were determined from the samples obtained.

Jaksch et al. (1983) maintain that Egyptian blue may have been manufactured in a multistage process rather than being just sintered or fritted. They suggested that the main ingredients were heated to melting, a flux being present to suppress

the temperature below 1,050°C, the temperature at which cuprorivaite would break down. The glass-bearing cake that resulted would then be ground and reheated several times to produce the pigment.

In summary, our knowledge about the preparation of Egyptian blue has been confirmed by producing a material with properties comparable to the early pigments. This material is obtained by mixing silica in the form of quartz powder or silica gel with calcium compounds such as calcium carbonate, gypsum, or calcium hydroxide and a copper compound (such as copper oxide) or a copper salt (such as malachite) in proportions that correspond to a ratio of $4SiO_2$:1CaO:1CuO, with or without a flux such as sodium carbonate, potassium carbonate, or modern equivalents such as borax or lithium carbonate. This mixture is heated to 1,000°C when no flux is added, or to 900°C when a flux is used, and maintained at temperatures of 800°C for a period ranging from ten to one hundred hours.

5.0 Identification and Characterization

5.1 Optical and Chemical Microscopy

According to Pabst (1959), cuprorivaite, the mineral corresponding to artificial Egyptian blue, is uniaxial: n_o=1.636, n_e=1.591. The birefringence is 0.045, which is a relatively high value. Egyptian blue is slightly pleochroic (fig. 7).

When observed under a microscope, Egyptian blue is characterized by its relatively large grain size and intense blue color. Crystal faces are never visible. When the product is crushed for use, the particles show irregular, angular fractures, which are not conchoidal like ground glass.

A crystal of synthetic Egyptian blue observed using scanning electron microscopy is shown in figure 8.

All the pigment components, including any glassy phase, and the relationship between them, can be observed in cross sections; analysis of the section by electron beam microprobe gives the chemical composition of the components (Tite, 1980; Jaksch et al., 1983; Tite, 1984).

Chemical tests under the microscope are practically impossible since Egyptian blue cannot be dissolved in those acids that are usually applied for microchemical reactions. This property distinguishes it from azurite, which is decomposed by acids.

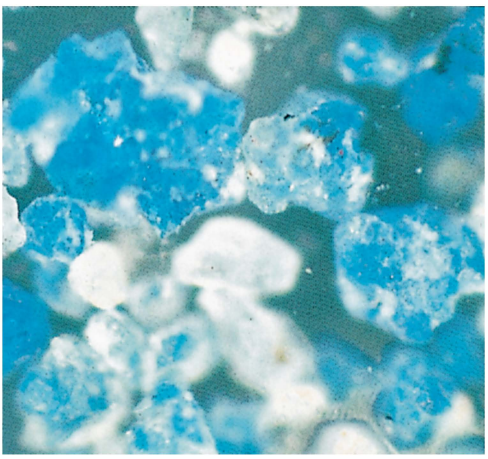

Fig. 7 Photomicrograph by transmitted light of Egyptian blue from an Egyptian wooden statue of Ikhnaton, Eighteenth Dynasty, c. 1362 B.C., Ägyptisches Museum, Berlin, inv. no. 21836. 460x.

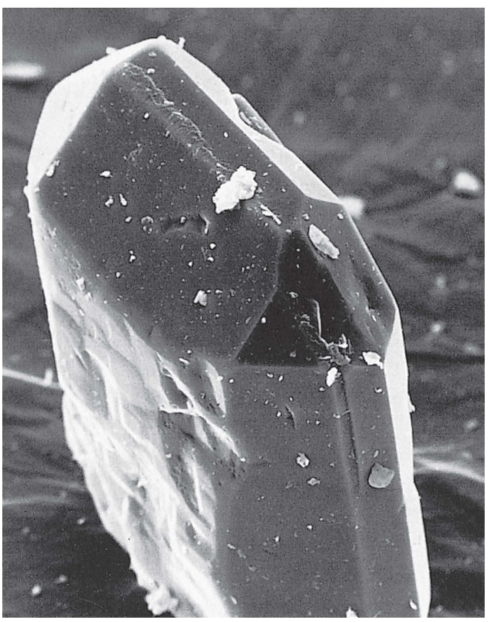

Fig. 8 Scanning electron micrograph of a crystal of synthetic Egyptian blue. From Bayer and Wiedemann (1976b). 660x.

5.2 Chemical Identification

The chemical identification of Egyptian blue is easiest with instrumental techniques such as emission spectrography or x-ray fluorescence analysis that require only minute samples or by electron beam microprobe analysis of cross sections (see

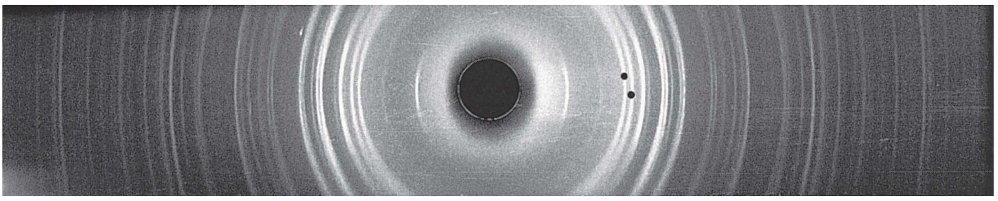

Fig. 9 X-ray diffraction powder pattern of Egyptian blue. Pigment labeled Pompeii blue, manufactured by Lefranc, Paris, 1937. Forbes Collection, Department of Conservation and Scientific Research, Freer Gallery of Art and Arthur M. Sackler Gallery, Smithsonian Institution, Washington. Not to be used for measurement purposes. The two tridymite lines (4.328, 4.107) marked by dots are impurities.

section 5.1). The identification of the three main elements—copper, calcium, and silica—is sufficient to indicate Egyptian blue is present.

Wet chemical analysis requires a decomposition of the pigment in a soda and potash flux or any comparable alkaline flux. Nitric acid is used to dissolve the residue of this decomposition; copper, calcium, and silica, as well as traces of other metals, can be identified by the usual spot tests.

5.3 Instrumental Methods of Analysis

5.3.1 ***X-ray diffraction.*** In 1940, Jope and Huse mentioned x-ray powder diffraction analysis as an easy and useful method for the study and identification of Egyptian blue. They compared samples of wall paints from Roman sites in England and pigment samples from Egypt to prove that they were the same crystalline substance; however, they did not give x-ray diffraction data. Their statement that they identified copper aluminate ($CuAl_2O_4$) by x-ray powder diffraction as the blue pigment on a pot from Tell el-Amarna more likely refers to a pot painted not with Egyptian blue but with cobalt blue ($CoAl_2O_4$), which is common on pottery from this site (Riederer, 1974). The x-ray diffraction data for copper aluminate ($CuAl_2O_4$) and cobalt blue ($CoAl_2O_4$) are so similar that precise identification by this method is possible only if the metal elements are determined by chemical analysis or other methods. Noll and Hangst (1975a) also identified cobalt aluminate on pottery from Tell el-Amarna.

Schippa and Torraca (1957a, b) published x-ray diffraction data of Egyptian blue of Roman origin and of a series of samples prepared in the laboratory (see section 4.3). They listed the *d*-values and the intensities of the Roman sample and recognized that Egyptian blue has the same crystallographic properties as the naturally occurring mineral cuprorivaite, which was described by Minguzzi (1938). Nicolini and Santini (1958) also published a series of x-ray powder diffraction diagrams of products that they obtained during their detailed studies on the synthesis of Egyptian blue.

Chase (1971) studied a series of samples, including two objects from Hasanlu made of Egyptian blue—a spade-shaped object and a goblet from the ninth century B.C. He listed all published x-ray diffraction data of the pigment of early and recent origin together with the data from both objects from Hasanlu and from his own experiments.

Saleh et al. (1974) published x-ray diffraction data for four ancient samples, and one of a freshly prepared sample, as well as the *d*-values and intensities of the eight strongest peaks of eight ancient and one modern sample.

In table 6, the x-ray diffraction data for cuprorivaite, quartz, and two other varieties of quartz, crystobalite and tridymite, are listed (*JCPDS*, 1988) with the data for synthetic pigments and ancient Egyptian blue of different origins. Figure 9 shows an x-ray powder diffraction pattern of an Egyptian blue sample in the E. W. Forbes Pigment Collection, Freer Gallery of Art.

5.3.2 ***Infrared, ultraviolet, and visible spectroscopy.*** To date there has been little study of Egyptian blue by infrared, ultraviolet, and visible spectroscopy since data from these methods do not provide possibilities for identification or distinction between different varieties of the pigment.

5.3.3 ***Neutron activation.*** A few analyses by neutron activation are available (see section 4.1 and table 5) that provide information on a large number of trace elements. Neutron activation analysis, like any other technique of trace element analysis, is of interest to determine the type of raw materials used in the manufacture of Egyptian blue, since the high amounts of tin, lead, or gold found in some samples establish that bronze was sometimes used as the source of copper.

5.3.4 ***Thermoluminescence.*** Although Egyptian blue is an ideal substance for thermolumines-

Table 6 **X-ray Diffraction Data for Egyptian Blue**[a]

	Cuprorivaite JCPDS 12-512			*α-quartz JCPDS 5-490*		*Cristobalite JCPDS 11-695*		*Tridymite JCPDS 18-1170*[b]	
hkl	*d* (Å)*	*d* (Å)**	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—
002	7.56	7.63	40	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—
102	5.25	5.22	15	—	—	—	—	—	—
110	5.16	—	—	—	—	—	—	—	—
112	4.26	—	—	4.26	35	—	—	4.328	90
—	—	—	—	—	—	4.05	100	4.107	100
—	—	—	—	—	—	—	—	3.867	20
004	3.78	3.78	90	—	—	—	—	3.818	50
200	3.65	3.66	25	—	—	—	—	—	—
—	—	—	—	—	—	3.52	4	—	—
104	3.36	3.36	80	3.343	100	—	—	—	—
202	3.29	3.29	100	—	—	—	—	—	—
211	3.19	3.19	50	—	—	—	—	—	—
—	—	—	—	—	—	3.14	12	—	—
114	3.05	3.05	40	—	—	—	—	—	—
212	3.00	3.00	90	—	—	—	—	2.975	25
—	—	—	—	—	—	2.841	14	—	—
213	2.740	2.736	5	—	—	—	—	—	—
204	2.626	2.629	40	—	—	—	—	—	—
220	2.581	2.585	40	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—
006	2.520	2.518	5	—	—	—	—	2.500	16
214	2.471	2.471	5	2.458	12	2.485	20	2.490	14
222	2.442	—	—	—	—	2.465	6	—	—
106	2.382	2.386	20	—	—	—	—	—	—
302	2.316	2.321	30	—	—	2.340	2	—	—
310	2.308	—	—	—	—	—	—	2.308	16
311	2.282	—	—	2.282	12	—	—	—	—
116	2.265	2.270	50	—	—	—	—	—	—
215	2.218	—	—	2.237	6	—	—	—	—
312	2.208	—	—	—	—	—	—	—	—
224	2.132	2.136	10	2.128	9	2.118	6	—	—
313	2.099	—	—	—	—	—	—	—	—
206	2.074	2.069	5	—	—	—	—	—	—
304	2.051	—	—	—	—	—	—	—	—
321	2.007	2.007	20	—	—	2.019	4	—	—
—	—	—	—	—	—	—	—	—	—
216	1.995	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—
314	1.970	1.970	20	1.980	6	—	—	—	—
322	1.956	—	—	—	—	1.929	6	—	—
008	1.890	1.890	15	—	—	—	—	—	—
323	1.879	—	—	—	—	—	—	—	—
315	1.835	—	—	—	—	1.870	8	—	—
108	1.830	1.831	60	1.817	17	—	—	—	—
—	—	—	—	1.801	<1	—	—	—	—

*Calculated, from Pabst (1959)

**Observed

a. Data from *JCPDS* (1988), all have additional weak lines.

b. Lines above $I = 8$ only

Samples from Tell el-Amarna

1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*16*
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	8.55
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	7.86
7.630	7.56	7.60	7.50	7.63	7.44	7.56	7.50	7.50	7.56	7.56	7.44	7.63	7.56	7.45	—
6.070	—	—	—	—	—	—	6.11	—	—	—	—	—	—	—	5.54
5.300	5.28	—	—	—	—	5.27	5.18	—	—	—	—	—	—	—	—
—	—	5.15	—	—	—	—	—	—	—	—	—	—	—	—	4.47
—	4.27	4.25	4.25	4.31	4.25	4.29	4.27	4.25	4.27	4.25	—	4.25	4.25	—	4.43
—	4.05	4.05	—	—	4.08	4.05	4.02	4.05	4.04	4.07	—	—	4.08	—	—
—	—	—	—	—	3.90	—	—	—	—	—	—	3.83	—	—	3.83
3.810	3.79	3.78	3.75	3.78	3.78	3.77	3.77	3.78	3.77	3.77	3.77	3.74	3.78	3.745	3.71
—	3.65	—	—	—	—	—	—	—	—	—	3.63	—	3.66	—	—
—	—	—	3.51	—	—	3.53	—	3.53	3.49	—	—	3.41	—	—	3.55
—	3.35	3.34	3.35	3.43	3.33	3.35	3.34	3.34	3.34	3.36	3.33	3.34	3.33	3.328	3.39
3.310	3.28	3.26	3.30	3.30	3.29	3.29	3.30	3.30	3.28	3.29	3.29	3.29	3.29	3.264	3.31
3.210	3.20	3.19	3.19	3.19	3.19	3.19	3.19	3.18	3.19	3.18	3.19	3.19	3.19	3.185	3.23
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	3.09
3.060	3.05	—	3.05	3.05	3.03	3.05	3.04	3.04	3.05	3.03	3.05	3.05	3.03	—	3.04
2.990	—	2.99	3.003	2.998	2.998	2.998	2.998	—	—	—	2.998	2.988	2.988	2.982	—
—	2.87	—	—	—	2.978	—	—	2.857	—	—	—	—	—	—	2.85
—	2.71	—	—	—	—	2.746	2.747	—	—	—	2.652	—	2.740	—	—
2.636	2.64	2.61	2.644	2.622	—	2.621	2.629	2.637	2.637	2.637	2.622	—	2.622	—	2.65
2.600	2.59	2.57	2.621	2.578	—	—	2.578	—	—	—	—	2.577	2.599	—	2.60
—	—	—	2.571	2.570	2.570	—	—	—	2.570	—	—	—	—	—	2.55
—	2.50	—	2.522	2.527	—	2.527	—	—	—	—	—	—	2.495	—	2.48
—	2.46	2.45	—	2.461	2.442	2.461	2.449	2.488	2.495	2.468	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
2.392	2.39	2.37	2.380	2.398	2.380	2.386	2.380	2.379	2.442	—	—	2.448	—	—	2.40
—	2.32	2.31	—	2.374	—	2.321	—	2.321	2.374	2.398	2.380	2.380	2.321	—	2.34
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2.30
2.281	2.28	2.28	2.270	—	2.264	2.270	2.276	2.276	2.276	2.276	2.280	2.281	2.281	2.26	2.29
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	2.227	—	—	2.232	—	—	—	—	—	—	—	2.225
—	2.14	2.12	2.127	2.130	2.132	2.136	2.127	2.131	2.136	2.127	—	—	—	—	2.143
—	—	—	—	—	—	—	—	2.094	2.094	—	—	—	2.099	—	2.096
—	—	—	—	—	—	—	—	—	—	—	—	2.076	—	—	2.069
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2.024
—	—	—	2.006	2.006	—	—	2.006	—	—	—	—	—	—	—	2.011
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2.000
—	1.98	1.99	—	—	—	—	—	—	—	—	—	1.993	—	—	1.988
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.981
—	—	—	1.977	1.977	1.973	1.977	—	1.973	1.973	1.981	—	—	1.965	—	1.973
—	1.92	—	—	—	—	—	—	—	—	—	—	—	1.914	—	1.907
1.895	—	—	1.891	1.891	1.888	1.891	1.891	1.888	1.891	—	—	—	1.880	—	—
—	1.88	—	—	—	—	—	—	—	—	—	1.841	—	—	—	1.845
1.835	1.83	1.82	1.831	1.830	1.824	1.831	1.827	1.824	1.827	1.827	1.827	1.824	1.827	1.824	1.831
—	—	—	—	—	—	—	1.817	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.797

Table 6 Continued

	Cuprorivaite JCPDS 12-512			*α-quartz JCPDS 5-490*		*Cristobalite JCPDS 11-695*		*Tridymite JCPDS 18-1170*[b]	
hkl	*d* (Å)*	*d* (Å)**	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
—	—	1.784	40	—	—	1.757	<2	—	—
—	—	1.758	20	—	—	1.730	2	—	—
—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—
—	—	1.704	40	—	—	—	—	—	—
—	—	—	—	—	—	1.690	4	1.695	12
—	—	—	—	1.672	7	—	—	—	—
—	—	—	—	1.659	3	—	—	—	—
—	—	1.636	20	—	—	1.634	2	—	—
—	—	—	—	1.608	<1	1.612	6	—	—
—	—	1.603	40b	—	—	1.600	4	1.600	10
—	—	1.573	5b	—	—	1.571	<2	—	—
—	—	—	—	—	—	1.567	<2	—	—
—	—	1.528	10	1.541	15	1.533	4	1.534	10
—	—	1.483	10	—	—	1.494	6	—	—
—	—	1.462	5	—	—	—	—	—	—
—	—	1.456	5	1.453	3	—	—	—	—
—	—	1.435	5	—	—	1.431	44	—	—
—	—	1.426	5	1.418	<1	1.419	4	—	—
—	—	1.398	20	—	—	1.398	4	—	—
—	—	1.380	20	1.382	7	1.379	<2	—	—
—	—	—	—	1.375	11	—	—	—	—
—	—	—	—	1.372	9	1.365	4	—	—
—	—	—	—	—	—	1.352	4	—	—
—	—	—	—	—	—	1.346	<2	—	—
—	—	1.336	25	—	—	1.333	4	—	—
—	—	1.315	10	—	—	—	—	—	—

b = Broad line

cence analysis, no detailed studies have been carried out by this method. When Egyptian blue was produced in antiquity at a temperature of approximately 850°C, the crystal lattice certainly was free from electrons brought to a higher energy state by radiation, trapped in defects in the lattice structure of the crystal. But two to five thousand years after its manufacture, Egyptian blue should have been exposed to a sufficient quantity of alpha, beta, and gamma rays from its own support and the environment so that thermoluminescence should be observed when a sample is heated to 500°C. In fact, Egyptian blue shows glow curves similar to those of ceramics although, depending on its mineralogical composition such as the amount of quartz and other siliceous phase, there are differences in the glow curves. Normally there is only one peak at 310°C to 315°C, which sometimes is accompanied by another peak at 110°C. Additionally, there are samples where the glow curve has peaks at 180°C, 250°C, 370°C, and 450°C.

Samples heated to 500°C and then cooled to room temperature and irradiated with a beta source show strong peaks at 105°C and 195°C. The equivalent β-dose in the temperature range between 300°C and 400°C is 4 to 5 Gy (Gray [Gy] is the SI unit for energy dose of the nuclear radiation) for Egyptian samples that are approximately four thousand years old. Samples exposed to x-rays develop peaks at 190°C, 240°C to 260°C, and 390°C.

5.3.5 ***Thermal analysis.*** The behavior of Egyptian blue at high temperatures was studied by Bayer and Wiedemann (1976a, b) in the course of synthesizing the pigment from calcite, malachite, and quartz powder (fig. 10). By means of a thermobalance, the change of the weight of the sample, the velocity of reactions, and the occur-

Samples from Tell el-Amarna

1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*16*
1.797	1.79	1.78	1.774	1.784	1.784	1.784	1.781	1.784	1.791	1.774	—	1.781	1.784	—	1.787
—	—	1.75	—	1.785	1.774	—	—	—	—	—	—	—	—	—	1.778
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.771
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.762
1.710	1.71	1.70	—	1.707	—	1.704	1.701	1.704	1.698	—	—	1.704	1.709	—	1.713
—	1.68	1.67	1.675	1.684	1.698	1.683	1.672	1.675	—	1.675	—	—	—	—	1.691
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.675
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.667
—	1.63	1.63	—	1.639	—	—	—	—	—	—	—	—	—	—	1.639
—	1.61	—	1.608	1.605	1.603	—	—	1.610	1.603	1.603	—	1.603	1.603	—	1.614
1.605	—	1.59	—	—	—	1.597	1.597	1.597	—	—	—	—	—	—	1.605
—	—	—	1.578	1.573	—	—	—	—	—	—	1.580	—	—	—	1.601
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.585
—	1.54	1.53	1.542	1.542	1.542	1.544	—	1.537	1.539	1.544	—	1.539	1.546	—	1.548
—	1.49	—	1.484	—	—	1.486	1.486	1.484	—	1.484	1.484	—	—	—	1.521
—	—	1.47	—	1.479	1.480	—	—	—	—	—	—	—	—	—	—
—	—	1.45	—	—	—	—	1.459	—	—	—	—	—	—	—	—
—	1.44	1.43	—	—	—	—	—	—	—	—	—	1.435	1.437	—	—
—	1.42	1.42	—	—	—	—	—	—	—	—	—	—	—	—	—
—	1.40	—	—	—	—	—	—	—	—	—	—	—	1.404	—	—
—	1.38	1.39	1.398	1.398	1.397	1.397	1.400	1.400	1.398	1.384	—	1.398	1.398	—	—
—	—	—	1.382	1.378	1.392	—	—	—	—	—	—	—	—	—	—
—	1.37	1.37	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	1.34	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	1.33	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

rence of endothermic or exothermic reactions could be studied. In the higher temperature range of the synthesis, between 600°C and 800°C, the reaction is endothermic and the sample experiences weight loss because of the decomposition of the calcium carbonate. After the formation of Egyptian blue at 800°C to 850°C, the product

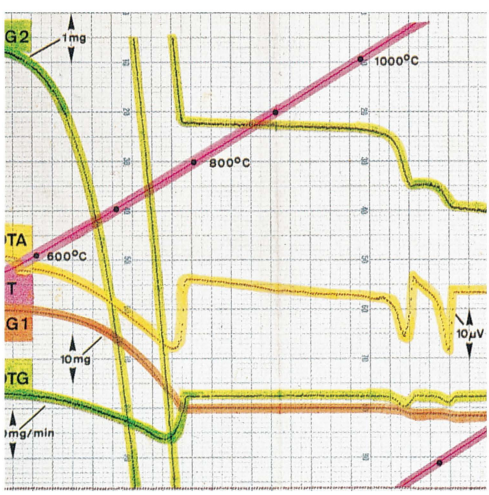

Fig. 10 Plot of investigation of Egyptian blue with a thermal balance. The weight curve (TG) shows changes in weight that occur depending on the temperature. The DTG curve is the first derivative of the weight curve, that is, it shows the rate of the reaction. The DTA (differential thermal analysis) curve shows changes in enthalpy. The temperature curve (T) shows the actual temperature. From Bayer and Wiedemann (1976a).

is stable until a temperature of about 1,080°C is reached. At that temperature, Egyptian blue decomposes to form glass, high-temperature modifications of silicon dioxide, and either copper(II) oxide in an oxidizing atmosphere, or copper(I) oxide in a reducing atmosphere.

5.4 **Criteria for Identification**

Egyptian blue can be identified by chemical analysis or by x-ray diffraction; both provide data that permit a clear distinction from any other blue pigment. If the sample is small, elemental analysis can be carried out by instrumental techniques such as x-ray fluorescence. If x-ray diffraction techniques are not available and the pigment sample is too small for a chemical analysis, the microscopic properties and microchemical tests for behavior with acids would be sufficient for identification. It should be kept in mind that Han blue closely resembles Egyptian blue microscopically, but x-ray diffraction and elemental analysis would differentiate the two. Azurite can be distinguished because of its solubility in dilute acids. Smalt as a glass is optically isotropic and has a lower refractive index. Ultramarine also has a refractive index well below that of Egyptian blue and it is soluble in dilute acids; the grain size of artificial ultramarine is very fine.

6.0 **Occurrences**

Numerous identifications of Egyptian blue on Egyptian objects have been made by the author by light microscopy, chemical analysis, and x-ray diffraction. These occurrences date from the Fourth Dynasty (2723–2563 B.C.) to the Ptolemaic period (332–30 B.C.) and were on tomb reliefs, sarcophagi, stone and wooden figures, cloth, and papyrus. The following lists a selected number of objects on which Egyptian blue was identified outside Egypt. The pigment's use, however, was far more abundant among ancient works of art than can be shown here.

Occurrences of Egyptian Blue in Locations Outside of Egypt

Date	*Site, Description Object, Collection, or Museum*	*Analyst and Method of Identification*
Greece		
3000–1100 B.C.	Knossos, wall paintings	Filippakis et al. (1976) Profi et al. (1976) micr., XRF, XRD
2500 B.C.	Keros Island, wall paintings	Filippakis et al. (1976) micr., XRF, XRD
before 1500 B.C.	Island of Thera (Santorini) Wall paintings	Filippakis et al. (1976) Profi et al. (1977) micr., XRF, XRD
1400–1100 B.C.	Mycenae, wall paintings	Profi et al. (1974) Filippakis et al. (1976) micr., XRF, XRD
1300 B.C.	Tiryns, wall paintings	Eibner (1926), chem.
580–500 B.C.	Aegina, facades of the temple	Riederer (1977b), XRD
400–108 B.C.	Pella, ancient Macedonia Wall paintings	Calamiotou et al. (1983) XRF, XRD
Roman Period		
1st C B.C.	Pompeii, Herculaneum Pigment from shops	Augusti (1967b) chem.
2nd C B.C.	Münsingen, Kanton Berne Switzerland Excavated wall paintings	Giovanoli (1969) XRD
2nd C A.D.	Hölstein, Kanton Basel-Land Switzerland Excavated wall paintings	Giovanoli (1969) XRD
2nd–3rd C A.D.	Cologne, Mainz, Bad Kreuznach Germany Excavated wall paintings	Riederer XRD
2nd–3rd C A.D.	England, various locations Wall paintings	Biek (1981) XRD
A.D. 350	Bø, Steigen parish, Norway Roman burial site, wooden shield	Rosenquist (1959) XRD
Middle Ages		
9th C A.D.	Church of San Clemente, Rome Wall paintings	Lazzarini (1982) XRD
9th C A.D.	Müstair convent, Switzerland Carolingian wall paintings	Mairinger and Schreiner (1986) LSA, micr., XRF, XRD

Method of Identification:
chem.=Chemical or microchemical tests
LSA=Laser emission spectroscopy
micr.=Light microscopy
XRD=X-ray diffraction
XRF=X-ray fluorescence spectroscopy

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2
Orpiment and Realgar

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1.0 Introduction

1.1 Pigment Definition

Orpiment is a yellow arsenic sulfide (As_2S_3) and realgar is a red arsenic sulfide (AsS or As_4S_4). Both pigments have been used in their natural and artificial forms. In the *Colour Index* (1971) orpiment is CI Pigment Yellow 39, nos. 77085, 77086. Realgar is not listed.

1.2 Current Terminology

Mineral orpiment; Artificial orpiment
English: orpiment; king's yellow
German: Rauschgelb, Operment; Königsgelb
French: orpiment; jaune royal, orpin artificiel
Spanish: oropimente
Italian: orpimento
Russian: аурипигмент; жёлтый мышьяк
Japanese: shiō, kiō, sekiō
Chinese: ci huang or shi huang (pinyin), tz'u huang or shih huang (Wade-Giles)

Mineral realgar
English: realgar
German: Realgar, Schwefelarsenik
French: réalgar
Spanish: rejalgar
Italian: realgar
Russian: реальгар
Japanese: yuō
Chinese: xiong huang (pinyin), hsiung huang (Wade-Giles)

In the seventeenth century the Japanese word *shiō* became the name for the yellow pigment gamboge and was replaced at that time by the name *sekiō* for orpiment (Oguchi, 1969).

2.0 History

2.1 Archaic and Historical Names

2.1.1 ***Orpiment.*** The Greek for orpiment, used by Theophrastus in the fourth century B.C. and by later Greek writers, was *arsenikon*. It was identified with *arsenikos*, male, from the belief that metals were of different sexes (Chemical Rubber, 1980–1981). The word is related to the Persian *zarnikh*, which is based on *zar*, the Persian for gold (Bailey, 1929). The Latin term *auripigmentum* or *auripigmento* (literally, gold paint) used by Pliny in the first century (Bailey, 1929) referred to the color and also to the fact that it was supposed to contain gold; this is the origin of the modern name (Palache et al., 1944). *Auripigmentum* was used by medieval writers such as Agricola (Hoover & Hoover, 1950) who also called it *operment*. The seventeenth-century Turquet de Mayerne manuscript refers to orpigment (De Mayerne, 1965–1967). In 1849 Mary Philadelphia Merrifield (1967) used the Spanish name *jalde* as well as *oropimente*. In the early nineteenth century orpiment imported to England from China was sold as Chinese yellow (Harley, 1982). Some modern names such as *Gelbe Arsenblende* or *arsenic sulfuré jaune* describe the color or chemical composition of orpiment.

2.1.2 ***Realgar.*** The Latin term used by Pliny (Bailey, 1932) was *sandarach*, which became the name *sandaraca* used by Agricola (Hoover & Hoover, 1950) who also referred to it as *rosgeel*. The name realgar comes from the Arabic *rahj al ghar*, powder of the mine (Palache et al., 1944). De Mayerne called it *rubis d'orpiment*. *Rote Arsenblende*, *Rauschrot*, and red orpiment are other terms that refer to its red color. Merrifield

gave it the Spanish name *jalde quemado* or *oropimente quemado*, that is, burnt orpiment. Artificial realgar is sometimes known as arsenic orange (Heaton, 1947), and the orange orpiment available in England in the nineteenth century (Carlyle, 1991) was probably realgar.

A watercolor sample labeled realgar in James Robert's *Introductory Lessons . . . painting in Water Colours* 1809 is, in fact, an earth color, therefore, it seems that other pigments were sold by that name for use as a watercolor (R. Harley, personal communication, 1986).

2.2 History of Use

In ancient Egypt orpiment and realgar were included in New Kingdom (sixteenth to eleventh century B.C.) offering lists (Iversen, 1955). Realgar has not been found on objects, but lumps of raw realgar and orpiment pigment were found in a fourteenth-century tomb (Saleh et al., 1974). Both were used in Egyptian cosmetics (Barthoux, 1925). Orpiment has been identified on objects and paintings from the thirty-first to the sixth century B.C. (see Occurrences and Spurrell, 1895; Lucas & Harris, 1962; Saleh, 1987). Orpiment has been identified on several third- to seventh-century Egyptian Coptic objects.

In ancient Mesopotamia both orpiment and realgar are listed in Assyrian medical texts (Partington, 1935). Orpiment was found mixed with beeswax on an eighth-century B.C. Assyrian writing board from Nimrud (Wiseman, 1953). Cakes of orpiment were found in the palace of Sargon II of about the same date (Forbes, 1955). A lump of orpiment was reported from the Hittite (thirteenth to eleventh century B.C.) remains in Zinjirli in Anatolia (Partington, 1935).

Realgar was used by Scythian and Sarmatian tribes (seventh to second centuries B.C.) in the area north of the Caspian Sea (Malevanny, 1968).

Although the classical writers were well acquainted with orpiment and realgar minerals as pigments, medicines, and poisons (Hoover & Hoover, 1950), few occurrences of the pigments have been reported on Greek objects. Realgar found at Corinth dates to the second century B.C. (Farnsworth, 1951). Both pigments occurred in the first century A.D. at Pompeii (Augusti, 1967), and realgar was found in Roman ruins at Silchester, England (Church, 1915).

An unusual occurrence of finely ground orpiment has been noted in the fourteenth-century painted decoration of the Al-Aqsa Mosque in Jerusalem (Lazzarini & Schwartzbaum, 1985). Both orpiment and realgar are mentioned in a manuscript on medieval Arab bookbinding of c. 1025 (Levy, 1962) and by a Persian author of c. 1606 (Minorsky, 1959). Orpiment has been identified on Armenian manuscripts from the eleventh to sixteenth centuries, on Arab fourteenth-century manuscripts, and on Persian miniatures from the early fourteenth to sixteenth centuries. Realgar has been reported on a sixteenth-century Armenian manuscript in the Walters Art Gallery, Baltimore. Both orpiment and realgar are described in fifteenth- to eighteenth-century recipes from Russia, Armenia, and Azerbaijan (Radosavijevic, 1976).

Orpiment is mentioned in Indian texts as early as the fourth century A.D. (Agrawal, 1969), and the pigment preparation by levigation of the ground mineral has been described (Bhattacharya, 1976). *Haritāla* is the most common Indian name for orpiment; for realgar it is *manaśśilā* (Bhattacharya, 1976). The earliest occurrence of orpiment on an Indian painting appears to be from the early twelfth century; it was used through the seventeenth century. A red, arsenic-containing pigment, suggested to be realgar, has been identified on sixteenth- to seventeenth-century Indian paintings (Cairns & Johnson, 1972; Johnson, 1972).

Orpiment and realgar are known to occur in Japan (Palache et al., 1944; Noguchi & Nakagawa, 1970). Both minerals were known there in the eighth century, although realgar was probably used only as a medicine (Uyemura, 1931). In the nineteenth century the best quality of both was said to be imported from China (Geerts, 1878). Realgar has not been found on Japanese objects, and orpiment occurs rarely. Orpiment has been found on a small number of ukiyo-e prints and paintings of the seventeenth to nineteenth centuries.

In China, both orpiment and realgar were known at an early date, at least by the second century B.C. and possibly by the fourth century B.C. (Needham, 1972). There are no references to their use as pigments, but they were important in Chinese medicine and metallurgy (Schafer, 1955). Neither orpiment nor realgar has been reported as a pigment on paintings or objects from China except that orpiment is known to have been used to color Chinese lacquer (Garner, 1963; Hornblower, 1963). Orpiment has been identified on Central Asian wall paintings from the sixth to the thirteenth centuries, and realgar was found on eleventh- to thirteenth-century wall paintings

from Kara Khoto (Gettens & Stout, 1966). Orpiment (*ser-po*) is listed as a typical pigment used for Tibetan paintings (Huntington, 1970), and it has been reported on Tibetan *thang-ka* paintings (Mehra, 1970). Various locations of the minerals were known to early Chinese writers; among the best-known sources were those in Kansu and Hunan provinces (Schafer, 1955). A more recent source in China for orpiment is Yunnan province (Watson, 1930).

In a traditional Thai painting technique, still in use today, yellow ink for writing and drawing on black paper manuscripts is made of orpiment (Boisselier, 1976).

Although orpiment has not been a common pigment on European works of art, it was used from the ninth-century *Book of Kells* (Sullivan, 1952) to late nineteenth-century impressionist paintings.

Medieval artists used orpiment imported from Asia Minor (Thompson, 1956), and it was listed as an item in African–Genoese trade in the twelfth century (Krueger, 1937). Theophilus described its use in the eleventh century (Hawthorne & Smith, 1963). Orpiment has been identified on Norwegian wooden altar frontals, polychrome sculpture, and folk art objects, including a crucifix (fig. 1). Orpiment and realgar were used in twelfth- to sixteenth-century icons from Bulgaria, Russia, and the former Yugoslavia (Filatov et al., 1965; Panev, 1979; Lelekova & Naumova, 1981). It was found in the early fifteenth-century palette of Jan van Eyck (Birren, 1965). In Venice, orpiment was purchased for a Romanian prince in 1600 (Filatov et al., 1965). Venice was well situated as a European source of pigment supplies as it was a port for trade with the East and a center of the cloth-dyeing industry (Plesters & Lazzarini, 1976). Orpiment and realgar have been mentioned in seventeenth-century pigment lists (De Mayerne, 1965–1967) and English seventeenth-century painting treatises (Talley, 1981); orpiment was used in seventeenth-century miniatures (Mascek, 1977). Thomas Bardwell listed orpiment among his pigments in 1756 but it has not been found in his paintings (Talley & Groen, 1975); it was also noted in Joshua Reynolds' palette in 1755 (Birren, 1965). Orpiment was used by J.M.W. Turner in late eighteenth- and early nineteenth-century oil paintings and oil sketches, but not in his later works (Townsend, 1993). Orpiment and realgar were reported in nineteenth-century pigment collections from Germany (Richter & Härlin, 1974) and Amsterdam (Pey, 1987). Kühn (1973), in a survey, identified orpiment on European paintings dating from 1300 to 1900.

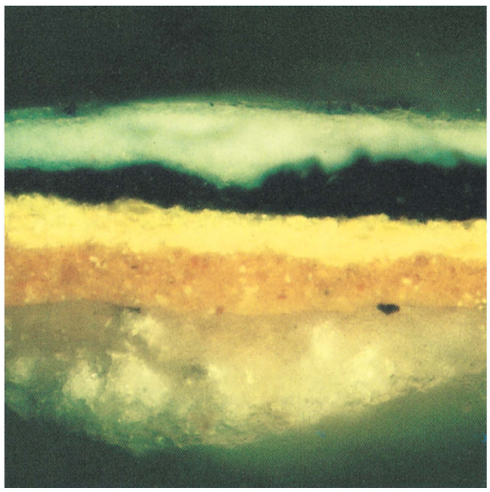


Fig. 1 Cross section, paint layers from wooden crucifix, Norway, 1150–1200. Universitetets Oldsaksamling, Oslo, no. 33267. The orpiment is underpainted with yellow ocher and covered with black with a superimposed white line on top from an adjacent area. From Unn S. Plahter. 230x.

Tintoretto (Jacopo Robusti) (1518–1594) made spectacular use of orpiment as well as realgar on some of his paintings. He used orpiment and realgar in the c. 1580–1585 *Portrait of Vincenzo Morosini* (fig. 2) in the National Gallery, London (Plesters, 1980). The composition of these pigments from Tintoretto's paintings is discussed in section 5.3.1.

In the Western Hemisphere orpiment has been identified on several eighteenth-century American oil paintings. King's yellow and "Orpiment, pale & deep" were listed by a shop in Boston in the 1760s as recent imports from London (Dow, 1927). In the late eighteenth century, François Baillairge in Quebec described an attempt to make "orpin" using arsenic. In describing orpiment, he used the term patent yellow; this term usually refers to the lead oxychloride pigment, and he also used it for that compound (Levenson, 1983). Orpiment has been found on a seventeenth-century painting from Peru.

Realgar has been identified with confidence on only a few works of art other than the Tintoretto occurrences cited above. Single examples are from an eleventh- to thirteenth-century manu-

Fig. 2 A. Tintoretto, *Portrait of Vincenzo Morosini*, c. 1580–1585, painting on canvas. Reproduced by permission of the Trustees, National Gallery, London, no. 4004.

script from Central Asia and a fifteenth-century Armenian manuscript. Realgar has been reported on Bulgarian icons dating from the Middle Ages to the Renaissance, and on Indian sixteenth- to seventeenth-century paintings. It was found on a painting by Titian (Tiziano Vicelli) (c.1480/1490–1576), paintings by Jean Chardin (1699–1779), and on an anonymous seventeenth-century American portrait painting. The brevity of this list may be some indication of the rarity of the pigment, but it may also reflect the limited identification methods available until recently for realgar.

2.3 **Dates of Use**

Orpiment, both natural and artificial, was used until the end of the nineteenth century. Because realgar has been so rarely identified, no definitive statement can be made about its use. Realgar's

B. Detail showing the use of orpiment and realgar in the embroidered stole on the figure's proper right shoulder (boxed area in 2A). The distinctive orange hue of realgar used alone is seen in the two patches of the narrow border on the proper right edge of the stole (Plesters, 1980).

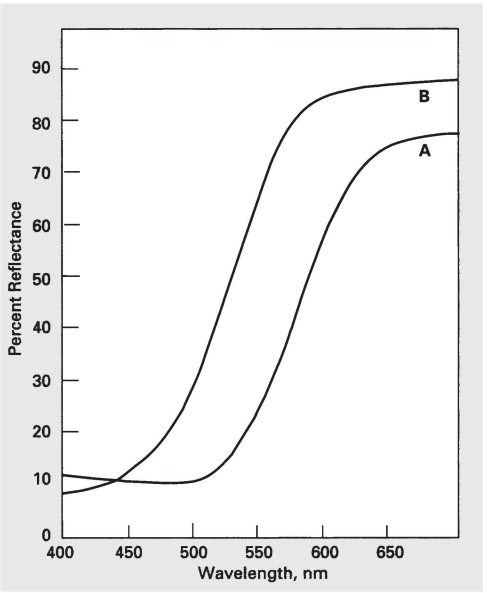


Fig. 3 Spectral reflectance of (A) natural orpiment and (B) realgar in parchment size. After Barnes (1939).

last known documented uses are in an eighteenth-century French painting and in a late-eighteenth- to nineteenth-century English pastel color box.

3.0 General Pigment Properties

3.1 Color and Spectral Reflectance

Orpiment is usually described as a lemon or canary yellow or sometimes as a golden or brownish yellow. Realgar is described as aurora-red to orange-yellow.

Orpiment is designated brilliant yellow, Munsell notation 4.4Y 8.7/8.9, and realgar is designated strong orange-yellow, Munsell notation 9.1YR 7.1/11.6 (Kelly & Judd, 1955).

Spectral reflectance curves have been published for orpiment and realgar (Barnes, 1939) (fig. 3).

3.2 Permanence

Early authorities described orpiment as fading readily (Weber, 1923), or at least to some degree (Laurie, 1914; Church, 1915) on exposure to light although Laurie (1967) also noted that the color of orpiment was unchanged on some illuminated manuscripts. Arsenic trisulfide is said to be stable to visible and ultraviolet light when dry; it decomposes slowly in cold water (faster in hot water) to arsenic trioxide and hydrogen sulfide, and is decomposed to arsenic trioxide by heating in air (Pascal, 1958). Orpiment showed severe color loss after exposure to ozone in the absence of light, converting to arsenic trioxide (Whitmore & Cass, 1988). Orpiment painted out in glue medium has partly altered to white arsenic trioxide after exposure to light for fifty years at the Fogg Museum of Art, Harvard University (Susan White, personal communication, 1984). Orpiment used to coat manuscript paper in Nepal to repel insects often turns white in time (Trier, 1972).

Realgar appears to be less permanent than orpiment and is known to change to orpiment after long exposure to light, with arsenic trioxide also forming (Weber, 1923; Palache et al., 1944; Reclus, 1956; Wells, 1975). The surface of two Chinese realgar figurines, probably from the eighteenth century, had oxidized to orpiment and arsenious oxide (Daniels, 1983). This yellow alteration product on realgar may, however, be pararealgar (Corbeil & Helwig, 1995). Laurie (1914) suggested that this change is evidenced by the presence of particles of realgar sometimes mixed with orpiment on illuminated manuscripts, but this realgar may be present as an impurity in the natural mineral and not because the orpiment is an alteration product. Museum specimens of realgar commonly show a yellow-orange alter-

ation (Clark, 1970). Heat or the presence of water vapor can accelerate the change (Pascal, 1958).

It has been reported that α-AsS, the high-temperature modification of realgar (see section 5.3.1), is considerably more permanent than realgar. When exposed to sunlight in both evacuated and open tubes for two years at 25°C, no change in the x-ray diffraction pattern was observed (Clark, 1970).

3.3 **Chemical Properties**

Orpiment powder darkens when heated. Its melting point is 300°C (Chemical Rubber, 1980–1981), although it has been cited as high as 325°C (Pascal, 1958). When heated in air it burns, producing arsenic trioxide (As_2O_3) and sulfur dioxide (SO_2). It sublimes between 703°C (Pascal, 1958) and 707°C (Chemical Rubber, 1980–1981). It decomposes slowly in water (see section 3.3). Artificial orpiment is more easily brought into solution than the mineral form due to its smaller particle size (Wallert, 1984). Orpiment is soluble in 3N hydrochloric acid (HCl), giving off hydrogen sulfide (H_2S), in concentrated nitric acid (HNO_3) giving off arsenic (As) and sulfuric acid (H_2SO_4), and in 4N sodium hydroxide (NaOH) (Plesters, 1956). It is also soluble in sulfuric acid (Larsen & Berman, 1934) and in solutions of ammonium carbonate and alkali sulfides (Mellor, 1961).

Realgar darkens when heated and returns to the original color when cooled (Pascal, 1968). When heated in air, it burns with a blue flame, producing arsenic trioxide and sulfur dioxide (Mellor, 1961). Its melting point is 307°C and it sublimes at 565°C (Chemical Rubber, 1980–1981). Realgar has the same solubilities as orpiment.

3.4 **Toxicity**

The toxicity of the arsenic sulfide pigments has been known since early times. Strabo described a *sandarach* mine in northern Anatolia where the mortality of the workers was so high that only criminals were sent there (Bailey, 1929). Artificial orpiment is extremely poisonous because of the presence of arsenic trioxide, a more soluble, and thus more toxic, compound than the sulfides (Reclus, 1956).

The toxic properties of orpiment have been used to advantage to repel insects. A recipe for treating Chinese book rolls with orpiment for this purpose is described in a fifth-century treatise (Van Gulik, 1958). Beginning in the sixteenth century in the Kathmandu Valley of Nepal, manuscript paper was coated with orpiment and yellow paper is still produced in the same way in Kathmandu (Trier, 1972).

Fig. 4 Detail of painting on paper, Firdawsi, *The Envoys of Salm and Tur before Faridun*, Iran (Shiraz) c. 1560, showing darkened lead white of face and turban of figure adjacent to a green background (an orpiment and indigo mixture) and a yellow robe (orpiment). Arthur M. Sackler Gallery, Smithsonian Institution, s1986.184. 22x.

3.5 **Compatibility**

Orpiment is said to be incompatible with lead- or copper-containing pigments (Weber, 1923). In the *Mappae Clavicula*, a twelfth-century medieval manuscript, this incompatibility with lead white and red lead was noted (Smith & Hawthorne, 1974), and fifteenth-century artisans knew that orpiment and copper-containing verdigris should not be used together (Thompson, 1956). The Strasburg Manuscript, however, recommends a mixture of orpiment and red lead to make golden flowers (Borradaile & Borradaile, 1966). Darkening of lead white adjacent to orpiment has been noted on Persian paintings in the Freer Gallery of Art, Smithsonian Institution, Washington (fig. 4) and in the Los Angeles County Museum of Art (Purinton & Watters, 1991).

Orpiment cannot be applied to wet plaster, a fact known to Pliny in the first century A.D. (Bailey, 1932) and noted by Cennino Cennini in the fifteenth century (Thompson, 1954).

A mixture of orpiment and indigo has been commonly used to produce green. This was noted by an eleventh-century Arab writer (Levey, 1962), in an Indian twelfth-century document (Coomaraswamy, 1934), and was known to Indian Mughal (1550–1750) painters (Brown, 1924). Cennini also noted this mixture (Thompson, 1954). It has been found on fourteenth- to sixteenth-century Indian and Persian paintings in the Freer Gallery of Art, and is common on thirteenth- to nineteenth-century Indian and West Asian paintings in the Arthur M. Sackler Gallery, Smithsonian Institution, Washington (FitzHugh, 1988). The orpiment-indigo mixture and orpiment mixed with red iron oxide to produce various shades of orange or pinkish brown have been found on Japanese ukiyo-e paintings in the Freer Gallery of Art.

Orpiment has been found mixed with azurite to give green on European late-medieval manuscript miniatures (Tosatti Soldano, 1980). A nineteenth-century set of pigments from Amsterdam included a mixture of orpiment, Prussian blue, and quartz labeled "Brownswijks groen" (Pey, 1987). Brunswick green is a term usually used for basic copper chlorides, but in the nineteenth century it also applied to mixed greens such as chrome yellow and Prussian blue (Harley, 1982). Green bice, a name occasionally given to artificial malachite, in the eighteenth century was sometimes applied to a mixture of orpiment and blue bice (at that time a name for smalt) (Harley, 1982).

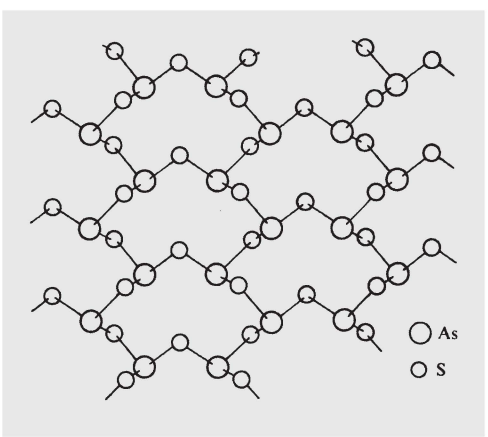


Fig. 5 A layer of the crystal structure of orpiment, As_2S_3. After fig. 20.12 in Wells (1975).

3.6 Oil Absorption and Grinding Properties

No data have been published on the oil absorption of orpiment. It is difficult to grind because of its micaceous structure. For this reason orpiment pigment is often quite coarse.

Francisco Pacheco in *El arte de la pintura* in 1649 mentioned the need to add a drier such as red lead or ground glass to a paint consisting of orpiment in linseed oil or to dry pigment (Veliz, 1982). The ground glass also served to facilitate grinding the pigment (Wallert, 1984).

4.0 Composition

4.1 Chemical Composition

Orpiment is arsenic trisulfide (As_2S_3) (fig. 5) and realgar is arsenic sulfide with the formula variously given as AsS, As_2S_2, and As_4S_4 (fig. 6).

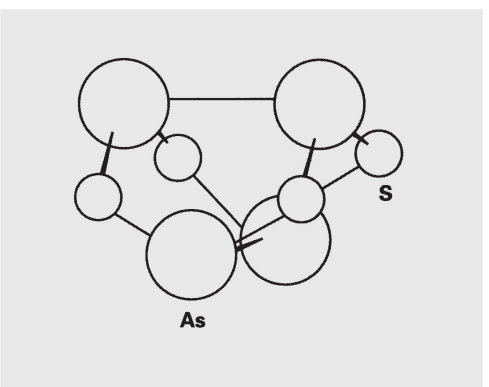


Fig. 6 Structure of a realgar molecule, As_4S_4. After fig. 20.11 in Wells (1975).

Realgar is known chemically as arsenic disulfide (As_2S_2). When sublimed in vacuo at temperatures up to 550°C, the vapor density corresponds to As_4S_4 and the structure of this molecule, shown in figure 6, is known (Wells, 1975). The molecular structure of mineral realgar consists of separate As_4S_4 molecules held together by Van de Waals forces (Ito et al., 1952). Orpiment and realgar are naturally occurring minerals both belonging to the monoclinic crystal system (fig. 7). Artificial orpiment (king's yellow) has the same composition as the mineral. It appears that other arsenic compounds can occur with the two more well-known minerals (see section 5.3.1).

Fig. 7 Mineral specimens, *left*: realgar from Manhattan, Nevada, no. R16948 and *right*: orpiment from Baden, Germany, no. 53044. Department of Mineral Sciences, Smithsonian Institution, Washington.

4.2 **Sources**

The mineral orpiment occurs as a low-temperature product in hydrothermal veins, as a hot-spring deposit, as a volcanic sublimation product, and in mine fires. It can be associated with stibnite, pyrite, fluorite, various lead sulfosalts, realgar, native arsenic, calcite, barite, and gypsum. It is a common alteration product of other arsenic minerals, especially realgar (Palache et al., 1944). It is found in Hungary, Romania, Germany, Austria, the former Yugoslavia, Greece, Switzerland, France, Italy, Turkey, republic of Georgia, Iran, Peru, China, Japan, and the western United States (Palache et al., 1944). It is also found in Iraq (Thompson, 1925), Myanmar (Burma) (Read & Pak, 1936), and in the Himalayas (Trier, 1972). According to the eleventh-century Arab scholar Al-Bīrūnī, orpiment came from the Pontus area of Turkey, Armenia, and Iraq (Hamarneh, 1973).

The mineral realgar occurs as a minor constituent in certain ore veins associated with orpiment and other arsenic minerals, with stibnite, and lead, silver, and gold ores. It occurs as a hot-spring deposit, as a volcanic sublimation product, in certain limestones or dolomites, and in clay rocks (Palache et al., 1944). It is found in Romania, the former Czechoslovakia, and the former Yugoslavia, Greece, Germany, Switzerland, Italy, Corsica, Japan, and the western United States (Palache et al., 1944). The world's largest mineral deposit of realgar is found in Hunan province, China (Yu, 1987). It is also found in Iraq (Thompson, 1925), the Caucasus, Iran, and Afghanistan (Malevanny, 1968) and, according to Al-Bīrūnī, in Nishapur, Iran (Hamarneh, 1973).

The classical writers were aware of many of the mineral deposits in northern Anatolia, Persia, and the Ukraine. Pliny also reported the existence of realgar on an island in the Red Sea (Bailey, 1932).

4.3 **Preparation**

Naturally occurring orpiment and realgar minerals were prepared by grinding and sometimes also by levigation. The difficulty of powdering orpiment was mentioned by Cennini, although he appears to have been referring to the artificial material, which would not have been as difficult to grind as the mineral (Thompson, 1954).

The Arab alchemists referred to realgar and orpiment as "the two kings" (Crosland, 1978) but it is unclear if this is the source of the term king's yellow for artificial orpiment. The term king's yellow and references to artificial orpiment are not found in English language sources before the eighteenth century, although the Dutch used the artificial material in the seventeenth century (Harley, 1982). Harley suggested that orpiment referred to the synthetic and natural material before the eighteenth century. A paint box from Ackermann of London, dated to between 1796 and 1827, now in the National Gallery Science Laboratory, London, contains two watercolor cakes labeled "King's Yellow" and "Red Orpi-

ment" (see section 5.3.1). The term king's yellow can also apply to chrome yellow or to a mixture of chrome yellow or cadmium yellow with zinc white (Weber, 1923; *Colour Index*, 1971).

Wallert (1984), who summarized methods of producing artificial orpiment and realgar, suggested the same terminology that is applied to the making of artificial vermilion. Production of orpiment by heating, with or without sublimation, can be referred to as "dry-process" methods and precipitation methods employing materials in solution can be called "wet-process" methods.

Pliny, in the first century, described orpiment as a natural pigment, as opposed to being manufactured (Bailey, 1932), evidently the earliest mention of the fact that an artificially prepared pigment existed. Cennini in the fourteenth century, referred to orpiment as "an artificial material . . . made by alchemy" (Thompson, 1954). Wallert (1984) suggested that Cennini may have prepared orpiment by sublimating the mineral with or without sulfur. Jehan le Begue, in the fifteenth century, described heating red sulfur and red orpiment to get a gold color (Merrifield, 1967). Wallert cited an unpublished early fifteenth-century Italian manuscript that discussed a preparation method that involved heating. The seventeenth-century Paduan manuscript published by Merrifield (1967), describes heating orpiment followed by grinding, with no reference to sublimation.

The first definite reference to the dry-process preparation of orpiment by sublimation appears to be by Robert Dossie in *The Handmaid to the Arts* (1758). He discussed "King's yellow or pure orpiment," which "must be prepared by mixing sulphur and arsenic by sublimation." He stated that king's yellow can also be obtained by subliming "comon orpiment" (the natural mineral), which he said was "very seldom employed in its unrefined state." In the nineteenth century, dry-process orpiment was made by sublimation of a mixture of sulfur and arsenic trioxide (As_2O_3) (Wallert, 1984).

Little is known about the history of artificial realgar. The seventeenth-century Paduan manuscript mentioned above describes melting, cooling, and grinding orpiment to get "red orpiment" (Merrifield, 1967). George Field noted that there were native and manufactured varieties of realgar in England in the early nineteenth century (Harley, 1982).

Wet-process methods of producing orpiment have been described, but there appears to be no evidence that the precipitated material was used as a pigment (see section 5.1).

At present, synthetic arsenic trisulfide (As_2S_3) can be prepared by fusing arsenic or arsenic trioxide (As_2O_3) with sulfur. Heating a mixture of pyrite (FeS_2) and arsenopyrite (FeAsS) will yield a mixture of orpiment and realgar by sublimation (Mellor, 1961). These methods yield impure mixtures, which must be further purified (Pascal, 1958). Arsenic trisulfide also results when hydrogen sulfide is passed through a hydrochloric acid solution of arsenic trioxide; this product is very toxic because some arsenic trioxide always remains (Reclus, 1956).

Synthetic realgar (AsS) is prepared by the same sublimation methods by varying the proportions. It can also be produced by fusion of sulfur and arsenic in the presence of carbon (Reclus, 1956). One method of preparation is by heating orpiment with arsenic (Mellor, 1961). There are other methods for preparing both compounds, but they are not used on a commercial scale (Pascal, 1958).

There is an 1846 Japanese reference to orpiment being produced by the burning of "arsenical stones" and also by heating arsenical ores with sulfur (Takamatsu, 1879–1880).

4.4 Adulteration and Sophistication

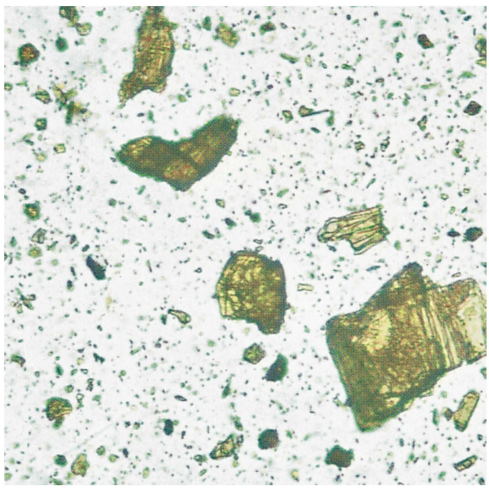
Mineral orpiment is always remarkably pure while synthetic orpiment is often contaminated with white arsenic trioxide (arsenolite), one of the compounds used in its preparation (see sections 4.3 and 5.3.1).

5.0 Identification and Characterization

5.1 Optical Microscopy

The refractive indices of orpiment are, α 2.4±, β 2.81, γ 3.02 (Larsen & Berman, 1934). In transmitted light the color is various shades of lemon yellow (fig. 8A). It is biaxial negative and strongly anisotropic. Distinctive yellow internal reflection masks interference colors (Short, 1964). The distinctive anomalous polarization colors of green to blue, as seen in figures 8B and 9, are useful for identification of orpiment (McCrone, 1982). The color in vertically reflected light, as seen in cross section, is gray (Short, 1964).

The mineral orpiment belongs to the monoclinic crystal system. In habit it is short prismatic and usually foliated, columnar, or in fibrous



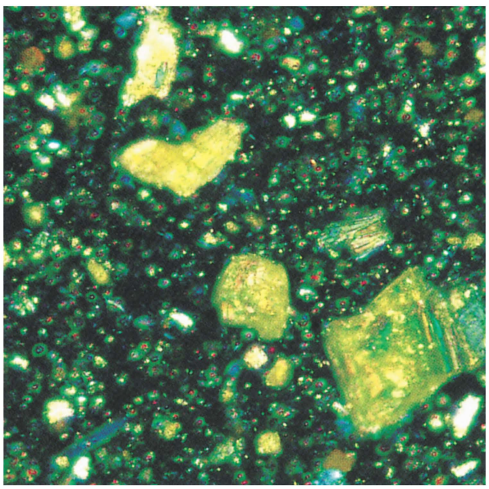


Fig. 8 Photomicrographs of orpiment from beeswax layer on Assyrian writing board from Nimrud, Iraq, eighth century. British School of Archaeology in Iraq. Mounted in Canada balsam, n=1.53. 230x.

A. By transmitted light.

B. Same field in crossed polars.

masses; it can occur as reniform or botryoidal aggregates and is sometimes granular or pulverulent (Palache et al., 1944). There is often perfect cleavage on {010} (Larsen & Berman, 1934). Its luster is pearly on the cleavage surface and resinous elsewhere. Its hardness is 1.5 to 2 and its specific gravity is 3.48 (calculated) (Palache et al., 1944).

Orpiment pigment particles are usually coarse, of somewhat limited transparency, and their foliated, micaceous structure is readily apparent on microscopic examination. The flat, shiny surface of the particles, particularly when coarse, often gives a glittering, sparkling appearance to the area where the pigment is used.

There is no objective way to distinguish between the naturally occurring mineral orpiment and the dry-process artificial material. Their properties are identical, except that the artificial material is more finely divided; the ground mineral can, however, include small as well as large particles. From x-ray diffraction we know that artificial orpiment may contain arsenolite (see section 5.3.1) and some differentiation might be based on the presence of this or other impurities. Scanning electron micrographs can show the structure of artificial orpiment in detail (see Wallert, 1984) and possibly further examination of the artificial material by this method would be productive.

It is presumed that the finely divided crystalline orpiment present in pigments supplied by nineteenth- and twentieth-century color makers is dry-process orpiment and not finely ground natural mineral. The king's yellow from the Ackermann paint box and that supplied by Roberson contain arsenolite; the smallest particle size in the latter was 10 μm. The particle size of orpiment used to color Chinese lacquer ranged from 10 to 12 μm (Hornblower, 1963); it is possible that this was artificial material, but no historical evidence exists that orpiment was prepared artificially in China. In contrast, in the pigment from a late nineteenth-century Japanese painting the largest particle size is about 30 μm, suggesting that it is ground mineral orpiment (see fig. 9).

Wet-process arsenic sulfide was prepared by John Winter, in the Department of Conservation and Scientific Research, Arthur M. Sackler Gallery and Freer Gallery of Art, by passing hydrogen sulfide through a hydrochloric acid solution of arsenic trioxide. This arsenic sulfide has a particle size of about 1 μm and did not yield an x-ray diffraction pattern, because it is amorphous and very finely divided. The round, regular appearance of the particles is typical of a precipitated material (fig. 10). There is no evidence to date that arsenic sulfide pigments prepared by the wet-process were ever used.

The refractive indices of realgar are, α 2.538, β 2.684, γ 2.704, slightly lower than orpiment

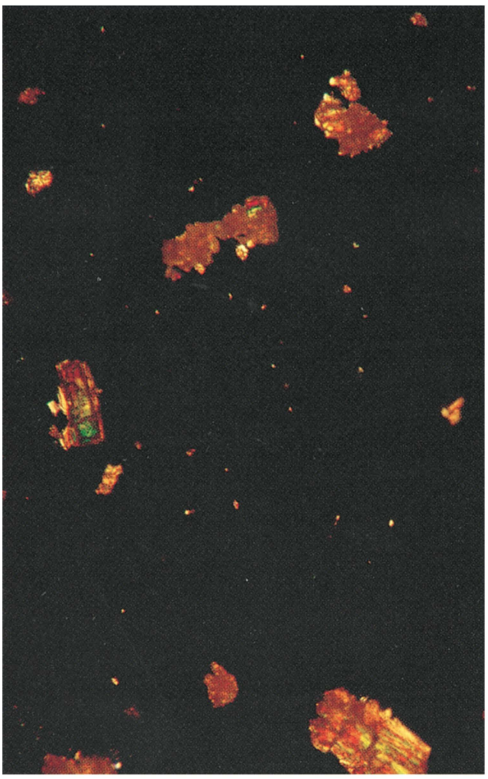
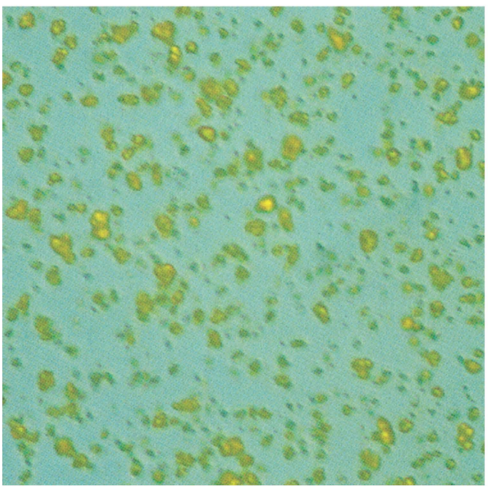


Fig. 9 Photomicrograph in crossed polars of orpiment from late nineteenth-century Japanese painting on silk, style of Hokusai, *Collecting Shellfish at Low Tide*. Freer Gallery of Art 03.2. Mounted in Aroclor 5442, n=1.66. 360x.

Fig. 10 Photomicrograph in partly crossed polars of artificial As_2S_3 produced by precipitation. Mounted in Aroclor 5442, n=1.66. 410x.



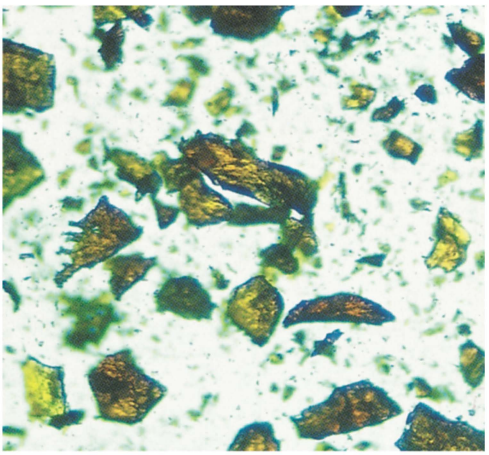
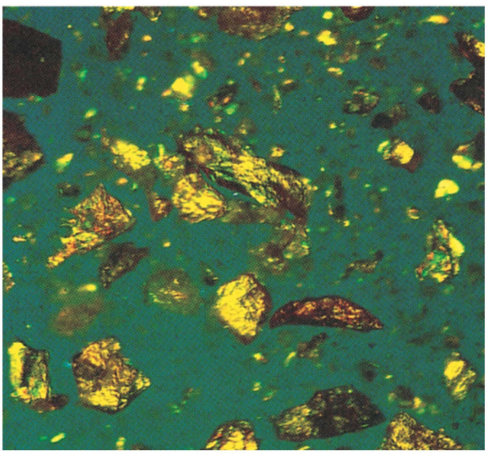


Fig. 11 Photomicrographs of realgar from Pompeii, slightly crushed for mounting. Mounted in Aroclor 5442, n=1.66. Sample from Selim Augusti. 60x.

A. By transmitted light.

B. Same field in partly crossed polars.



(Palache et al., 1944). In transmitted light the color is orange-red (fig. 11). Realgar is isotropic (Short, 1964) and shows distinctive orange internal reflection. The color in vertically reflected light, as seen in cross section, is bluish gray (Short, 1964).

The mineral realgar is also monoclinic. In habit it is short prismatic and striated. It is usually granular, coarse to fine, or compact, or as an encrustation. Cleavage is good on {010}. Small conchoidal fractures are sometimes seen. Its luster is resinous to greasy. Its hardness is 1.5 to 2 and its specific gravity is 3.59 (calculated) (Palache et al., 1944).

Little is known about the microscopic properties of artificial realgar.

5.2 Chemical Microscopy

On heating, orpiment becomes colorless because of its oxidation to white arsenic trioxide (As_2O_3). De Wild (1929) wrote that these crystals of arsenic trioxide can be condensed and observed on a microscope slide.

The effect of acids on orpiment and realgar has been described (see section 3.4). R. J. Gettens (unpublished) noted that when orpiment is treated with concentrated nitric acid on a microscope slide, arsenic trioxide (As_2O_3) forms as tiny refracting octahedra in little clusters at the edge of the drop; the clusters do not have the tendency to dendritic formation shown by lead nitrate ($Pb(NO_3)_2$), although they can be confused with lead nitrate octahedra.

Several tests for arsenic (or arsenate) are possible by chemical microscopy.

The ammonium molybdate test for arsenic is sensitive, subject to practically no interferences, and is not difficult to carry out. Orpiment or realgar are decomposed with aqua regia and the residue is taken up with 1:7 nitric acid (HNO_3) and the solution is evaporated almost to dryness. A drop of ammonium molybdate solution (1.5% in 1:7 nitric acid) is added and slowly evaporated. Tiny lemon-yellow crystals of ammonium arseni-molybdate form. These crystals are very small and nearly spherical and therefore their octahedral shape cannot always be seen; tiny crosses are common and give the solution a scintillating appearance before it goes to dryness (fig. 12). If 1:7 nitric acid is added, it will dissolve any excess ammonium molybdate. The crystals are isotropic in polarized light. The limit of detection is 0.01% ammonium arseni-molybdate (Chamot & Mason, 1940; Short, 1964).

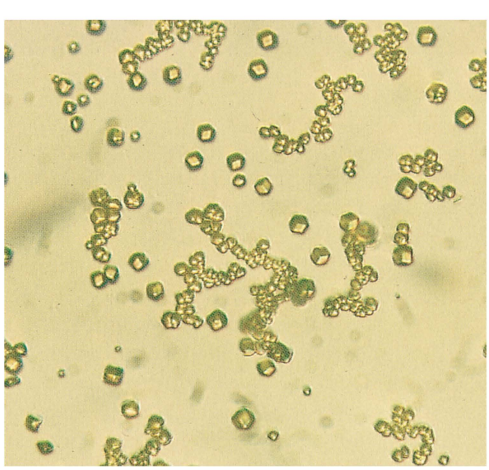


Fig. 12 Test for arsenic with ammonium molybdate. By transmitted light. 360x.

In the test with stannous chloride, metallic arsenic forms (Plesters, 1956). The pigment is dissolved in concentrated hydrochloric acid, and a drop or two of saturated stannous chloride solution is added. Arsenic precipitates as a blackish brown solid.

For the test utilizing the formation of silver arsenate, the unknown is warmed with ammonia and 10% hydrogen peroxide in a platinum crucible and then acidified with acetic acid and one to two drops of 1% silver nitrate ($AgNO_3$); red-brown silver arsenate forms (Chamot & Mason, 1940; Plesters, 1956).

Other tests by chemical microscopy include the potassium iodide and cesium double-iodide tests (Chamot & Mason, 1940; Short, 1964), detection as arsine in an adaption of the Marsh test, or reduction to metallic arsenic and subsequent oxidation to arsenic trioxide, and various other tests for arsenate (Chamot & Mason, 1940).

Tests may also be made for sulfur or sulfide, although these are not generally necessary.

Several spot tests are available for arsenic. The most sensitive is the detection of arsenic(III) with kairine and ferric chloride. The limit of detection is 0.005γ arsenic (Feigl & Anger, 1972).

5.3 Instrumental Methods of Analysis

5.3.1 *X-ray diffraction.*

Orpiment and realgar. Orpiment is readily identified by x-ray powder diffraction. Identification of realgar by x-ray diffraction should be carried out with care, however, because of the possible presence of other orange-red arsenic sulfides. See tables 1, 2, and 3 for *d*-spacings and figure 13 for x-ray diffraction patterns of orpiment, realgar, and related minerals.

Other arsenic sulfide minerals. A number of reddish orange and yellow arsenic sulfide minerals are known to occur with orpiment and realgar; these are listed in table 4. One of these minerals is pararealgar (AsS), a polymorph of realgar, which varies in color from bright yellow to orange-yellow to orange-brown (Roberts et al., 1980). Pararealgar has recently been identified on a sixteenth- to seventeenth-century European painting, *Holy Family and Saint* (Winnipeg Art Gallery G36-107) (Corbeil & Helwig, 1995).

Table 1 **X-ray Diffraction Data for Orpiment, Realgar, and Arsenolite**

King's Yellow Ackermann Freer F1685		*Red Orpiment Ackermann Freer F1711*		*Arsenolite JCPDS 4-0566**		*Orpiment JCPDS 19-84**		*Realgar JCPDS 24-77**		*Tintoretto Santo Stefano Orange Pigment Freer F2085*		*Tintoretto San Rocco Yellow Pigment Freer F2088*	
d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
—	—	—	—	—	—	—	—	—	—	—	—	10.78	20
—	—	—	—	—	—	—	—	—	—	9.83	<10	—	—
—	—	—	—	—	—	—	—	—	—	7.57	20	—	—
—	—	—	—	—	—	7.50	5	—	—	—	—	—	—
—	—	—	—	—	—	—	—	7.406	8	—	—	7.44	20
7.25	10	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	6.758	18	6.76	10	6.81	20
6.37	30	6.37	80	6.394	63	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	6.026	35	—	—	6.03	70
5.99	10	—	—	—	—	—	—	—	—	—	—	—	—
—	—	5.83	100	—	—	—	—	—	—	—	—	—	—
5.79	10	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	5.728	55	5.72	20	5.75	80
—	—	—	—	—	—	—	—	—	—	5.57	100	—	—
—	—	—	—	—	—	—	—	5.505	20	—	—	—	—
—	—	—	—	—	—	—	—	—	—	5.47	<10	—	—
5.37	30	—	—	—	—	—	—	5.411	100	—	—	5.37	100b
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	5.04	10	—	—	—	—	—	—	5.10	100	5.10	40
—	—	—	—	—	—	—	—	—	—	4.96	20	—	—
4.82	100	—	—	—	—	4.85	100	—	—	4.82	20	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	4.618	16	—	—	4.62	10
4.40	<10	—	—	—	—	4.44	5	—	—	—	—	—	—
—	—	4.31	<10	—	—	—	—	—	—	—	—	4.29	20
4.25	<10	—	—	—	—	—	—	4.244	6	4.25	20	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	4.068	14	—	—	4.06	20
—	—	—	—	—	—	4.02	50	—	—	—	—	—	—
3.95	20	3.93	10	3.920	<1	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	3.790	6	3.79	<10	—	—
—	—	—	—	—	—	—	—	—	—	3.75	90	3.75	30b
—	—	—	—	—	—	—	—	3.726	12	—	—	—	—
3.68	20	—	—	—	—	3.71	20	—	—	—	—	—	—
—	—	—	—	—	—	—	—	3.677	8	—	—	—	—
—	—	—	—	—	—	—	—	3.604	12	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
3.36	20	3.35	10	—	—	—	—	—	—	3.43	<10	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	3.29	80	—	—
3.20	70	3.19	90	3.195	100	3.22	30	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	3.18	10
—	—	—	—	—	—	—	—	3.164	80	3.18	20b	3.16	100
3.07	20	3.05	60	—	—	3.07	20	3.048	55	3.09–3.01	60	3.06	70
—	—	—	—	—	—	—	—	—	—		—	—	—

Intensities of *JCPDS* 24-77 and 4-0566 measured by diffractometer; *JCPDS* 19-84 measurement method not given; all others determined visually.

*From JCPDS International Centre for Diffraction Data (*JCPDS*, 1990).

b=Broad line

Table 1 Continued

King's Yellow Ackermann Freer F1685		*Red Orpiment Ackermann Freer F1711*		*Arsenolite JCPDS 4-0566**		*Orpiment JCPDS 19-84**		*Realgar JCPDS 24-77**		*Tintoretto Santo Stefano Orange Pigment Freer F2085*		*Tintoretto San Rocco Yellow Pigment Freer F2088*	
d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
2.98	>10	2.99	60	—	—	3.02	5	—	—	—	—	—	—
—	—	—	—	—	—	—	—	2.983	50	—	—	—	—
2.95	>10	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	2.943	35	—	—	—	—
—	—	—	—	—	—	—	—	2.925	60	2.93–	40	2.93	60
2.85	50	2.89	70b	—	—	2.89	20	—	—	–2.87	—	2.87	30
—	—	—	—	—	—	—	—	2.861	16	—	—	—	—
2.80	50	—	—	—	—	2.79	30	—	—	2.80	70	2.81	20
—	—	—	—	—	—	—	—	2.776	10	—	—	—	—
—	—	—	—	2.768	28	—	—	—	—	—	—	—	—
2.72	50	—	—	—	—	2.72	30	2.722	70	—	—	2.74	30
—	—	—	—	—	—	—	—	2.698	25	—	—	—	—
—	—	—	—	—	—	—	—	2.650	8	—	—	—	—
—	—	—	—	—	—	—	—	2.591	25	—	—	2.59	10
2.54	20	2.54	40	2.541	38	2.56	20	—	—	—	—	—	—
—	—	—	—	—	—	—	—	2.515	12	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	2.486	18	—	—	—	—
2.46	20	—	—	—	—	2.47	40	—	—	—	—	—	—
—	—	—	—	—	—	—	—	2.465	35	—	—	—	—
—	—	—	—	—	—	—	—	2.442	25	—	—	—	—
2.40	>10	2.40	>10	—	—	—	—	—	—	—	—	—	—
2.35	>10	—	—	—	—	2.34	5	—	—	—	—	—	—
2.30	>10	—	—	—	—	2.32	5	—	—	—	—	—	—
—	—	2.27	30	2.262	12	—	—	2.261	30	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	2.22	5	—	—	—	—	—	—
—	—	—	—	—	—	—	—	2.191	20	—	—	2.19	10
—	—	—	—	—	—	—	—	—	—	—	—	—	—
2.13	30	2.13	>10	2.132	17	2.14	10	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	2.12	20
2.08	20b	—	—	—	—	2.09	30	—	—	—	—	—	—
2.02	10	—	—	—	—	2.04	20	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
1.95	10	1.95	10	1.958	27	1.969	5	—	—	—	—	—	—
1.90	10	—	—	—	—	1.914	20	—	—	—	—	—	—
1.86	10b	—	—	1.873	6	1.862	10	—	—	—	—	1.85	20b
1.82	>10	—	—	1.846	5	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
1.75	20b	—	—	—	—	1.755	40	—	—	—	—	—	—
1.71	>10	—	—	—	—	1.710	5	—	—	—	—	—	—
1.68	30b	—	—	1.670	21	1.689	30	—	—	—	—	—	—
1.63	10b	—	—	—	—	1.642	10	—	—	—	—	—	—
—	—	—	—	—	—	1.600	5	—	—	—	—	—	—
—	—	—	—	1.599	10	—	—	—	—	—	—	—	—
1.54	20b	—	—	1.551	22	—	—	—	—	—	—	—	—
				+ weak additional lines		+ weak additional lines							

Table 2 **X-ray Diffraction Data for Arsenic Sulfide Minerals Other Than Orpiment and Realgar**[a, b]

Alacranite JCPDS 25-27		*Pararealgar JCPDS 33-127*		*Duranusite JCPDS 25-1479*		*Dimorphite I JCPDS 26-125*		*Dimorphite II JCPDS 26-126*	
d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
5.75	80	5.56	90	5.62	90	6.27	50	4.89	100
3.93	70	5.14	100	5.04	90	5.16	100	2.14	50
3.20	80	3.75	80	3.38	60	3.12	60	1.620	50
3.08	70	3.299	50	3.20	50b	2.96	50		
3.01	100	3.025	50	3.02	70				
2.89	100	2.795	70	2.919	100				
2.82	60			2.808	70				
				2.682	80				
				1.969	90				
				1.788	90				
				b=Broad line					

a. Data from *JCPDS* (1990).
b. All lines of *I*-50 and above.

Duranusite (As_4S), another mineral that occurs with realgar, is reddish orange. A specimen of duranusite with realgar from the Duranus Alps, Maritimes, France, was examined and sampled (13203, Department of Mineral Sciences, Smithsonian Institution). The x-ray diffraction pattern obtained was that of realgar alone; if present in sufficient quantities, duranusite should be identifiable by x-ray diffraction. Duranusite and realgar could not be differentiated in the sample when examined in a microscope slide at low magnification.

Alacranite (α-AsS), a high-temperature structural modification of realgar (β-AsS) was found with realgar in Chile (Clark, 1970) and has also been synthesized (Roland, 1972; Yu & Zoltai, 1972; and *JCPDS*, 1990, file no. 24-78). Alacranite is slightly paler and more yellowish in color than the realgar from the same deposit, which is described as being a richer reddish orange than most realgar specimens. Alacranite is monoclinic and its optical properties in a polished cross section are not noticeably different from those of realgar (Clark, 1970). It was identified at the Conservation Analytical Laboratory, Smithsonian Institution, on an early Colonial-era Mexican painted deerskin, now in the Firestone Library, Princeton University, using x-ray powder diffraction and x-ray fluorescence (J. Mishara, personal communication, 1986).

Another yellow modification of realgar, which is probably triclinic, develops on light-radiated realgar (Cahoon, 1965). This photochemical reaction product was found on a realgar specimen in the E. W. Forbes Pigment Collection that had been on display in the Fogg Art Museum, Harvard University, and exposed to light for over thirty years. This alteration product also formed on realgar exposed to light and mounted in collodion on a microscope slide for several weeks (Stodulski et al., 1984). The three strongest lines are at 5.59, 5.12, and 2.80 Å (table 3); this compound is not listed in the *JCPDS* 1988 file. It has not been found used as a pigment, but could conceivably form as an alteration product in conditions where a painted object or painting was exposed to light. It has been pointed out that this alteration product may be pararealgar (Corbeil & Helwig, 1995).

Dimorphite (As_4S_3) is a yellow mineral associated with orpiment and realgar. Orange-yellow crystals of dimorphite were first identified in 1849 by A. Scacchi, who suggested that two forms of the mineral existed (Palache et al., 1944). Whitfield synthesized the compound As_4S_3 and purified it by vacuum sublimation to yield either α- or β-dimorphite, depending on the temperature at which it condenses; he determined the crystal structure of α-dimorphite, which is similar to dimorphite I. The *JCPDS* 1990 file lists two dimorphite patterns (see table 2). The type specimen of dimorphite supplied by Scacchi in 1876 is a dull yellow, rather like a yellow ocher in color (R364, Department of Mineral Sciences, Smithsonian Institution). It is chiefly dimorphite II with possibly some of a third dimorphite (*JCPDS*, 1988, file no. 17-2907), which is no longer listed

Table 3 **X-ray Diffraction Data for Reaction Product from Realgar Radiated by Sunlight**[a]

d (Å)	*I*
9.74	5
6.89	5
6.38	20
5.59	100
5.12	100
4.93	10
4.82	10
4.20	5
3.75	70
3.43	10
3.34	10
3.29	60
3.20	10
3.10	20
2.98	30
2.91	10
2.80	100
2.66	5
2.61	5
2.53	10
2.45	10
2.37	5
2.31	5
2.28	10
2.22	5
2.19	5
2.13	5
2.11	5
2.06	5
2.03	10
1.97	5
1.86	5
1.84	5
1.82	5
1.81	5
1.78	5
1.74	5
1.71	5
1.68	5
1.55	5

a. Data from Cahoon (1965).

in the JCPDS file, and with some unidentified lines. Dimorphite I and II, chiefly the latter, have been identified with orpiment in ancient (third millennium B.C.) Egyptian paintings from Giza (Noll, 1981).

Pigments from Tintoretto paintings. Samples (see fig. 13F–G) of realgar from two paintings in Venice by Tintoretto supplied by Joyce Plesters (while at the National Gallery, London), are from an orange robe in *The Last Supper* in the Church of Santo Stefano and a yellow robe in *The Israelites Gathering Manna*, in the Scuola di San Rocco (Plesters & Lazzarini, 1976).

Both samples had the microscopical appearance of realgar and gave a positive test for arsenate with the ammonium molybdate test by chemical microscopy. X-ray powder diffraction confirmed the presence of realgar in the sample from the Scuola di San Rocco (see table 1 and fig. 13F). All strong realgar lines, with intensity of 50 and above, except *d* 2.983 Å, are present and there is some indication of the presence of pararealgar. Of the non-realgar lines in the San Rocco sample of intensity 30 and above, 5.10 and 3.75 Å may represent pararealgar and 2.87 Å may be duranusite.

The x-ray diffraction pattern of the sample from the Church of Santo Stefano (see table 1 and fig. 13G) shows no realgar lines, probably because of the small sample size. It seems to show very definite pararealgar lines at 5.57, 5.10, 3.75, and 2.80 Å.

Alacranite may be present in these Tintoretto pigments, but the strong lines coincide so closely with those of realgar that no definite conclusion can be drawn about the presence or absence of this mineral. There are so many overlapping lines among these arsenic sulfide minerals that definite identification is extremely difficult. The presence of other minerals is possible; several arsenic sulfides of uncertain structure are listed in the *JCPDS* 1990 file.

Artificial arsenic sulfide pigments. A study by x-ray powder diffraction of manufactured arsenic sulfide pigments shows arsenolite (As_2O_3) to be a major constituent (see table 1). The two Ackermann's watercolor cakes made between 1796 and 1827 contain arsenolite. The cake labeled "King's Yellow" is a mixture of orpiment, realgar, and arsenolite. The cake labeled red orpiment contains arsenolite, and possibly some alacranite, as indicated by the presence of lines at 5.75, 3.08, 3.01, and 2.89 Å. If realgar is present, it is in amounts too small to show in the x-ray diffraction pattern.

Two twentieth-century "orpiments" in the Arthur M. Sackler Gallery and Freer Gallery of Art, Department of Conservation and Scientific Research collection from the two supply houses of Fezandie and Sperrle and C. Roberson and Co. Ltd. are also chiefly composed of arsenolite. Since arsenolite is one of the starting materials for the preparation of artificial orpiment and realgar,

Table 4 **Arsenic Sulfide Minerals Associated with Orpiment and Realgar in Nature That Might Occur in Orpiment and Realgar Pigments**

Mineral Name	*Composition*	*Occurrence*	*Crystal Form*	*Color*	*JCPDS No.*	*Reference*
Pararealgar	AsS	With realgar	Monoclinic	Bright yellow to orange-yellow to orange-brown	33-127	Roberts et al., 1980
Duranusite	As_4S	With realgar	Orthorhombic	Reddish orange[a]	25-1479	Johan et al., 1973
Alacranite	α-AsS	With realgar	Monoclinic	Reddish orange	25-27	Clark, 1972
Dimorphite	As_4S_3	With orpiment and realgar	Orthorhombic	Orange-yellow	26-125 Dimorphite I 26-126 Dimorphite II	Whitfield, 1970

a. Color description in the *JCPDS* file as pale gray is incorrect. The pale gray refers to the color of a polished section in vertically reflected light (Johan et al., 1973).

its presence in these pigments is not surprising. Presumably it might also represent an alteration product (see section 3.3).

Twentieth-century Persian pigments. Two sets of dry pigments used for miniature painting, purchased in Iran in 1935, are in the Arthur M. Sackler Gallery and Freer Gallery of Art, Department of Conservation and Scientific Research. One was obtained by Myron Bement Smith in Isfahan, the other by a Mr. Herzel in Rome. From the descriptive lists that accompany them, both sets appear to have come from the same source. Microscopic examination reveals them to be similar. The orpiment in the Smith set is labeled no. 2, yellow, *zarnikh-i zard.* The list with the Herzel set carries the explanation, "Ground from a stone which comes from a Kasivin quarry." These pigments consist of a mixture of portlandite ($Ca(OH)_2$), calcite, and quartz as shown by x-ray diffraction. Microscopic examination also reveals the presence of orpiment, which is not present in sufficient quantities to appear in the x-ray diffraction pattern. It is of interest that portlandite is reported as a yellow powder in fumaroles on Vesuvius (Minguzzi, 1937). It seems likely that the portlandite, a white mineral, was in this case colored with orpiment. Evidently portlandite can occur in areas where orpiment forms, which might have been the case in the Kazivin quarry.

5.3.2 ***Infrared spectroscopy.*** The infrared and Raman spectra of orpiment and realgar mineral samples have been published (Forneris, 1969). The one strong infrared absorption peak for orpiment (fig. 14) is at 305 cm^{-1}, with medium peaks at 183, 348, 354, and 361 cm^{-1}. Realgar has strong peaks at 170, 225, 367, and 373 cm^{-1} (tables 5 and 6).

5.3.3 ***X-ray spectrometry (x-ray fluorescence) and electron beam microprobe.*** The main arsenic lines are $K\alpha_1$ 10.5keV (1.17987 Å), $K\beta_1$ 11.7keV (1.05730 Å, and $L\beta_1$ 1.32keV (9.4141 Å) (Goldstein et al., 1992). Arsenic was identified by x-ray fluorescence in a watercolor cake labeled king's yellow in an English early nineteenth-century paint box, and in the yellow pigment on an American watercolor and a fraktur (both c. eighteenth or nineteenth century) in the Henry Francis du Pont Winterthur Museum (Carlson & Krill, 1978). It is inferred from the presence of arsenic that the latter two pigments are king's yellow or orpiment. Orpiment is known to have been used to provide a yellow color for lacquer in China and Japan. Arsenic was identified by electron beam microprobe in the yellow layer, assumed to be orpiment, in a fifteenth-century Chinese lacquer box (Hornblower, 1963). Raman laser microprobe analysis has been used to identify orpiment on a painted Egyptian death mask from the Thirteenth Dynasty (c. 1780–1680 B.C.) (Guineau, 1984).

5.3.4 ***Spectrochemical analysis.*** Arsenic is readily detectable by emission spectroscopy. In the ultraviolet range the prominent lines are 2780.2, 2349.84, and 2288.12 Å, with a sensitivity of 0.1% (Waring & Annell, 1953). There are no lines in the visible range.

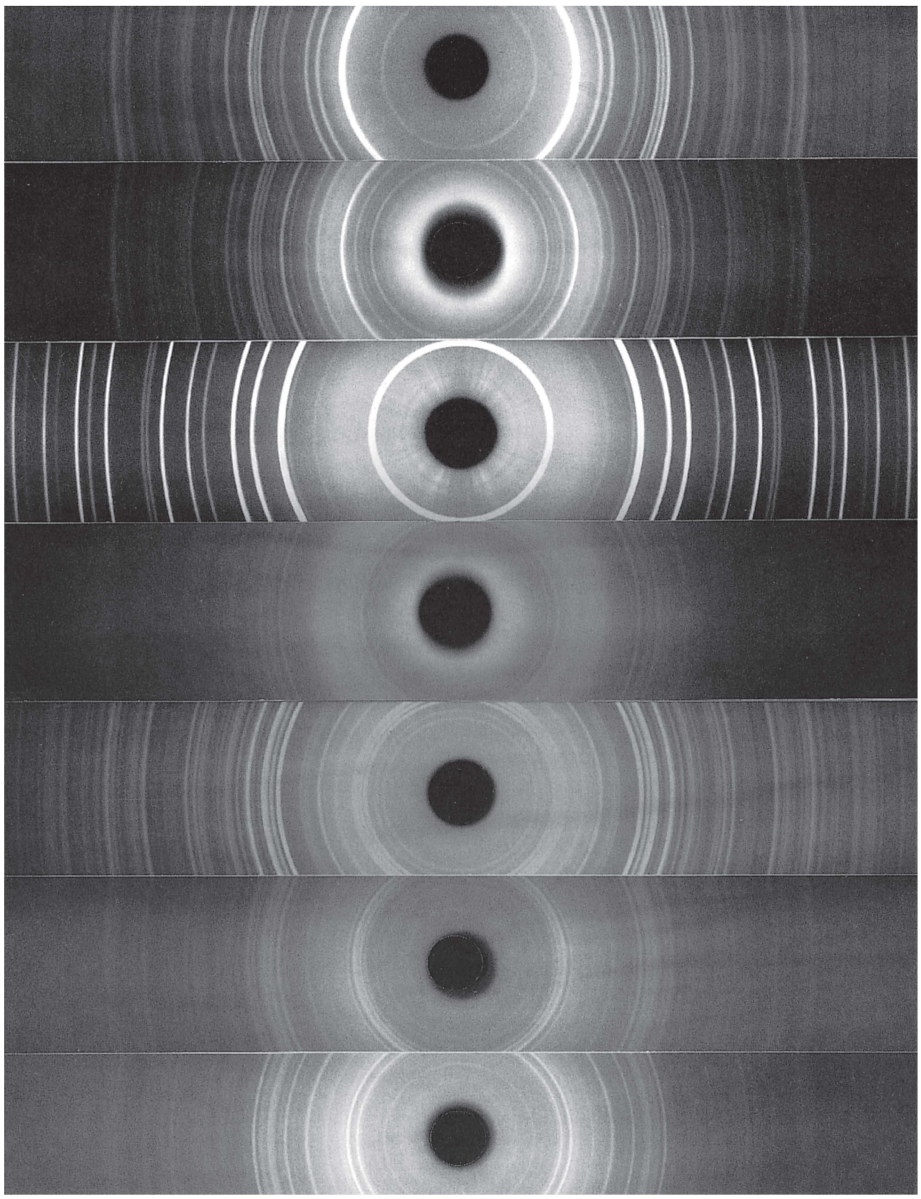


Fig. 13 X-ray diffraction powder patterns. Photographs not to be used for measurement purposes. All films from Freer Gallery of Art, Smithsonian Institution, Washington.

A. Orpiment from Greece, province of Macedonia. Department of Conservation and Scientific Research, Arthur M. Sackler Gallery and Freer Gallery of Art.

B. King's yellow. Watercolor cake from Ackermann of London, c. 1800–1825.

C. Arsenolite, synthetic. Department of Mineral Sciences, Smithsonian Institution, no. B4668(S).

D. Red orpiment. Watercolor cake from Ackermann of London, c. 1800–1825.

E. Realgar, occurring with duranusite from Duranus Alps, France. Department of Mineral Sciences, Smithsonian Institution, no. 13205.

F. Orpiment and realgar in the yellow robe of *The Israelites Gathering Manna*, by Tintoretto, Scuola di San Rocco, Venice. Sample from Joyce Plesters, formerly of the National Gallery, London.

G. Orpiment and realgar in the orange robe of *The Last Supper*, by Tintoretto, Church of Santo Stefano, Venice. Sample from Joyce Plesters.

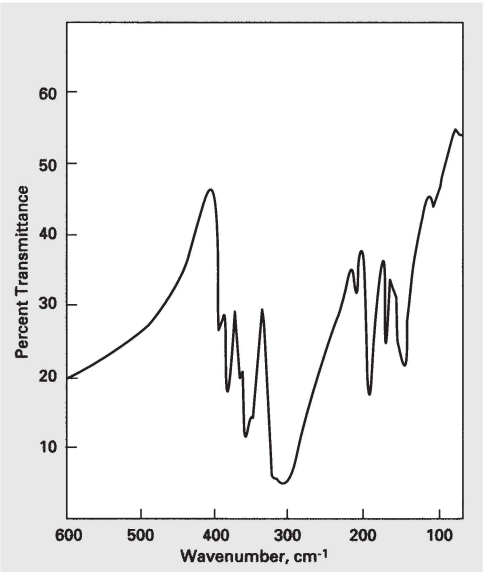


Fig. 14 Infrared absorption spectra of mineral orpiment from Nye County, Nevada. Fourier transform infrared spectroscopy from G. L. Carlson and Robert L. Feller, Carnegie Mellon Research Institute, Pittsburgh.

5.3.5 ***Neutron activation.*** Neutron activation autoradiography was used to identify arsenic-bearing pigments in paintings by Ralph Blakelock, a nineteenth-century American artist (Cotter & Sayre, 1971).

5.3.6 ***Mass spectrometry.*** Spark source mass spectrometry was used to identify arsenic in yellow and red pigments on sixteenth- and seventeenth-century Mughal Indian paintings; it was suggested that these pigments were orpiment and realgar (Cairns & Johnson, 1972; Johnson, 1972).

5.3.7 ***X-radiography.*** Orpiment shows strong x-ray absorption. Although its absorption is not quite as high as that of lead white and cinnabar it is higher than that of the earth pigments, which have moderate absorption. Identification of orpiment from x-radiography alone would not be possible since other yellow pigments such as lead-tin yellow also have strong absorption (Rees-Jones, 1975).

5.4 Criteria for Identification

The appearance of orpiment in a microscope slide in ordinary transmitted and polarized light, followed by a positive test for arsenic, have generally been accepted as sufficient criteria for identification. Confirmation can be supplied by x-ray diffraction. The same criteria apply to realgar, but because other orange-red arsenic sulfide minerals may be present, x-ray diffraction methods should always be used for a firm identification. In view of the information given in section 5.3.1, the name realgar as a pigment name might best be used to refer to any red arsenic sulfide pigment.

Table 5 **Observed Infrared Spectra of Orpiment (As_2S_3) (Nujol mull)**[a]

cm^{-1}	*Intensity*
52	w
139	vs
160	vw
183	m
202	vw
305	s
348	m
354	m
361	m
381	w
393	w

v=Very, w=Weak, m=Medium, s=Strong
a. Data from Forneris (1969).

Table 6 **Observed Infrared Spectra of Realgar(As_4S_4) (Nujol mull)**[a]

cm^{-1}	*Intensity*
37	vw
47	w
141	vw
148	vw
170	s
183	m
194	m
205	m
211	m
225	s
258	vw
269	vw
284	vw, sh
330	m
343	vs
358	m
367	s
373	s

v=Very, sh=Shoulder, w=Weak, m=Medium, s=Strong
a. Data from Forneris (1969).

6.0 **Occurrences**

Orpiment has been used throughout the world over a wide range of dates, although rarely in large amounts. Realgar has been used only sparingly.

Occurrences of Orpiment and/or Realgar

Date, Country, or School	*Artist, Title or Description* *Collection or Location*	*Analyst and Method* *of Identification*
East and Central Asia		
Central Asia, East Turkestan, 6th–10th C	Wall paintings, Museum für Indische Kunst, Berlin	Riederer (1977) micr., XRD, ES, IR, orp.
Chinese Central Asia 6th–11th C	Mural paintings, Xinjiang province	Kostrov and Shenina (1961)† orp.
Central Asia, 7th–8th C	Mural paintings, Pjandzkent, near Samarkand	Kostrov and Shenina (1961)† orp.
Chinese Central Asia 9th–10th C	Paintings on silk Stein collection, British Museum	M. Bimson*,‡ micr., XRD, orp.
Chinese Central Asia 10th–11th C	2 paintings on silk, Dunhuang FGA 30.36, 35.11	R. J. Gettens, W. T. Chase*,‡ micr., XRD, orp.
Central Asia, 11th–13th C	Mud wall paintings, Kara Khoto FGA study collection SC-PA-143	Gettens and Stout (1966) micr., orp. and realg.
Chinese Central Asia 12th C	Wall paintings, Dunhuang caves	Hsü et al. (1983) micr., XRD orp. and realg.
Chinese, Yuan Dynasty 14th C	Pigment on surface of a lacquer box Arthur M. Sackler Gallery Smithsonian Institution s87.0390	J. Douglas* XRD, orp.
Chinese, 15th C	Pigment embedded in lacquer box H. Garner collection	Garner (1963) ES, orp.
Tibetan, 15th–19th C	*Thang-ka* paintings on cotton	Mehra (1970) spot tests, orp.
Japanese, Ukiyo-e School 17th–18th C	Print, Art Institute of Chicago	Grove (1971) micr., orp.
Japanese, Ukiyo-e School late 17th–early 19th C	13 paintings, FGA	FitzHugh (1979) micr., chem., XRD, orp.

*Personal communication
†Method not noted
‡E. W. FitzHugh
chem.=Chemical or microchemical tests
EBM=Electron beam microprobe
ES=Emission spectroscopy
FGA=Freer Gallery of Art, Smithsonian Institution, Washington
micr.=Light microscopy
orp.=Orpiment found
realg.=Realgar found
SEM/XES=Scanning electron microscopy with energy-dispersive spectroscopy
XRD=X-ray diffraction
XRF=X-ray fluorescence spectroscopy

Date, Country, or School	*Artist, Title or Description* *Collection or Location*	*Analyst and Method of Identification*
Egypt, West Asia, and India		
Egyptian, 1st–4th dynasty (31st–25th C B.C.)	Wall paintings, Giza	Noll (1981) XRD, XRF, orp.
Egyptian, 12th dynasty (21st C B.C.)	Wooden shrine FGA 07.4	W. T. Chase* XRD, orp.
Egyptian, Middle Kingdom (21st–18th C B.C.)	Wooden coffin Museum of Fine Arts, Boston	Young and Whitmore (1968) micr., ES, XRD, orp.
Egyptian, 18th dynasty (16th–14th C B.C.)	Wall and stone paintings Thebes	Noll (1981) XRD, XRF, orp.
Egyptian, 13th dynasty (c.1780–1680 B.C.)	Plaster death mask, Necropolis of Mirgissa, Nubia	Guineau (1984) Raman micr., orp.
Egyptian, 13th dynasty (c.1780–1680 B.C.)	Inlay of cartouche in a wooden haft British Museum	Bimson (1987) XRD, XRF, IR, orp.
Egyptian, 21st dynasty (10th C B.C.)	Wood sarcophagus Vleeshuis, Anvers	Goetghebeur (1969) micr., orp.
Egyptian, 22nd–26th dynasty (10th–6th C B.C.)	Mummy case, exterior, Petrie Museum University of London, UC 14230	J. Plesters and A. Roy* micr., ES, orp.
Mesopotamia, Assyrian (8th C B.C.)	Coloring in beeswax, ivory writing board, Nimrud, Iraq British School of Archaeology in Iraq	R. J. Gettens*, ‡ micr., XRD, orp.
Egyptian, Coptic, 3rd C	Fayum portrait Toledo Museum of Art, Toledo, Ohio	Buck and Feller (1972) XRD, orp.
Egyptian, 3rd–4th C	Painting on canvas Private collection	Sack et al. (1981) micr., orp.
Egyptian, Coptic, 4th C	Pottery fragment, Monastery of Phoebammon	Iskander (1961) chem., orp.
Egyptian, Coptic, 5th C	Fragment, painting on wood panel Dumbarton Oaks, Washington 46.1	R. J. Gettens* micr., orp.
Egyptian, Coptic, East Christian, 7th C	Painted wooden book covers "Washington MS of the Four Gospels" FGA 06.297, 06.298	R. J. Gettens* micr., XRD, orp.
Armenian, 10th–16th C	8 illuminated manuscripts Walters Art Gallery; FGA; Pierpont Morgan Library; Patriarchate of St. James, Jerusalem	Cabelli et al. (1984) Cabelli and Mathews (1982 1984), micr., XRD, orp.
Indian, Bengali, Buddhist early 12th C	Painting on paper, FGA 30.86	‡ micr., orp.

*Personal communication
‡E. W. FitzHugh
chem.=Chemical or microchemical tests
EBM=Electron beam microprobe
ES=Emission spectroscopy
FGA=Freer Gallery of Art, Smithsonian Institution, Washington
micr.=Light microscopy
MS=Mass spectroscopy
orp.=Orpiment found
Raman micr.=Raman microspectroscopy
realg.=Realgar found
SEM/XES=Scanning electron microscopy with energy-dispersive spectroscopy
XRD=X-ray diffraction
XRF=X-ray fluorescence spectroscopy

Date, Country, or School	*Artist, Title or Description* *Collection or Location*	*Analyst and Method* *of Identification*
Egyptian, Copto-Arabic 3rd quarter, 12th C	Painting on parchment, first page of a religious codex, FGA 55.11	R. J. Gettens* micr., orp.
Armenian, c.1200	Illuminated manuscript "The Four Gospels," FGA 50.3	R. J. Gettens* micr., orp.
Indian, Mughal, and Rajasthani 13th–17th C	Miniature paintings, Los Angeles County Museum of Art	Johnson (1972) Cairns and Johnson (1972) MS, orp. and realg.
Persian, Indian, Iraqi Turkish, Egyptian, Syrian 13th–19th C	32 paintings on paper, Vever Collection Arthur M. Sackler Gallery Smithsonian Institution, Washington	FitzHugh (1988) micr., chem., XRD, orp.
Armenian, c.1300	Glajor gospel manuscript MS Arm. 1, University of California, Los Angeles	Orna and Mathews (1981) micr., XRD, orp.
Persian, Mongol period Shiraz School, early 14th C	Tabari's "Universal History" Manuscript pages, FGA 47.19, 57.16	R. J. Gettens*, ‡ micr., XRD, orp.
Persian, various schools early 14th–16th C	8 paintings on paper, FGA 28.11, 30.4, 31.14 32.51, 37.8, 40.14, 67.7, 67.8	‡ micr., orp.
Arabic, 1315	"Automata of Al-Jazari" manuscript FGA 30.73	‡ micr., orp.
Arabic, Mamluk, 1345–1350	Paintings, wooden ceiling of the dome Al-Aqsa Mosque, Jerusalem	Lazzarini and Schwartzbaum (1985), micr., orp.
Arabic, Iraqi, 1370	"Wonders of Creation" manuscript Qazwini, FGA 54.33, 54.114, 57.13	‡ micr., orp.
Indian, Gujarati 15th C	"Vasanta Vilasa" illuminated scroll on cotton, FGA 32.24	R. J. Gettens*, ‡ micr., XRD, orp.
Indian, Hindu, 15th C	Painting on paper, FGA 39.35	‡ micr., orp.
Indian, Sultanate period, mid- or second half 15th C	4 manuscript pages with paintings "Khamse" of Amir Khusraw Dihlavi FGA 59.1–59.4	R. J. Gettens* micr., orp.
Armenian, Khatchatur of Khizan, 1455	Illuminated manuscript, Walters Art Gallery, Baltimore 543	Cabelli and Mathews (1982) Cabelli et al. (1984), micr. XRD, realg.
Persian, various schools late 15th–late 16th C	9 paintings on paper Harvard University Art Museums (Fogg)	S. M. White* micr., SEM/XES, orp.
Turkish, 16th C	Painting on paper, FGA 29.75	‡ micr., orp.
Indian, Mughal 16th–19th C	5 paintings, Cincinnati Art Museum	Purinton and Newman (1985) micr., XRD, EBM, orp.
Indian, Mughal period Akbar School, 3rd quarter 16th C	Paintings on cotton "Hamza Nama," FGA 49.18, 60.14, 60.15	R. J. Gettens* micr., orp.
Indian, Rajasthani School early 18th C	Scroll painting on paper Museum and Picture Gallery, Baroda	Shah (1976–1977) micr., orp.

Date, Country, or School	*Artist, Title or Description* *Collection or Location*	*Analyst and Method* *of Identification*
European		
European, 8th–15th C	18 Illuminated manuscripts including Byzantine manuscripts	Laurie (1914) micr., orp.
Irish, 9th C	*Book of Kells*, Trinity College Library Dublin	Sullivan (1952) micr., orp.
Norwegian, 850–900	Rudder from Viking ship Universititetets Oldsaksamling Oslo 10391	U. Plahter* micr., XRD, orp.
European, 10th–13th C	3 manuscripts, Bibliothèque Nationale, Paris	Flieder (1968) micr., orp.
German, 11th C	Painted wooden ceiling St. Michel's Church, Hildesheim	Denninger (1969) micr., orp.
Norwegian, second half 13th C	*Virgin and Child*, polychrome wood Church of Dal, University Museum of National Antiquities, Oslo	Plahter and Wiik (1970) micr.
Norwegian, 1250–1350	Painted wooden altar frontals Church of Tingelstad and others	Plahter et al. (1974) Plahter and Plahter (1976) Plahter (1984), micr., XRD orp.
Flemish, 14th C	"*Virga Jesse*," polychrome sculpture Sint-Kwintinuskerk Hasselt, Belgium	Serck-Dewaide et al. (1978–1979) micr., orp.
European, 14th–15th C	Late Medieval manuscript miniatures, private collection	Tosatti Soldana (1980) micr., XRD, ES, orp.
England (or possibly France) c.1395	*The Wilton Diptych* Oak panels, National Gallery London 4451	A. Roy* micr., SEM/XES orp. combined with indigo
England, probably 15th C	Polychromed stone figure, west front Exeter Cathedral Devon	J. Plesters and A. Roy* micr., orp.
Italian, 16th C	Michelangelo (attributed) *Madonna and Child, St. John and Angels*, National Gallery London 809	Ruhemann and Plesters (1964) micr., orp. and realg.
Italian, 16th C	Raphael, *Sistine Madonna* Staatlichen Kunstsammlungen, Dresden	Weber (1984) micr., orp.
Italian, 16th C	Leonardo da Vinci, *Last Supper* wall painting Santa Maria delle Grazie, Milan	Kühn (1985) micr., chem., ES, XRD, orp.
Scottish, c.1600	Ceiling paintings, Crathes Castle and Mary Somerville's house	J. Plesters and A. Roy* micr., orp.
Austrian, 1614–1784	Polychromed wooden altar retables and sculpture from upper Austria and Salzburg	Mairinger (1974) micr., XRD, XRF, orp.
English, 1622	John Hazard, harpsichord Knole, Kent, National Trust	A. Mactaggart* micr., orp.

*Personal communication
†No method given
chem.=Chemical or microchemical tests
EBM=Electron beam microprobe
ES=Emission spectrographic analysis
micr.=Light microscopy
XRD=X-ray diffraction
XRF=X-ray fluorescence spectroscopy

Date, Country, or School	*Artist, Title or Description* *Collection or Location*	*Analyst and Method of Identification*
French, 1629–1630	Nicolas Poussin *Rebekah Quenching the Thirst of Eliezer*, Collection of Dennis Mahon	Plesters (1965) micr., orp.
Belgian, 1651(?)	Andreas Ruckers, harpsichord Private collection	J. Plesters and A. Roy* micr., orp. mixed with lampblack to make green
French, 18th C	Jean-Baptiste Siméon Chardin *Kitchen Utensils with Leeks, Onions and Eggs,* Cleveland Museum of Art 80.37	I. Fiedler* micr., orp. and realg.
French, 18th C	Jean-Baptiste Siméon Chardin, various paintings, Museum of Fine Arts, Boston and National Gallery of Art, Washington	Merrill (1981) XRF, orp. and realg.
French, probably 1720	Jean Antoine Watteau, *Italian Comedians* National Gallery of Art Washington 1946.7.9	Fisher (1984) micr., XRF, orp. and realg.
French, 18th C	Follower of Jean-Baptiste Pater *Fête Champêtre*, Art Institute of Chicago 1954.295	I. Fiedler* micr., orp. and realg.
French, c.1728–1731	Jean-Baptiste Siméon Chardin *Glass of Water and Coffeepot* Carnegie Museum of Art, Pittsburgh 66.12	I. Fiedler* micr., orp. and realg.
French, 1745–1750	François Boucher, *Bathing Nymph* Art Institute of Chicago 1931.938	I. Fiedler* orp. and realg.
French, 1760	Harpsichord built by Benoît Stehlin Paris, anonymous decorator Smithsonian Institution, S.I. musical instrument lab. sample 133.0	S. Odell* micr., orp.
French, 1765	Harpsichord built by François-Etienne Blanchet II, Paris, anonymous decorator Collection of Robert Rosenbaum, S.I. musical instrument lab. sample 122.0	S. Odell* micr., orp.
French, 1769	Jacques-Louis David, *Portrait of Madame Buron*, Art Institute of Chicago 1963.205	I. Fiedler* micr., orp.
French, 1770	Harpsichord built by Jean Mari Dedeban Paris, anonymous decorator, Corcoran Gallery of Art, Washington	Germann and Odell (1978) micr., XRD, orp.
English, 1770–1772	Joseph Wright of Derby *Mr. and Mrs. Coltman*, National Gallery, London 6496	J. Plesters and A. Roy* micr., LSA, orp.
English, 1773	Joshua Reynolds, *Lady Cockburn and Her Three Sons*, National Gallery London 2007	J. Plesters and A. Roy* micr., ES, orp.
Italian, 1775–1793	Francesco Guardi, *Ruined Archway* Art Institute of Chicago 1933.1080	M. H. Butler* micr., EBM lower of two layers of ground is 80% orp.
English, 1782	Joshua Reynolds, *General Sir Banastre Tarleton* National Gallery, London 5985	J. Plesters and A. Roy* micr., ES, orp.

Date, Country, or School	*Artist, Title or Description* *Collection or Location*	*Analyst and Method* *of Identification*
French, Paris, c.1790	Painted wooden panels, Mme. Serilly's boudoir, Victoria and Albert Museum, London	J. Plesters and A. Roy* micr., XRD, ES, orp. and realg.
Late 18th–early 19th C	Pastel color box belonging to Elizabeth Cary (1770–1831), pastel Victoria and Albert Museum, London P42-1922	J. Plesters and A. Roy* micr., LSA orange color, realg. yellow pastel color, orp.
European, 19th C	7 paintings in the Schack Galerie Munich	Kühn (1969) ES, XRD, orp.
Norwegian, early 19th C	Folk art objects, Norsk Folke-Museum, Oslo	Skaug (1978) micr., XRD
Spanish, 1812–1814	Francisco Goya, *The Duke of Wellington,* National Gallery London 6322	J. Plesters and A. Roy* micr., LSA, orp.
French, 1879–1883	Paul Cézanne, *Bay of l'Estaque* 3 occurrences in *Portrait of Mme. Cézanne* in layer below *Bay of l'Estaque*, Philadelphia Museum of Art 63-116-2	Butler (1984) micr., orp.
French, 1883	Paul Cézanne, *View of the Bay of Marseilles with the Village of Saint-Henri*, Philadelphia Museum of Art 67-116-3	Butler (1984) micr., orp.
Western Hemisphere		
American, 17th C	Manuscript no. 996, University of Chicago Manuscript Collection	M. H. Butler* micr.
Peruvian, Cuzco School early 17th C	Anonymous, *Virgin de la Leche* Collection of Elvin A. Duerst	R. J. Gettens* micr., orp.
American, 1670–1680	Anonymous, *Elizabeth Paddy Wensley* Museum of Fine Arts, Boston	England and Van Zelst (1982) XRF, realg.
American, New York State early 18th C	Dutch scripture history paintings Albany Institute of History and Art and Columbia County Historical Society	Zucker (1980), micr. M. Gifford*, micr., orp.
American, Massachusetts c.1711–1721	Anonymous, *Henry Gibbs* Art Institute of Chicago 1967.171	I. Fiedler* micr., realg.
Upper Hudson Valley New York State, c.1719**	Anonymous, *Girl with Flower* Butler Institute of American Art Youngstown, Ohio	R. L. Feller* XRD, orp.
English or American first quarter 18th C**	Anonymous, *Portrait of a Lady* High Museum of Art Atlanta, Georgia	R. J. Gettens*, micr. ‡, XRD, orp.

*Personal communication
**Information from E. S. Quandt, Washington, D.C.
‡E. W. FitzHugh
chem.=Chemical or microchemical tests
micr.=Light microscopy
SEM/XES=Scanning electron microscopy with energy-dispersive spectroscopy
XRD=X-ray diffraction
XRF=X-ray fluorescence spectroscopy

Date, Country, or School	*Artist, Title or Description* *Collection or Location*	*Analyst and Method of Identification*
Upper Hudson Valley New York State, c.1741**	The Gansevoort limner, *Mrs. Myndertse with Her Daughter Sarah* Private collection	R. L. Feller*, XRD ‡, micr., orp.
American, c.1760	John Singleton Copley, *Dorothy Murray* Harvard University Art Museums (Fogg) Cambridge, Mass. 1929.321	Shank (1984) micr., XRD, SEM/XES, orp.
American, 1799	John Ritto Penniman, *Meeting House Hill, Roxbury, Massachusetts* Art Institute of Chicago 1979.1461	I. Fiedler* micr., orp.
American, 19th C	Anonymous, *Boy of Hallett Family with Lamb*, Art Institute of Chicago 1938.1334	I. Fiedler* micr., orp.

Date, Country, or School	*Artist, Title or Description* *Collection or Location*	*Analyst*[a] *and Method of Identification*
Venetian Paintings		
Late 15th C	Giovanni Santi, *The Virgin and Child*, National Gallery, London 751	micr., LSA, orp.
16th C	Tintoretto (Jacopo Robusti), *The Israelites Gathering Manna* Scuola di San Rocco, Venice	Plesters and Lazzarini (1976) micr., ‡, XRD, realg. and orp.
1504	Giovanni Battista Cima da Conegliano *The Incredulity of St. Thomas* National Gallery, London 816	Dunkerton and Roy (1986) micr., LSA, realg.
c.1510	Titian (Tiziano Vecelli), *The Holy Family and a Shepherd*, National Gallery London 4	Lucas and Plesters (1978) micr., LSA, realg. and orp.
1514	Giovanni Bellini, *The Feast of the Gods*, National Gallery of Art Washington 1942.9.1	Bull and Plesters (1990) micr., XRF, orp. and realg.
1515–1516(?)	Palma Vecchio, *Portrait of a Poet*, National Gallery, London 636	micr., realg.
c.1516	Giovanni Battista Benvenuto, known as Dell'Ortolano, altarpiece, *St. Sebastian, St. Roch, and St. Demetrius* National Gallery, London 669	micr., orp. and realg.
1519	Sebastiano del Piombo, *The Raising of Lazarus*, National Gallery London 1	micr., LSA realg.
c.1520	Niccolò Giolfino (ascribed to) *Portraits of the Giusti Family of Verona*(?) National Gallery, London 749	micr., realg.

‡E. W. FitzHugh
LSA=Laser emission spectroscopy
micr.=Light microscopy including confirmation, in some cases, by microchemical tests
orp.=Orpiment found
realg.=Realgar found
XRD=X-ray diffraction
XRF=X-ray fluorescence spectroscopy
a. Carried out, except where noted, by Joyce Plesters and Ashok Roy, National Gallery, London. For discussion of some of these paintings, see Plesters and Lazzarini (1976) and Plesters (1980).

Date, Country, or School	*Artist, Title or Description Collection or Location*	*Analyst*[a] *and Method of Identification*
1522–1523	Titian, *Bacchus and Ariadne* National Gallery, London 35 and orp.	Lucas and Plesters (1978) micr., LSA, realg.
c.1545	Tintoretto, *Apollo and Diana Killing the Children of Niobe* Princes Gate Collection London 119	micr., LSA, XRD realg.
1547	Lorenzo Lotto, *Family Group* National Gallery, London 1047	micr., LSA orp. and realg.
1548	Tintoretto, *Miracle of St. Mark*, Accademia Galleries Venice	micr., realg. and orp.
c.1550s	Tintoretto, *The Deposition* National Gallery of Scotland	micr., LSA realg. and orp.
c.1552	Tintoretto, *The Presentation of the Virgin*, Church of the Madonna dell'Orto, Venice	micr., LSA orp. and realg.
c.1556	Tintoretto, *Christ Washing His Disciples' Feet*, National Gallery, London 1130	micr., orp. and realg.
c.1560	Tintoretto, *Miracle of the Loaves and Fishes* Metropolitan Museum of Art New York	micr., LSA, XRD orp. and realg.
c.1560–1662	Tintoretto, *Last Judgment* Church of the Madonna dell'Orto, Venice	Plesters and Lazzarini (1976) micr., orp.
Early 1560s(?)	Tintoretto, *The Last Supper* Church of Santo Stefano, Venice	‡ micr., orp. and realg.
1562–1564	Tintoretto, *Adoration of the Golden Calf*, Church of the Madonna dell'Orto, Venice	micr., LSA, XRD realg. and orp.
1570s(?)	Paolo Veronese, *The Family of Darius before Alexander*, National Gallery, London 294	micr., LSA realg. and orp.
1573	Paolo Veronese, *Feast in the House of Levi,* Accademia Gallery, Venice 137	micr., LSA orp. and realg.
Last quarter 16th C	Paolo Veronese, *Allegory of Love, II* National Gallery, London 1324	micr., LSA realg.
Last quarter 16th C	Paolo Veronese, *Allegory of Love, IV* National Gallery, London 1326	micr., LSA, XRD realg.
c.1578	Tintoretto, *The Origin of the Milky Way*, National Gallery, London 1313	micr., realg. and orp.
c.1580–1585	Tintoretto, *Portrait of Vincenzo Morosini,* National Gallery, London 4004 (see fig. 2)	micr., LSA orp. and realg.
1581–1584	Tintoretto, *Doge Mocenigo Presented to the Redeemer* Metropolitan Museum of Art, New York	micr., LSA realg.

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Fig. 1 Hishikawa Moroyasu, *A* Yujo *Arranging Her Hair*, Japan, Edo period, eighteenth century; painting, color on paper. Freer Gallery of Art, Smithsonian Institution, Washington 98.114. The stripes on the robe are rendered in indigo mixed with shell white (calcium carbonate), identified by microscopy and chemical tests by Elisabeth West FitzHugh.

3
Indigo and Woad

HELMUT SCHWEPPE

1.0 Introduction

1.1 Pigment Definition

Indigo is the name used uniformly in the United States, Germany, and France for the blue dye or artists' pigment that was prepared from plants, until the end of the nineteenth century. These plants were of the families Papilionaceae (*Indigofera tinctoria* L., Cruciferae/Brassicaceae (*Isatis tinctoria* L., also known as woad and dyer's woad), Polygonaceae (*Polygonum tinctorium* L., also called dyer's knotgrass), and others. The reader should be aware that changes in the botanical names have occurred over the years.

Natural indigo is CI Natural Blue 1, no. 75780, in the *Colour Index* (1971); synthetic indigo is CI Vat Blue 1, no. 73000, and CI Pigment Blue 66, no. 73000, depending on whether it is referred to as a textile dye or a pigment. Indigo is listed under number 1301 in the color tables by Schultz (1931).

After pioneering work by A. Baeyer, who in 1870 succeeded in the first synthesis of indigo from isatin (Baeyer & Emmerling, 1870), and the development of simplified syntheses from phenylglycine and phenylglycine carboxylic acid by Heumann (1890a, b), synthetic indigo was made available commercially in 1897 in the purest form by Badische Anilin Soda Fabrik (BASF) and quickly replaced the natural coloring matter.

1.2 Current Terminology

English: indigo, indigotin
German: Indigo, Indigotin
French: indigo
Spanish: anil, indigo
Italian: indaco
Portuguese: anil, azul-indigo
Russian: индиго
Japanese: ai
Chinese: lan dian (pinyin), lan tien (Wade-Giles)

English: woad, wood
German: Waid, Färberwaid
French: guède, pastel
Spanish: glasto, pastel
Italian: guado
Portuguese: pastel dos tintureiros
Russian: вайда
Chinese: song lan (pinyin), sung lan (Wade-Giles)

2.0 History

2.1 Archaic and Historical Names

Woad. In antiquity a distinction was made between woad and indigo, the latter being imported from India. Dioscorides gave the Greek name for woad, *isatis*, in the first century A.D. Vitruvius called it *vitrum* in *De Architectura* written in the first century B.C. (Reinking, 1924). Vitruvius is known to have frequently used older Greek sources, now lost. In the first century A.D. Pliny the Elder mentioned the Gallic name for woad, *glastum*. The names that appear in middle Latin are *uvatum*, *guattum*, *gadus herba* (Roosen-Runge, 1974) and also *guadium* and *gaida* (*Bayer*, 1970).

Dyer's woad is called *weit* or *weid* in Old High German and Middle High German (Ploss, 1952); these names are related to the *waisdo*, *wisdilo*, and *erwaisda* used in the Carolingian manuscript *Capitulare de villis* (Roosen-Runge, 1974). The Sumerians knew dyer's woad as *sam* ZA.GIN.NA,

(Levey, 1959). In the *Papyrus Graecus Holmiensis* from the third century A.D. the harvested, crushed, and dried woad was called *anthrax* (Lagerkrantz, 1913; Reinking, 1925). In the fourteenth century, Geoffrey Chaucer used the Saxon name *wod* (Brown, 1943), from which the later English terms wood and then woad developed (*Bayer*, 1970). In earlier French literature, the best type of woad was called *pastel* (*Bayer*, 1970).

Indigo. Indigo was called *n-tinkon* in ancient Egypt (*Bayer*, 1970). Dioscorides indicated that indigo imported from India was called *indikon* in Greek. Pliny used the Latin term *indicum* (Book 35, par. 30) and other Latin names were *pigmentum indicum* and *color indicus* (Heermann, 1930). Vitruvius wrote about indigo as an artist's pigment (Vetterli, 1950) and Byzantine writers called indigo *azorium Romanum* (Church, 1890).

In medieval shop literature, indigo is referred to as *lulax* or *indicum*. From 1228, indigo from Baghdad listed in the Marseilles tariffs was called *indigo bagadel* (Roosen-Runge, 1974), and in his book on dyeing, Rosetti (1548) called Indian indigo *endego de Bagad*. Cennino Cennini wrote of Baghdad indigo in the fifteenth century (Thompson, 1933) and the name Baghdad, in various forms, was applied to indigo by other writers (Merrifield, 1967). Interestingly, in a set of German nineteenth-century pigments, a pigment labeled *indaco* was a mixture of indigo and smalt (Richter & Härlin, 1974b). In the Middle Ages in Germany, indigo imported from Italy was called *lamptschen endich*, that is, Lombardy indigo (Roosen-Runge, 1974). The fifteenth-century Strasburg Manuscript mentions London indigo and *lamptschen endaco*, possibly referring to woad indigo rather than the Indian kind (Borradaile & Borradaile, 1966). The names used most frequently in Germany in the Middle Ages for indigo were *indich*, *endich*, *endig*, and *endit* (Ploss, 1952). Seventeenth-century English color lists used the term *indico* as a replacement for the earlier names *indebaudias* and *inde blew* (Harley, 1982).

When indigo was first imported into Europe, it was thought by some to be a mineral and "indigo from mines" was cited as late as 1705 in a British patent (Leggett, 1944).

In China, any indigo-yielding plant was called *lan cao* (pinyin) (*lan tsa'o* [Wade-Giles]) (Watson, 1930). Other names were *dian hua* (pinyin) (tien hua [Wade-Giles]) and flower blue (*hua ging* [pinyin], *hua ch'ing* [Wade-Giles]) (March, 1935). Japanese names were *ai*, *seitai*, *aibana*, and *tenka*, while *aibo* was the name given an ink stick of indigo (Oguchi, 1969). A Japanese painting with extensive use of indigo is shown in figure 1.

Names in pre-Columbian Mexico for several plants that contained indigo were *matlalli*, *tezotli*, *oxoxovic*, *xiuhquilitl*, and *pitzahoac* (Margival, 1955; Bruyas, 1970). An early Guatemalan name for the indigo plant (*Indigofera tinctoria* L.) was *jiquilite* (Bruyas, 1970).

In ancient India the word for indigo was *nilah*, meaning dark colored, black blue, which also characterized the shade well, as dark blue shades can be obtained more easily than light shades in primitive dyeworks. The Indian word was borrowed in Persian as *nilae*, and from this the Arabic word *nila* was derived. The Arabic form of the name was combined with the article *al-*, and from *al-nil* developed the form *anil*, which was adopted by the Portuguese (Ploss, 1960; see also Levey, 1962).

2.2 History of Preparation and Use

Vitruvius in the first century B.C. was the first to mention indigo (Book 7, chap. 14) (Morgan, 1926). Dioscorides wrote in *Materia Medica* (Book 5, chap. 107), "The dye that is called indigo comes from India. It forms as spontaneous exudation on a type of reed growing there." Pliny wrote (Book 35, par. 46 [König, 1960; see also Bailey, 1932]):

> [Tyrian purple] is followed by indigo in value. This comes from India, where it attaches itself as mud to the foam of the reeds. When it separates in this manner it is black; on dilution, however, it yields a beautiful blue-to-purple color. A second kind of indigo floats on the vats in the purple dye houses, which is the foam of purple.

The comment, "where it attaches itself as mud to the foam of the reeds" indicates, according to König, the method of preparation of indigo, where the *Indigofera* species were cut when flowering and allowed to ferment in large vats in the presence of water. According to Pliny, the separated liquor was aerated as thoroughly as possible by beating with tools such as sticks and shovels when the insoluble indigo separated in a black mass. The indigo "foam of purple," may have been concentrated in the foam on the purple liquor by the light-induced release of bromine atoms from part of the principal dye component, the purple compound 6,6'-dibromoindigotin, in the solution. This photochemical reaction was

known and used by Driessen-Hengelo (1944) for the identification of purple dye in antique textiles.

Indian indigo was probably used by the Greeks and Romans in antiquity solely as a painting pigment, and not as a textile dye, for which the indigenous woad (*Isatis tinctoria* L.) was available. It is significant that the preparation of woad and the starting of the woad liquor are described in detail in the Egyptian *Papyrus Graecus Holmiensis* (third century A.D.), whereas indigo is mentioned only in the instructions for coloring of stones (Lagerkrantz, 1913; Reinking, 1925; Vetterli, 1950). Julius Caesar wrote in book five of *De Bello Gallico*, "All Britons paint themselves with woad [*vitrum*], which grows wild and produces a blue dye. This gives them a terrifying appearance in battle." Pliny the Elder confirmed this observation (Book 22, par. 2): "There they have a plant similar to plantain which is called 'glastum' in Gaul, with which the women and daughters in Britain paint their bodies at certain festivities; they go naked and are similar to the Ethiopians in the color of their bodies." The word *glastum* used by Pliny is derived from the Celtic expression *glas*, which means blue. Ovid in the first century reported that the early Teutons colored their gray hair black with woad (see Brown, 1943).

Dyer's woad and its use for dyeing wool and linen was first described in the early Middle Ages in the *Capitulare de villis*—instructions for the management of the Carolingian possessions. The use of woad for preparing mixed pigments and dyes was reported repeatedly during this epoch. Vegetable remains of *Isatis tinctoria* L. (woad) were identified in the c. ninth-tenth century deposits at York (Tomlinson, 1985). Woad is mentioned as a component of a blue mixed pigment and in *lazurin* recipes in the *Mappae Clavicula* (Phillips, 1847; see also Smith & Hawthorne, 1974). Indigo from India is listed in numerous shop manuals from the Middle Ages, including the *Mappae Clavicula*, Heraclius (see Ilg, 1888), and Alcherius (in Jehan le Begue, no. 294; see Merrifield, 1967). Bettey (1978) described the cultivation of woad in seventeenth-century England.

Glen (1911) noted that indigo may have been used in ancient Egypt on a robe from Thebes dated as early as approximately 3000 B.C. Ruggli (1932) reported indigo on the bandages of mummies from graves dated approximately 1580 B.C. and Serchi and Morandi (1951) identified it on ancient Egyptian fabrics. It is not known if *Isatis tinctoria* or *Indigofera tinctoria* was used for these dyes.

Pfister (1935) reported the use of indigo for dyeing in the Hellenistic Orient. Abrahams and Edelstein (1964, 1967) found indigo on textiles discovered in a cave in Israel dated to the time of the Bar Kochba rebellion (A.D. 135). Indigo was used as a pigment at Dura Europos in Syria about A.D. 200 (Roosen-Runge, 1974). Al Bīrūnī, an Arab scholar and scientist (A.D. 973–1048), mentioned the indigo plant as a source of cloth dye native to Arabia (Hamarneh, 1973).

Marco Polo (1254–1324) was the first to report to the West on the main indigo preparation sites in India, when he described the process in the Kulam kingdom on the west coast, in addition to the manufacturing centers of Guarat and Cambai in northwestern India (Vetterli, 1950). Indigo is thought to have been used in India as early as 2000 B.C., and was referred to in a twelfth-century Sanskrit text (Coomaraswamy, 1934). Its main use was as a textile dye, but it was also used in paintings on paper and in wall paintings (Agrawal, 1969; Agrawal & Jain, 1984). It has been found on palm leaf manuscripts from Bengal, Nepal, and west India (Bhattacharya, 1976). Until the discovery of America, India was the sole source of indigo for Europe (Leggett, 1944).

As early as the twelfth century, imported indigo appeared in European merchants' account books and in customs tariffs. It usually came from Baghdad, which was the main trading center for Indian and Persian indigo. The Venetians and Genoese later took over the trade and bought indigo directly from Persian traders at centers in Tauris and Lajazzo in Asia Minor and Hormuz on the Persian Gulf. Indigo appears in weight tax rates and bills dated 1140 in Genoa, 1228 in Marseilles, and 1276 in London (Vetterli, 1950). In the fourteenth century Holland imported indigo from India (Leggett, 1944).

With the rise of East Indian trade in later centuries, indigo became, like spices, a major trading item. It was sent to Europe in increasingly larger quantities and began to compete with the indigenous woad. In a struggle that lasted several centuries and led to strict enactments against importation of Indian indigo, the latter finally prevailed over woad in the seventeenth century because of its higher pigment content.

As a result of the heavy demand, it began to be cultivated more extensively. In 1783, British colonists started indigo plantations in Bengal, and

from 1805 to 1814 exports averaged 5.6 million pounds annually. The cities of Madras, Bombay, Broach, and Karachi were engaged in indigo trade with East Asia. During the nineteenth century, with intensive cultivation, indigo production in British India increased considerably and in 1896/1897 reached a maximum of more than 9.5 million kg. The average value of the Indian production was estimated at 75 million Swiss francs for the years 1880/1881 to 1895/1896, compared to 25 million Swiss francs for indigo produced in Java, Ceylon (Sri Lanka), Guatemala, El Salvador, Nicaragua, Mexico, Venezuela, and elsewhere (Vetterli, 1950).

In China, the native indigo plant, *Polygonum tinctorium*, was used possibly as early as 2000 B.C. (Ruggli, 1932). Indigo from *Indigofera tinctoria* was first imported by China via Persia in A.D. 717 and was called "blue kohl" (*ging dai* [pinyin], *ch'ing tai* [Wade-Giles]) because of its use as a cosmetic. It was later cultivated in south China. *Isatis tinctoria* is also found in China, but it was probably not introduced there until the sixteenth century (Schafer, 1963; Needham, 1986).

Margival (1955) reported on the use of indigo from the plants *matlalli* and *anil* in pre-Columbian times in the New World. See table 1 and section 4.2 for some of the plant species used for indigo production. Tagliani and Wiazmitinow (1934) found indigo on numerous early Peruvian textiles of the Paracas culture. Indigo was identified by absorption spectroscopy and chromatography on pre-Inca fabrics from Peru (sixth-seventh and thirteenth-fourteenth centuries) (Kashiwagi, 1976).

The pigment Maya blue is prepared by precipitating indigo on the white clay mineral attapulgite (fig. 2). It was used on wall paintings and painted ceramics in pre-conquest Mexico. The identification of an attapulgite component (Gettens, 1962) was followed by identification of indigo as the coloring agent and synthesis of the pigment (Van Olphen, 1966; Kleber et al., 1967).

The Spanish introduced *Indigofera tinctoria* from India into their colonies in Venezuela and Guatemala in the seventeenth century. Indigo cultivation quickly spread to the West Indies. It was grown by French settlers there from the seventeenth century (Pinault, 1987). By 1672 there were sixty indigo plantations in Jamaica and by 1787 Santo Domingo (the present-day island of Haiti and the Dominican Republic) had 3,150 (Vetterli, 1950). In North America, the first indigo

Fig. 2 Maya blue on a wall painting fragment from Bonampak, southeast Mexico, c. eighth century A.D. 37x.

plantations had been established about 1700 in South Carolina, where Great Britain in 1773 obtained more than one million pounds of indigo (Pinckney, 1976).

In 1897, BASF succeeded in producing synthetic indigo at a price of sixteen marks per kg and was then able to compete with the plant dye. By 1904, the price of synthetic indigo had fallen to seven marks per kg. By 1913 it had almost completely replaced the natural product. Indigo exports from Germany rose from 0.5 million kg in 1897 to 33.35 million kg in 1913; during the same period, indigo exports from India declined from 8.6 million kg to 0.5 million kg (Vetterli, 1950).

2.3 Dates of Use

Indigo was used in Egypt in the sixteenth century B.C. and possibly earlier. It is still in use as a textile dye, notably for dyeing denim (Hughey, 1983). It was not used by painters in oil after the seventeenth century, but it continues in use today as a watercolor pigment (Harley, 1982).

3.0 General Pigment Properties

3.1 Color and Spectral Reflectance

In the pure form, indigo is a dark blue powder. Seufert (1955) wrote of the color of indigo:

> Indigo is the darkest blue in the spectrum and in the color wheel, as dye a deep dark blue, a blackish blue; it has a dull, dusky greyish quality, stemming from extra-

Table 1 **Plant Species Producing Indigo**

Species[a]	*Areas Grown*	*Reference(s)*[b]
Indigofera tinctoria L.	India and elsewhere	e.g. 1
I. anil L.	South America (pre-Columbian and modern)	1, 2, 3
I. disperma L.		1
I. argentea	Asia	1
I. angustifolia L.		1
I. arcuata Willd.		1
I. caroliniana Walt.		1
I. cinerea Willd.		1
I. coerulea Roxb.		1
I. endecaphylla Willd.		1
I. erecta Thunb.	South America	1, 3
I. glabra L.		1
I. hirsuta L.		1
I. indica Lam.		1
I. mexicana L.		1
I. emarginata Perr.		1
I. sumatrana=I. tinctoria	India	4
I. arrecta	Natal	4
I. paucifolia	Madagascar	4
I. secundiflora	Guatemala	4
I. suffruticosa Miller	The Americas (pre-Columbian and modern)	2
I. guatemalensis	The Americas (pre-Columbian and modern)	2
I. pseudotinctoria	India (?)	5
Isatis tinctoria L. (dyer's woad)	Europe and elsewhere	e.g. 6
Polygonum tinctorium W. T. Aiton (dyer's knotgrass)	East Asia (mostly)	e.g. 6
Strobilanthes flaccidifolius Nees=*S. cusia* Imlay	China, Japan	6, 7
Mercurialis leiocarpa	Possibly Japan	8
Nerium tinctorium= Wrightia tinctoria (oleander tree, pala indigo plant, genipapo tree)	Southern India	9
Lonchocarpus cyanescens (gara plant)	Nigeria, Sierra Leone, western Sudan, Cameroon	10
Sophora tinctoria L.= *Baptisia tinctoria*	North America	11
Baptisia tinctoria (wild indigo)	North America	12
Fuchsia parviflora	Pre-Columbian Central and South America	2
Jacobinia spicigera	Pre-Columbian Central and South America	2
Chiropetalum lanceolatum	Pre-Columbian Central and South America	2

a. Other names used are in parentheses.

b. References: (1) Von Georgievics, 1892 (2) Bruyas, 1970 (3) Zimmerman, 1923 (4) Schultz, 1931 (5) Haller, 1950 (6) Hayashi, 1979 (7) Sewell et al., 1939 (8) Takamatsu, 1879–1880 (9) Mell, 1922 (10) Perkin, 1970b (11) Bühler, 1950 (12) Adrosko, 1971.

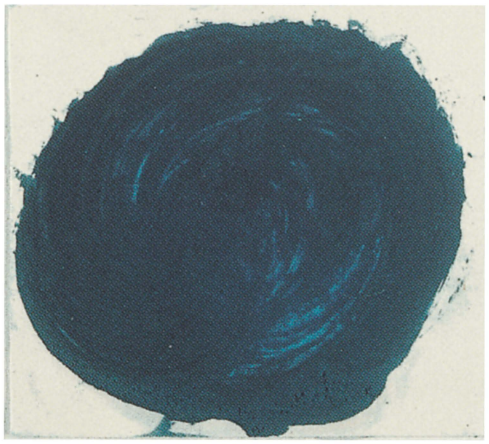


Fig. 3 Paint out of natural indigo mixed (1:1) with calcite. The binder in this paint out is "Medium III (quick drying)" from the Lucas Company (Dr. Fr. Schoenfeld and Co.). This binder contains cyclohexanone resin, acrylic resin, oil of turpentine, and white spirit.

Fig. 4 Paint out of natural indigo mixed (1:3) with calcite containing same binder as in figure 3.

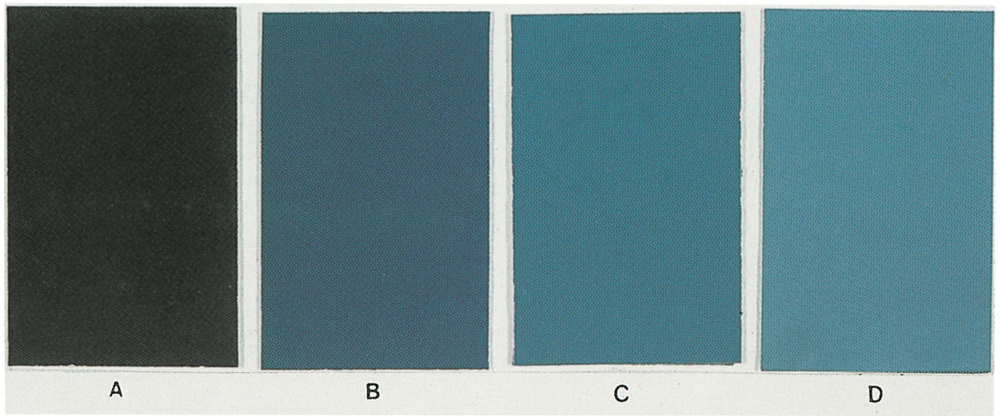


Fig. 5 Paint outs of pure BASF indigo in nitrocellulose binder: (A) at full hue (B) extended with titanium white 1:2 (C) extended with titanium white 1:4 (D) extended with titanium white 1:9.

neous parts in the natural indigo such as indigo brown and indigo red, which the synthetic indigo does not contain and therefore lacks the slight turbidity. Natural indigo is more a deep ink blue; the artificial indigo in powder form is more a black blue.

Figure 3 shows a color sample of natural indigo (ordinary Manila indigo) extended 1:1 with calcium carbonate; figure 4 shows the same at a 1:3 ratio. Maya blue has a more pronounced green tint than indigo alone (see fig. 2).

Figure 5 shows paint outs of BASF indigo, pure, and extended with titanium white at the ratios 1:2, 1:4, and 1:9. Unextended indigo appears almost black.

At one time the color of indigo, especially at the fractures of lumps, was an important characteristic in evaluating its quality, as it was believed that good indigo should be "fired," that is, having a good dark blue color showing a purple-blue reflection at its fracture. The best types of indigo, such as Bengal, acquires on rubbing with the fingernail a very beautiful copper luster on the fracture surface. In addition, the red-violet types of Bengal indigo that exhibited a higher density,

Fig. 6 Lump of commercial natural indigo from India. Photo from Bayer AG (*Bayer,* 1970).

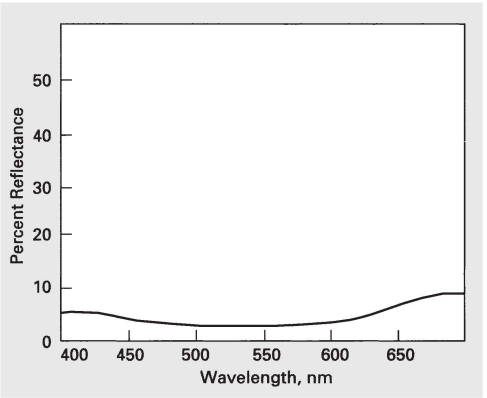


Fig. 7 Spectral reflectance of indigo in parchment size. After Barnes (1939).

were harder, and showed a lustrous fracture surface were considered very valuable.

Less valuable, however, were the light blue varieties because they were less compact than the better indigo. The Bengal indigo types of the lowest value were those that appeared light blue with a gray or green tint (Von Georgievics, 1892).

Specific names were chosen for the various types of natural indigo based on their color: superfine blue, fine blue, blue violet, purple violet, fine violet, fine red, good red, fine coppery, and low coppery (Von Georgievics, 1892). Figure 6 shows a lump of the commercial form of natural indigo.

A typical spectral reflectance curve for indigo is given in figure 7. With CIE illuminant type C, the tristimulus values are X=4.22, Y=3.62, and Z=5.43; the trichromatic coefficients are X=0.3180, Y=0.2728, and Z=0.4092. The dominant wavelength is 540c nm, relative brightness is 3.6%, and excitation purity is 19.0% (Barnes, 1939). Spectral reflectance curves have been used to identify indigo (see section 5.3.3).

3.2 **Permanence**

Used as a textile dye, indigo has an excellent lightfastness of grade eight on wool, but only a moderate grade four on cotton (based on a scale of one as the lowest and eight as the highest degree of lightfastness) (*Colour Index*, 1971). Crews (1987) described it as one of the most light resistant of the natural dyes. Kuramoto and Kitao (1982) studied the mechanism of photofading of indigo.

As a pigment ground with substrates, indigo has good lightfastness. Saunders and Kirby (1994) have published results on the wavelength dependence of its fading. Its resistance to water is good; to alcohol it is good to moderate, and to oil it is low. It is heat resistant to 150°C (Schultz, 1931). Tholen (1950) reported indigo as resistant to air and stable when exposed to hydrogen sulfide when used as an artist's pigment. When exposed to ozone in the absence of light, indigo was very reactive in terms of its fading rate (Whitmore et al., 1987). When exposed to atmospheric nitrogen dioxide it is described as reactive (Whitmore & Cass, 1989); it showed much less change upon exposure to traces of nitric acid in the atmosphere (Salmon & Cass, 1993). Changes in the spectral reflectance of Japanese indigo exposed to "soft white" fluorescent lamps have been reported by Feller et al. (1984).

3.3 **Chemical Properties**

Indigo is insoluble in water, dilute alkali solutions, and acids. It is difficult to dissolve in hot ethanol, amyl alcohol, acetone, ethyl acetate, and pinene and is more readily soluble in chloroform and glacial acetic acid. It is readily soluble in boiling aniline, nitrobenzene, naphthalene, phenol, and phthalic anhydride (Fierz-David, 1926).

Indigo crystallizes from phthalic anhydride in beautiful blue prisms; in other cases, it forms blue-black needles, sometimes with a strong copper luster. The crystals are rhombic. In nonpolar solvents, indigo dissolves to give a red solution; in polar solvents, such as aniline, phenol, glacial

acetic acid, and dimethylsulfoxide, it gives a blue solution in which the solute has a double molecular weight. Some polar solvents such as dimethylformamide destroy the indigo when it is dissolved in them with boiling. The absorption maximum of indigo is 599 μm in xylene solution and 601.5 μm in tetraline solution. In these solvents it has a violet-blue color.

Indigo melts at 390°C to 392°C and sublimes undecomposed. It dissolves in concentrated sulfuric acid to give a yellow-green solution containing salts that are decomposed by water to form very finely divided indigo (BASF, 1899). This process is used on a large scale to manufacture commercial types of indigo, for example, "Indigo rein BASF" (Thiess, 1957). Strong oxidizing agents such as concentrated nitric acid convert it to the yellow isatin (the lactam of 2-aminophenylglyoxylic acid, fig. 8A). Indigo is resistant to hydrochloric acid, and remains unchanged when treated with dilute sodium hydroxide; with concentrated sodium hydroxide the sodium salt forms. Chrysanilic acid, anthranilic acid, and indoxylaldehyde are formed on boiling (Schultz, 1931).

Leucoindigo (fig. 8F) is a white crystalline product that dissolves to yellow in alkali and reoxidizes to indigo in the air. It is formed by reduction in the presence of alkalies, with zinc dust, ferrous hydroxide, dithionites (hydrosulfites), or catalytically activated hydrogen, and by biochemical reduction in a fermentation vat. This reduction process is the basis for vat dyeing. The *cis* form of indigo probably separates from the vat liquor (Thiess, 1957), but is then changed into the *trans* form within a short time (fig. 8B).

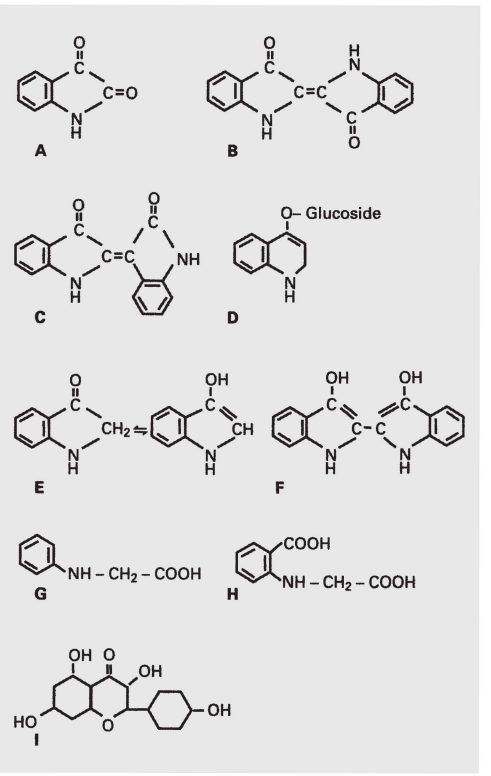


Fig. 8 Formulas for indigo and related compounds: (A) isatin (B) indigo (C) indirubin (D) indican (E) indoxyl (F) leucoindigo (G) phenylglycine (H) phenylglycine-o-carboxylic acid (I) kaempferol.

3.4 **Compatibility**

Indigo is not resistant to waterglass (sodium silicate) or lime. It is stable in mixtures, opaque, and can form glazes (Tholen, 1950). Indigo is suitable for the graphic arts, watercolors, and tempera painting (Schultz, 1931). It has found application in these as well as in glue medium and oil paints, but not to the same extent as azurite, ultramarine, or Prussian blue. In an oil medium it may bleed since it is somewhat soluble; nevertheless, it was listed in oil colors sold by Winsor and Newton and other English color makers in the nineteenth century (Carlyle, 1991). Generally, indigo is not used for murals since its lightfastness is inadequate. In the past it was frequently used for coloring stucco; however, noticeable fading usually occurred in the areas most exposed to light.

Indigo has been widely used in mixtures, most commonly with yellow to produce green. On an eighth-century painted temple ceiling in Nara, Japan, it was mixed with yellow ocher and with red iron oxide (Mogi et al., 1975). The indigo and yellow ocher mixture was also used in Japan in tenth-century paintings on wood (Yanagisawa, 1985) and in eleventh-century wall paintings (Yamasaki, 1958). During the fourteenth to nineteenth centuries, painters in the Islamic world from Turkey to India commonly used a mixture of orpiment and indigo to produce varying shades of green (FitzHugh, 1988) and Cennino Cennini mentioned the use of the same mixture in fifteenth-century Florence (Thompson, 1933). Cennini noted that indigo was mixed with lead white or lime white and an early eleventh-century Persian author also listed indigo and lead white, although he commented that ultramarine with lead white was preferred (Minorsky, 1959). The orpiment-indigo mixture was identified on a

fourteenth-century Flemish painting (Serck-Dewaide et al., 1978–1979), and indigo was mixed with lead-tin yellow by the fifteenth-century Dutch painter Dirck Bouts to give a blue-green (Bomford et al., 1986).

3.5 Oil Absorption and Grinding Properties

Grinding in oil requires approximately 90 to 100 parts oil to 100 parts indigo. Without the addition of drying pigments such as lead white the color dries poorly. The covering power of indigo is relatively low, but its coloring capacity is considered very good. Wehlte (1982) places oil absorption of indigo in the normal range.

4.0 Composition

4.1 Chemical Composition

Indigo has the two halves of the molecule linked together at the respective 2- positions, the structure shown in figure 8B. In addition to indigo, natural and synthetic indigo pigments contain greater or smaller amounts of the isomer indirubin, also called indigo red, which has the same two moieties linked between the 2- and 3-positions (fig. 8C) (CI no. 75790, Schultz no. 1327). Indian types such as Bengal indigo contain 2% to 4% indirubin, however the Javanese type occasionally contains as much as 15% (BASF, 1907). Indirubin is soluble in ethanol and in 10% sulfuric acid and can be extracted by boiling with ether to give pure indigo (BASF, 1907; Gentele, 1909).

Titration with sodium dithionite can be carried out to determine the quantity of indigo blue and indirubin in an indigo sample since the blue indigo is reduced first, followed by the red indirubin. The end of the titration for blue is recognized when the color changes from blue to violet. The volume of dithionite consumed is recorded, the titration is continued until the red color disappears, and the volume is recorded again. The difference between the two figures corresponds to the amount of indirubin present (BASF, 1907).

A yellow component, kaempferol, 3,5,7,4'-tetrahydroxyflavone (fig. 8I), occurred at one time as an additional component in some natural indigo, particularly indigo prepared from the leaves of the indigo species *Indigofera arrecta*, which is indigenous to Natal. Perkin (1907a) demonstrated that the dried leaves of Natal indigo contain approximately 4% kaempferitrin (kaempferol rhamnoside). There is a relatively high kaempferol content in Javanese indigo because it was produced from *Indigofera arrecta* imported into Java from South Africa by Dutch traders. The crude indigo mud was treated with dilute sulfuric acid to purify it. In this process, kaempferol is formed from kaempferitrin by glycoside cleavage and remains as a water-insoluble compound in the indigo.

In analyzing types of indigo rich in indirubin, Perkin also found isatin (see fig. 8A) (Rupe, 1909), which indicates that indirubin is formed during the synthesis of indigo from isatin and indoxyl (fig. 8E). It appears that indirubin forms readily in plant indigo when the extract of the fermented plant is oxidized in the presence of weak alkalies.

Additional organic secondary components of natural indigo products have fanciful names and are of indefinable composition. Indigo gluten is a substance similar to vegetable glutens and can be extracted from indigo by treating it with dilute sulfuric acid followed by filtration. Indigo brown includes brown amorphous substances that do not attach themselves to the fiber when indigo is used as a textile dye, but they appear to be present in the indigo that is bound to lime. When indigo is separated from indigo gluten by means of sulfuric acid, and subsequently digested with potassium hydroxide, the brown material dissolves, with a little indigo, and colors the solution dark brown, almost black (Gentele, 1909).

Depending on the quality of the natural indigo, its ash content may vary from 10% to 90% primarily due to the presence of calcium and magnesium carbonate and, to a lesser degree, alumina and iron oxide (Von Georgievics, 1892). The content of indigo blue varies between 20% and 90% in natural indigo products. The best types contain 70% to 90% indigo, more inferior types contain 40% to 50%, and the most inferior frequently contain only 20% (Heermann, 1930).

Synthetic indigo, if not extended, contains approximately 98% indigo blue and also some indirubin and iron oxide.

4.2 Sources of Natural Indigo in the Plant Kingdom

Indigo (see fig. 8B) is formed by enzymatic or acid hydrolysis of indican (indoxyl glucoside, see fig. 8D) to give indoxyl (3-hydroxyindole, see fig. 8E), which is subsequently oxidized by atmospheric oxygen to give leucoindigo (dihydroindigo, see fig. 8F), and then indigo. Indican occurs in numerous plants (see table 1). Studies have shown that indigo is in the *trans* form, as

Fig. 9 Indigo plant (*Indigofera anil* L.). From Elisabeth Blackwell *Sammlung der Gewächse* (Nuremburg, 1754).

Fig. 10 Woad plant (*Isatis tinctoria* L.). From Elisabeth Blackwell *Sammlung der Gewächse*.

represented in figure 8B (Lüttke & Klessinger, 1964).

The main sources of indigo are plants of the genus *Indigofera* cultivated from 20° to 30° north latitude in India, and also in Java, Sumatra, Madagascar, the Philippines, China, Japan, South Africa (Natal), Central America, Venezuela, and Brazil. Various other *Indigofera* species have been cultivated for indigo in different parts of the world and are listed in table 1. In India, much of the largest amount of natural indigo was obtained from *Indigofera tinctoria*. Figure 9 shows an *Indigofera anil* plant illustrated in the 1754 edition of Elisabeth Blackwell's (1750–1773) *Sammlung der Gewächse*. *I. pseudotinctoria* is said to be superior with respect to the quality of the indigo obtained (Haller, 1950).

In addition to the *Indigofera* species, other plants important as indigo sources have been dyer's woad, dyer's knotgrass, the indigo-containing oleander, the gara plant, and several plants found in the Western Hemisphere. The latter included wild indigo *Sophora tinctoria* (Bühler, 1950) also known as *Baptisia tinctoria* (Adrosko, 1971) that was used by the early colonists of Pennsylvania and the Carolinas as a source of blue dye.

In the past, dyer's woad (*Isatis tinctoria* L.) was cultivated on a large scale in Normandy, Provence, and Languedoc, and also in England and Germany. In Germany, cultivation was prevalent in Silesia, Brandenburg province, and in the area of Magdeburg. It was produced extensively in Thuringia, where in 1616 three hundred villages made a living from woad cultivation: Erfurt, Gotha, Arnstadt, Langesalza, and Tannstadt were five towns engaged exclusively in the woad-producing trade (Von Georgievics, 1892). Figure 10 is a woad plant illustrated in Blackwell's *Sammlung der Gewächse*.

In Japan, China, and Manchuria dyer's knotgrass (*Polygonum tinctorium* T. W. Aiton) has been cultivated for the preparation of indigo. In relation to the weight of dried leaves of the plant, it gave a very good indigo yield. Dyer's knotgrass was introduced with some success in 1835 to the Russian territories in the Caucasus. In 1936 in the province of Szechwan in China, seven mil-

lion pounds of crude indigo were produced from *Polygonum tinctorium* and another indigo plant, *Strobilanthes flaccidifolius* Nees, now *S. cusia* Imlay (Sewell et al., 1939). Table 1 lists other indigo plants available in China and Japan. In Europe, indigo production from dyer's knotgrass was negligible, although *Polygonum* plantings grew well in various regions of France, Bohemia, and Carinthia (Von Georgievics, 1892).

In the nineteenth century in southern India, the botanist Roxburgh raised the indigo-containing oleander *Nerium tinctorium* (also called *Wrightia tinctoria*), which does not require good soil for cultivation. Also called the "pala indigo plant" or "genipapao tree," it can grow to a height of twelve to fifteen feet (Mell, 1922).

Even today, the gara plant, *Lonchocarpus cyanescens* (family Papilionaceae) is planted as a source of indigo in some parts of the southern provinces of Nigeria, Sierra Leone, western Sudan, and Cameroon. Commonly known as "yoruba indigo," this plant is a climber that reaches ten to forty feet. Its leaves and buds are pressed into balls like "woad balls" and dried in the sun (Perkin, 1907b).

4.3 Preparation

4.3.1 ***Preparation of natural indigo from indigo plants.*** The metabolite present in all the above-mentioned dye plants is the water-soluble indoxyl glucoside (Indican, see fig. 8D). To obtain indigo, the glucoside bond must first be broken by enzymatic or acid hydrolysis leading to the formation of indoxyl (see fig. 8E) and glucose. Indigo (see fig. 8B) is formed from indoxyl by dehydrogenation with atmospheric oxygen by way of leucoindigo (see fig. 8F). Fermentation of the plant material results in a hydrolysis of the glucoside catalyzed by an enzyme present in the cells of all plants that produce indigo.

Probably because of its low dye content (approximately 1/30 of the amount of dye in *Indigofera* species [Rupe, 1900]), dyer's woad was not used as raw material for the production of indigo. After drying, woad was crushed into a pulp in wet grinding mills and stacked in heaps approximately one meter high. The mass was allowed to ferment for approximately two weeks and from it round woad balls were then formed and placed on trays to dry. The woad balls were then placed in a vat with water and again allowed to ferment; this produced a liquor that, when warmed, was used to dye textiles (Ruggli, 1932; *Bayer*, 1970).

In India the dye was obtained from the *Indigofera* species, described by Heermann (1930):

> The harvested leafy branches that are approximately 0.5–1 m long are placed diagonally in successive, closely packed layers in large, cemented, oblong stone basins. The top layer is covered with bamboo canes and then weighted down with heavy beams. Water is then allowed to run into the basins, until the entire mass of leaves is submerged in the water. The basins are located in the open and are only protected against rain and sun by a roof.
>
> In the cold-water process, the extraction of the indican is complete in six to nine hours. After approximately ten hours, the water is drawn off and a few minutes later a semiliquid blue deposit forms. The liquid is vigorously brought into contact with atmospheric oxygen by beating, and all of the indoxyl is converted into indigo within approximately two hours. The crude indigo, which has settled in the beating basins, the "crude paste," is transferred to filters for draining, leached with water or boiled and then subjected to a thorough chemical purification. The purified product is pressed into small bricks and finally dried in artificially heated chambers.
>
> Warm-water process. Water above 50°C is used, which accelerates the entire process considerably. The extraction process begins after only fifteen minutes and is essentially complete within three to four hours. The bond scission in indigo formation described above is not brought about bacterially but by an enzyme present in the cells. Indigo is also obtained from dried leaves in some areas. The average yield from 100 kg dried plants is approximately 1.5 to 2 kg indigo.
>
> Commercial form. The better types of indigo are sold mostly in the form of brick-shaped or cubic pieces (approximately 6 cm long), or in broken pieces of varying sizes. On the surface they usually bear a stamped mark indicating the factory and the region from which the indigo comes. All cubes and bricks have a gray efflorescence on the surface, and those from India also show a net-like impression from the linen cloth on which they lay while drying, on one or several surfaces.

An eighteenth-century illustration (fig. 11) shows the steps in the production of indigo in the West Indies. Similar illustrations have been published by Pomet (1694) and in other seventeenth- and eighteenth-century French sources (see Pinault, 1987).

4.3.2 ***Preparation of synthetic indigo.*** Baeyer and Emmerling (1870) were the first to prepare synthetic indigo by using isatin (see fig. 8A) as the starting material; another possible synthesis from *o*-nitrobenzaldehyde and acetone was reported by Baeyer and Drewsen (1882). Baeyer (1883) determined the correct structural formula for indigo. Heumann (1890a) demonstrated that indigo is formed when *N*-phenylglycine (fig. 8G) readily obtainable from chloroacetic acid and aniline, is fused with alkali hydroxide; indoxyl (see

fig. 8E) is initially produced by a ring closure and is then converted to indigo by oxidation.

Heumann's patents for his indigo synthesis were transferred to BASF, Ludwigshafen, and the Hoechster Farbwerke. The yield from Heumann's first indigo synthesis could not be increased above 10% of the theoretical yield with the means available at that time, whereas significantly higher yields were obtained in Heumann's second synthesis starting from phenylglycine-o-carboxylic acid (fig. 8H; Heumann, 1890b). The commercial production of indigo at BASF started in 1897 when the first "Indigo rein BASF" was released and by 1913 amounted to 4,800 tons. From 1925, BASF produced all of its indigo from phenylglycine nitrile (cyanomethyl aniline). In 1926, sodium amide replaced alkali hydroxide in the fusion reaction and amounts of indoxyl were obtained that were 90% of the theoretical yield.

Initially, Heumann's indigo synthesis based on fusing phenylglycine with alkali to close the five-membered heterocycle resulted in low yields. Pfleger (1901) improved production by adding sodium amide to the alkali hydroxide melt to form indoxyl in high yields. This process was transferred to the Hoechster Farbwerke and they entered the market with a synthetic indigo known as Indigo MLB.

Prior to World War I, the factory production of indigo was limited mainly to Germany. Later, indigo factories developed in England, France, Switzerland, the United States, and Japan, and probably all of them used the phenylglycine/sodium amide process.

Holzach (1948) and Von Nagel (1968) have given detailed descriptions of the history of commercial indigo syntheses.

4.4 Adulteration and Sophistication

To better identify the natural types of indigo, special descriptive names indicating quality and origin were used. Examples include Bengal indigo, Java indigo, or statements of color such as superfine violet, fine violet, clear blue, purple violet, violet blue, ordinary blue, fine coppered, and low coppered. Names used included sandy indigo (*sablé*), which shows sandy patches in its interior; spotty indigo (*piqueté*), which contains pin-head size blue and white spots; burnt indigo (*brulé*), a too strongly dried product; indigo covered with a salt efflorescence (*éventé*); and banded indigo (*rubané*), which shows various layers at the surface of the fracture (Haller, 1950). Because of the demand for natural indigo, it was adulterated in many ways in the countries of origin. In India it was frequently mixed with such adulterants as ashes, washed earth, sand, slate dust, and brick dust, and the adulterations were characterized by high ash content; in eastern India gum or extract of a fruit known as *Embryopteris gelatinifera* was often added, which could be detected by a slimy appearance and the softening of such indigo in water.

Natural indigo was frequently adulterated in Europe; additions included starch, finely crushed blue wool and silk rags, Prussian blue, soot, and resin. Occasionally the indigo was stored in damp locations to raise its normal moisture content and thus increase the weight by 3% to 6%. Other common adulterants were gypsum, clay, chalk, and steatite (Church, 1890).

Usually adulterations in lump or powdered indigo are readily detectable. When indigo contains starch it turns black on contact with concentrated sulfuric acid, and an aqueous extract gives a violet-to-blue color with iodine solution. The presence of blue rags is easy to detect with a magnifying glass or a reflected-light microscope. If indigo adulterated with Prussian blue is boiled in sodium hydroxide (1N concentration) the Prussian blue dissolves; addition of dilute sulfuric acid and ferric chloride to the filtrate causes the Prussian blue to reprecipitate. A resin content is detected by the odor produced when an indigo sample is burned. Soot is detected by boiling a sample in concentrated nitric acid; the blue indigo is oxidized into yellow isatin (see fig. 8A), while the soot remains black. When the nitric acid is diluted with water and then filtered, the filter will contain the black residue of soot. The moisture content of an indigo sample can be determined by weight loss when dried (Von Georgievics, 1892; Schweppe, 1977).

Von Georgievics gave comprehensive criteria for the evaluation of indigo:

> It should never be granular, but of a fine pasty condition, indigo must be very dense but still have a low specific weight and not be hard. When the fracture surfaces are of a floury consistency and covered by a thin skin, it is said: "The indigo is open"; in contrast to the so-called closed indigo, which does not have these characteristics and is of lower quality. The color is supposed to be a beautiful blue or reddish blue, brighter at the fracture than on the outside. The purer the indigo, the more readily it will burn and the lower the amount of remaining ash; the latter is rust-colored for good types, gray for lower quality. Further, it should be completely dry and

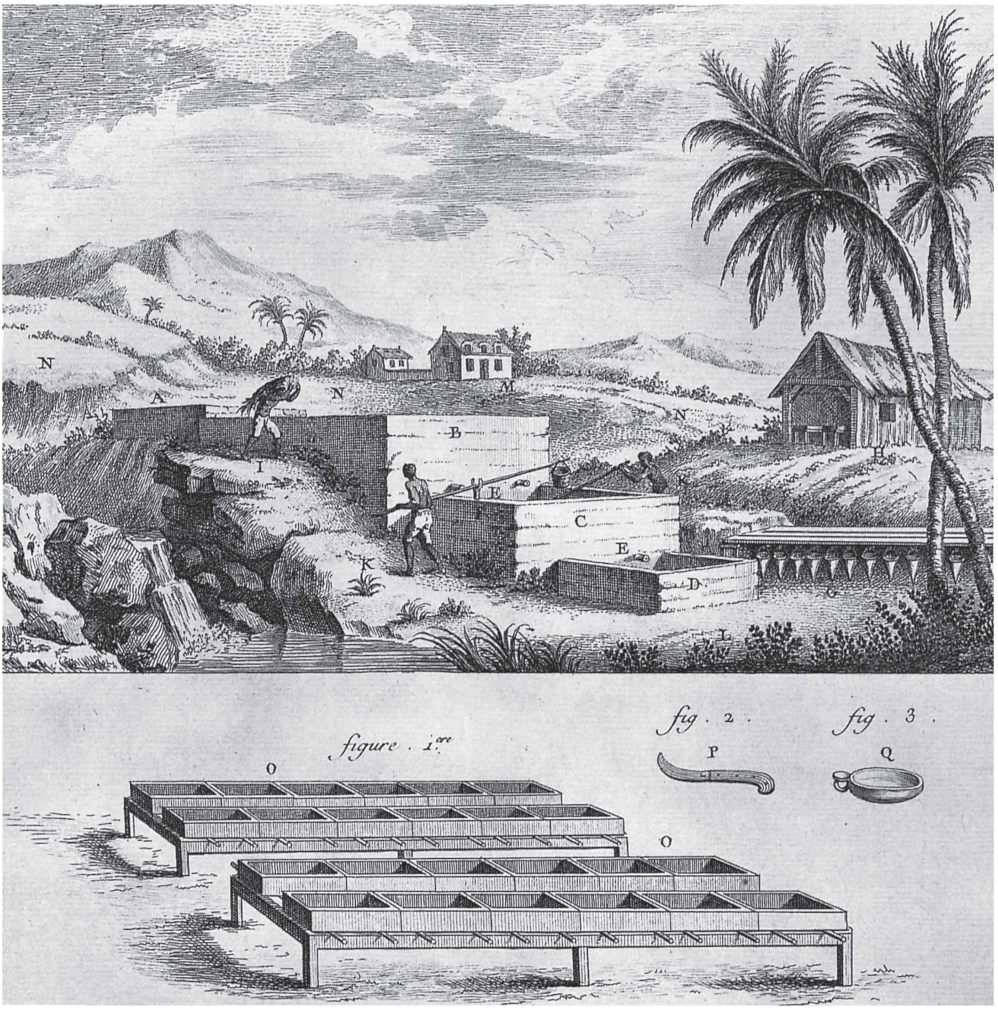


Fig. 11 Indigo plantation in the West Indies. From Diderot (1751–1765).

A. Tank for pure water.
B. Soaking tank.
C. Beating tank.
D. Settling tank where blue sediment precipitates in the bottom.
E. Taps through which liquid passes from one tank to a lower tank.
G. Cloth bags filled with indigo, hanging to drain.
H. Drying shed.
K. Workers continually agitating the dye in the beating tank with pierced buckets attached to long poles.
1.O Wood containers on trestles on which the indigo dries in the drying shed.
2.P Curved knife for cutting the indigo.
3.Q Polished silver cup used to examine the dye particles, which form in the beating tank.

break easily. A good indigo, when moistened makes a streak on white paper that looks beautifully blue when it is spread with water.

Synthetic indigo may be mixed with dextrose, molasses, or glucose, and the author has found adulterations with chalk and gypsum. Titration methods such as the hydrosulfite titration (BASF, 1907), and gravimetric methods (BASF, 1907; Whittaker, 1923) are important for detecting adulterations and determining how far the indigo has been extended and hence the value of an indigo sample. A comparison dye test is equally important to the expert for determining the dye content. Additional aids for determining its value are the colorimeter and the spectrum in the visible range.

5.0 Identification and Characterization

5.1 Optical and Chemical Microscopy

Indigo is easily confused with Prussian blue in artists' paints because of its color as well as its extremely fine state of subdivision. Individual pigment granules often cannot be recognized under the light microscope. Layers of paint pigmented exclusively with indigo appear black in reflected light and blue or greenish in transmitted light if the pigment layer is thin. In an oil film, indigo can appear dissolved in the medium. To distinguish it from Prussian blue a drop of 10% potassium hydroxide or 5% sodium hydroxide is dropped on the sample; Prussian blue is decolorized while indigo remains unchanged. The application of dilute nitric acid will decolorize indigo while Prussian blue is unaffected. This test can be carried out on small samples under the microscope. The nitric acid test fails when the indigo is in the form of artists' pigment in a preparation with clay minerals (attapulgite) such as Maya blue (Kleber et al., 1967). Specific tests for indigo include solubility in chloroform giving a deep blue solution and bleaching by sodium hypochlorite (Plesters, 1956).

5.2 Chemical Identification

The chemical tests apply mostly to indigo-dyed textiles but may, in some cases, be adapted to test for indigo applied as a pigment.

5.2.1 ***Sublimation test.*** This is probably the oldest test used to identify indigo since it is mentioned by Pliny the Elder in *Historia Naturalis* (Bailey, 1932; see also König, 1960), where he said: "Indigo is tested on hot charcoal, for pure indigo gives a flame of a fine purple color."

Indigo sublimes into a red-violet vapor at approximately 230°C and on cooling is deposited in characteristic blue-black crystalline needles that are easily recognized with a magnifying glass or under a reflected light microscope (Fierz-David, 1926; Heermann, 1930; Thiess, 1957). Rathgen (1921) described an experimental procedure in which the sublimation test is performed in a carbon dioxide atmosphere at a defined temperature. This procedure prevents any accompanying substances such as fibers or binding agents from being charred and the indigo crystallization from being obscured by cracking products. In many cases it is sufficient to perform the sublimation test in a small ignition tube or in a closed-end glass capillary of 1 mm inside diameter, which is heated over a Bunsen burner.

The sublimation test may also be carried out by burning a fiber that is dyed with indigo and holding the burning fiber against a cold, white porcelain dish. The sublimed blue dye condenses on the porcelain (Whittaker, 1923).

5.2.2 ***Nitric acid test.*** One drop of concentrated nitric acid is placed on a sample of textile. When an indigo dye has been used a yellow spot surrounded by a green edge is formed (Whittaker, 1923). When indigo is in the form of pigment a small sample of a few micrograms is crushed on a small piece of filter paper supported on a hard surface. The nitric acid test is then carried out on the filter paper. A pigment sample may also be treated with a sodium hydroxide/hydrosulfite liquor to first dye a piece of cotton (see section 5.2.3), and the nitric acid test is then carried out on the dye. Indigo is oxidized to the yellow isatin (see fig. 8A) by treatment with nitric acid, the green edge formed in the test is a mixing zone of yellow isatin and blue indigo.

Since other vat dyes in addition to indigo turn yellow on being treated with nitric acid (for example, Indanthrenblau RS [Indanthrene Blue, CI no. 69800]), the spot obtained with nitric acid is placed in an acid solution of tin–II–chloride (10g tin–II–chloride, 50 ml hydrochloric acid, 50 ml water). If it is indigo the yellow spot remains while the original blue color returns with vat dyes such as Indanthrenblau RS (Siebel, 1960).

5.2.3 ***Hydrosulfite test.*** Sodium hydrosulfite (sodium dithionite, $Na_2S_2O_4$) reduces indigo to the leuco form, sometimes called indigo white (see fig. 8F). A small sample of dye or pigment is shaken with an alkaline solution of the reagent (50 g sodium dithionite, 50 g sodium hydroxide in 1 liter water), or warmed for about one minute on a water bath; the solution then turns yellow. If a short cotton thread (about 0.5–1 cm long) or a cotton swatch (about 2 x 2 mm along the edges) is placed in this so-called vat for approximately fifteen minutes at room temperature, the cotton is dyed yellow; the color changes to blue on exposure to the air as indigo is re-formed by oxidation.

Hofenk de Graaff (1974) modified the hydrosulfite test as follows: a few drops of ethyl acetate are added to the hydrosulfite solution after cooling. When it is shaken the ethyl acetate layer turns blue in the presence of indigo. The reaction is very sensitive; as little as approximately five

micrograms of indigo can be identified. This test distinguishes indigo from other natural violet or blue dyes such as logwood, archil, tannin, and Tyrian purple as none of the latter dyes have been found to give the same reaction. Some synthetic vat dyes can have the same color reaction, therefore, a chromatographic comparison may be necessary in some instances.

Brilliant indigo varieties—synthetic halogen substitution products of indigo—can be differentiated from indigo dyes by placing a dye sample in hydrazine. Dyes with indigo remain blue, whereas brilliant indigo dyes immediately turn yellow-brown (Schweppe, 1977).

5.2.4 ***Solubility tests.*** Indigo dissolves in boiling glacial acetic acid to give a blue solution. Glacial acetic acid is capable of stripping indigo quantitatively from plant and animal fibers (see BASF, 1907) and is suitable for separating indigo from alumina lakes of various natural dyes such as weld lake and buckthorn lakes. To further identify the indigo, the glacial acetic acid solution is evaporated to dryness in a porcelain dish on the water bath, the residue is washed several times with water and ethanol and then used for a hydrosulfite test (see above) or to obtain the infrared spectrum (see section 5.4).

The solubility properties of indigo are summarized in section 3.3. It dissolves in paraffin to give a wine red color. Rathgen (1921) reported that microchemical identification of indigo may be obtained by saturating a single blue thread liberally with paraffin, placing it in a melting-point tube, and cautiously heating it over the pilot flame of a Bunsen burner. A wine red solution in the melted paraffin, characteristic for indigo, then appears and can frequently be seen with the naked eye but better with low magnification.

A yellow color first results when indigo is dissolved in cold, concentrated sulfuric acid, a short time later it turns olive in color. When the solution stands for an extended period of time, the color slowly changes to green and then to deep blue. No change in color occurs when water is added; the solution remains blue. The indigo undergoes sulfonation to turn into indigo carmine (indigodisulfonic acid). When a short, wool thread is added to the blue solution and the solution is boiled, the wool thread is dyed blue (Whittaker, 1923).

5.2.5 ***Thin-layer chromatography.*** A comparison against a known indigo sample by thin-layer chromatography frequently is useful for positive identification of indigo mixed with other dyes or pigments.

Hofenk de Graaff (1974) used the indigo solution obtained by shaking the dyeing liquor with ethyl acetate (see section 5.2.4) for thin-layer chromatography on plates coated with acetylcellulose obtained from Polygram Cel AC-30, manufactured by Macherey, Nagel and Co., Düren, Germany. The solvent mixture was ethyl acetate/ethanol/water (2:1:1); indigo gave a blue spot of Rf-value of approximately 0.50. Some samples gave a second violet spot at Rf-value 0.55, which was probably indirubin. A separation on Merck silica gel-60 plates is possible for indigo, indirubin, and isatin using 9:1 toluene/glacial acetic acid (1) and 9:1 chloroform/tetrahydrofuran (2) to obtain the following Rf-values (Schweppe, 1977):

	(1)	*(2)*	*Color of Spots*
Indigo	0.29	0.54	blue
Indirubin	0.26	0.31	red
Isatin	0.08	0.26	yellow

Solutions in ethyl acetate, glacial acetic acid, or tetrahydrofuran can be used for spotting on the thin-layer plate.

Thin-layer chromatography has been used to identify indigo in Indian nineteenth-century textiles (Kharbade & Agrawal, 1988) and to analyze synthetic organic pigments, including indigo, used in artists' commercial oil paints (Strauss, 1984). High-performance liquid chromatography was used to identify indigo in a Dutch nineteenth-century pigment collection (Pey, 1989).

5.3 Instrumental Methods of Analysis

5.3.1 ***X-ray diffraction.*** X-ray diffraction data for indigo have been published (table 2). This method can be useful in identifying indigo if sufficient material is available, but this is rare with pigments on objects or paintings.

5.3.2 ***Infrared spectroscopy.*** Infrared spectroscopy as a method for identifying naturally occurring organic pigments has been described by Kühn (1961, 1964), Abrahams and Edelstein (1964, 1967), Flieder (1968), Masschelein-Kleiner and Heylen (1968), and Van't Hul-Ehrnreich (1970). Infrared analyses of polyatomic molecules such as indigo (30 atoms, 84 normal vibration modes) can lead, with considerable effort, to a complete listing of all observed bands corresponding to the (mechanically possible) normal modes of vibration.

Table 2 **X-ray Diffraction Data for Indigo (CuKα 1.5418 Å)**[a]

d (Å)	*I/I*
8.48	90
6.69	20
6.31	90
5.14	10
4.76	10
3.92	50
3.73	50
3.39	100
3.13	30
2.86	10
2.77	30
2.49	10
2.26	10
2.21	30
1.98	30
1.84	10
1.80	10
1.69	10
1.62	10
1.56	10

a. *JCPDS Powder Diffraction File* 4-0508. From *JCPDS* (1988).

Table 3 **Infrared Absorption Maxima of Indigo**[a]

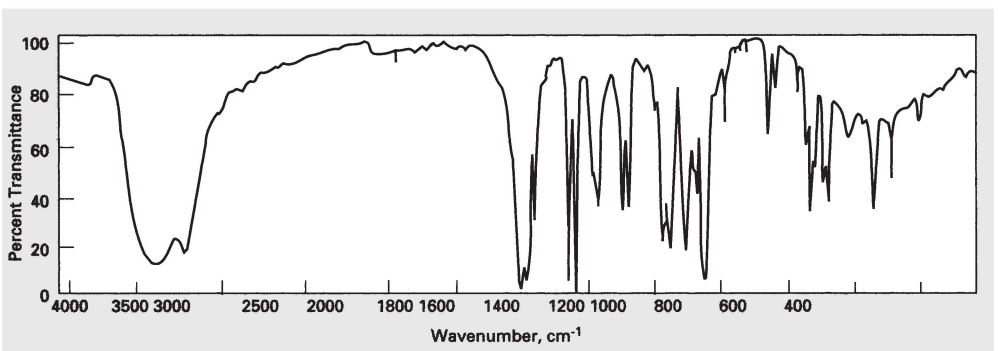
Wavenumbers (cm^{-1})	*Wavenumbers in Order of Decreasing Intensity* (cm^{-1})
1626.2	1626.2
1613.0	1613.0
1585.2	1074.1
1482.1	1461.0
1461.0	1128.5
1393.4	1482.1
1318.3	1174.6
1299.6	1198.9
1221.5	1318.3
1198.9	1393.4
1174.6	1585.2
1128.5	1299.6
1095.5	1095.5
1074.1	563.4
1011.5	697.6
878.6	753.2
858.7	711.8
789.7	509.3
763.7	878.6
753.2	1221.5
711.8	1011.5
697.6	763.7
563.4	418.5
509.3	858.7
418.5	789.7

a. Recorded with a Perkin-Elmer infrared spectrophotometer 283 (instrument specification for the complete wavenumber range 1.5 cm). The wavenumber were corrected according to the polystyrene spectrum that was also recorded. All bands are given that decrease the transmission at least 1%.

Figure 12 shows the infrared spectrum of pure indigo, recorded in the form of a pressed KBr pellet. The infrared spectral bands are listed in table 3 in order of wavenumber and decreasing intensity.

Compared to similar carbonyl compounds with five-membered rings indigo is conspicuous for having a very low C==O stretching frequency of 1626 cm^{-1} (by comparison, cyclopentanone has a carbonyl stretching frequency of 1742 cm^{-1}). Lüttke and Klessinger (1964) attribute this unusually low-carbonyl frequency to hydrogen bonding, citing the broad N—H bands observed at 3246 cm^{-1} in crystalline indigo in support. These hydrogen bonds can be inter- and intramolecular (Klessinger & Lüttke, 1966).

Fig. 12 Infrared spectrum of pure indigo.



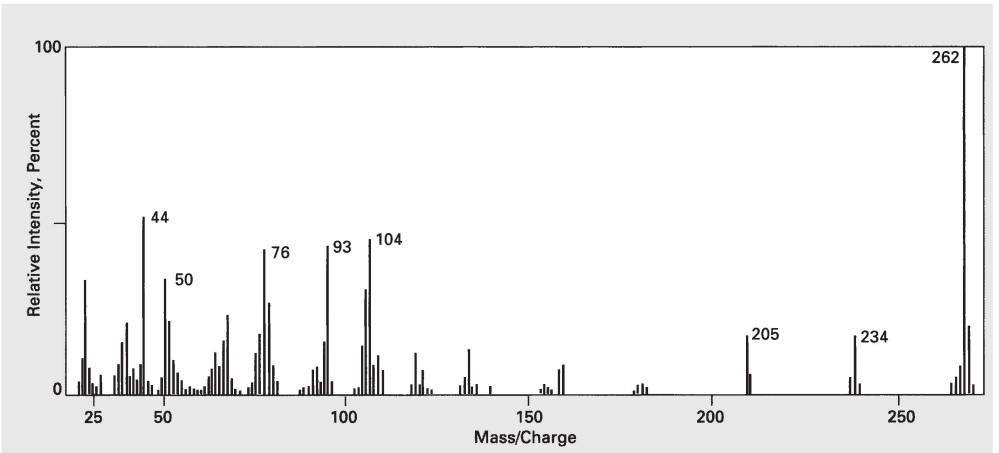


Fig. 13 Mass spectrum of indigo. The mass 262 corresponds to the molecular weight of indigo. After splitting-off of carbon monoxide, a fragment of mass 234 is formed.

When determining the infrared spectrum of an unknown pigment sample a preceding purification is essential. This can be accomplished by extracting the indigo into glacial acetic acid solution, evaporating the extract to dryness, and treating the residue with dilute ammonia and ethanol. An infrared spectrum is recorded on the insoluble portion. Another possibility for pretreatment is to use the hydrosulfite test described by Hofenk de Graaff (section 5.2.3). After treatment of the analytical sample with alkaline sodium dithionite solution, enough ethyl acetate must be added to dissolve sufficient indigo to obtain the spectrum (approximately 20 µg for microtechniques). For the same reason, reoxidation to indigo while shaking the solution in air should also be maximized, possibly by the addition of an excess of ammonium persulfate.

5.3.3 ***Visible spectroscopy.*** Saltzman (1978) along with others (1963) used absorption spectroscopy in the visible range for the identification of dyes on old textiles, including indigo; they measured the transmission of an indigo solution in chloroform. Johnston and Feller (1963) used spectral reflectance curves to identify various artists' pigments and in many cases were able to analyze them nondestructively. Identification of indigo or indigo mixtures on Japanese prints has been carried out by this method (Feller et al., 1984). A combination of wet chemistry and ultraviolet visible spectroscopy was used to differentiate between indigo, Prussian blue, and iron-mordanted logwood on textiles (Cordy & Yeh, 1984). Formanek (1928) recorded the position of the absorption maximum for indigo as 5990 Å (in xylene) and 6015 Å (in tetraline) in his comprehensive work on the absorption spectra of indigo and its substitution products. The author's measurement in pyridine solution produced a value of 6100 Å.

5.3.4 ***Mass spectrometry.*** Figure 13 shows the mass spectrum of indigo. Fragmentations occurring in this spectrum are not very pronounced as is generally the case with aromatic compounds.

5.3.5 ***Other instrumental methods.*** Emission-spectrographic analysis can provide negative evidence for indigo. The presence of iron would indicate Prussian blue or the presence of other elements such as copper, cobalt, or sodium would indicate other blue pigments such as azurite, cobalt blue, or ultramarine, respectively.

Indigo has been identified by Raman-microprobe analysis with related techniques of absorption microspectrophotometry and fluorometric analysis (Guineau, 1989).

5.4 Criteria for Identification

As with most organic colorants, optical microscopy is of limited value for positively identifying indigo. Chemical tests conducted under the microscope can distinguish between indigo and various other blue pigments such as Prussian blue but are more difficult with mixtures. Where chemical tests can be applied on a slightly larger scale in micro test tubes or similar apparatus,

more flexibility in establishing identification is available. Of such tests, the reduction to leucoindigo by sodium dithionite followed by extraction into ethyl acetate and reoxidation to indigotin appears to be a reliable and positive method.

Thin-layer chromatography requires a minimum of sample material and is especially useful when mixtures are suspected. Of the instrumental methods, infrared spectroscopy is usually only definitive if it is combined with a separation technique to remove other organic compounds such as media, support constituents, or other colorants. When separation is possible this method may be regarded as positive. Similar limitations may apply to mass spectroscopy. Hyphenated gas chromatography–mass spectroscopy is now fairly widely available and might be useful in testing for indigo. If a large enough sample is available, x-ray powder diffraction is a positive identification method. The visible spectrum of indigo has a characteristic shape that in most cases can establish positive identification; if mixed with other colorants indigo can be difficult to identify especially when reflectance spectroscopy is used. Fading or other chemical deterioration of most organic colorants makes identifications more difficult and no absolute criteria can be set for such cases.

6.0 **Occurrences**

The occurrences list gives some published identifications of indigo, many of which were made before the general application of chromatographic and spectrometric methods to pigment analysis. They supplement the discussion in section 2.2 of the historical aspects of the pigment.

Occurrences of Indigo

Date, Country, or School	*Artist, Title or Description* *Collection or Location*	*Analyst and Method of Identification*
Europe		
Russia, 13th–15th C	Icons	Filatov et al. (1965) micr., chem., IR, see also Lelekova and Naumov (1981)
Norway, 1250–1350	Painted wooden altar frontals	Plahter (1984), micr.
Germany, 1466	Herlin Altarpiece, Church of St. James, Rothenberg	Broekman-Bokstijn (1970) micr., IR
Italy, c.1431–1495	Cosimo Tura, *Allegorical Figure* National Gallery, London	Dunkerton et al. (1987) micr.
Netherlands, c.1415–1475	Dirck Bouts, two paintings National Gallery, London	Bomford et al. (1986) micr.
Italy, 1495–1497	Leonardo da Vinci, *Last Supper* Monastery of Santa Maria delle Grazie, Milan	Kühn (1985) micr., chem.
16th C	*Madonna and Child* (panel painting) said to have come from Mary of Guise's House, Blyth's Close, Edinburgh	Townsend (n.d.) micr., chem.
Netherlands, 1611–1614	Peter Paul Rubens, *Descent from the Cross*, Antwerp Cathedral	Coremans and Thissen (1962) micr.
Netherlands, 1625/1626–1679	Jan Steen, three paintings in the John G. Johnson Collection Philadelphia Museum of Art	Butler (1982–1983) micr.
Dutch, 1654–1655	Jan Vermeer, *Christ in the House of Mary and Martha*, National Gallery of Scotland, Edinburgh	Kühn (1968) micr.
German, 19th C	Collection of pigments, Darmstadt	Richter and Härlin (1974a) micr.
Dutch, 19th C	Hafkenscheid Collection of pigments Technical University of Delft Netherlands	Pey (1989) HPLC
German, 19th C	Collection of pigments of Arnold Böcklin, Swiss painter (1827–1901)	Richter and Härlin (1974b) micr.
English, 19th C	Oil paintings and sketches, works on paper, and palettes of J.M.W. Turner (active c.1792–1850)	Townsend (1993) micr., UV micr.
Asia		
Central Asia, East Turkestan, 6th–10th C	Wall paintings, Museum of Indian Art, Berlin	Riederer (1977) micr.

chem.=Microchemical tests
HPLC=High-performance liquid chromatography
IR=Infrared
micr.=Light microscopy
TLC=Thin-layer chromatography
UV micr.=Ultraviolet microscopy
XRD=X-ray diffraction

Date, Country, or School	*Artist, Title or Description* *Collection or Location*	*Analyst and Method of Identification*
China, 9th–10th C	Buddhist wall paintings Dunhuang, China	Warner (1938) micr.
China, Tang dynasty (A.D. 618–906) and Jin dynasty (12th C)	Polychrome terra-cotta sculpture and wood sculpture	Larson (1988) micr.
Central Asia, 11th–13th C	Mud wall paintings, Kara Khoto Freer Gallery of Art Study Collection SC-PA-143	Gettens and Stout (1966) micr.
Tibet, 15th–19th C	*Thang-ka* paintings on cotton	Mehra (1970) micr., TLC
Arabia, Mamluk 1345–1350	Paintings, wooden ceiling of the dome, Al-Aqsa Mosque, Jerusalem	Lazzarini and Schwartzbaum (1985) micr.
Persia, India, Iraq Turkey, Egypt, and Syria 13th–19th C	32 paintings on paper Vever Collection, Arthur M. Sackler Gallery, Smithsonian Institution, Washington	FitzHugh (1988) micr., chem.
India, Mughal	9 paintings, Cincinnati Art Museum	Purinton and Newman (1985) micr.
Japan, 17th C Edo period	Scroll painting	Taguchi and Taguchi (1977) spectrophotometry (absorption spectra)
Japan, 16th–early 17th C	Hand-colored print, on paper	Magurn (1942) micr., chem.
Japan, Ukiyo-e School late 17th to early 19th C	13 paintings Freer Gallery of Art, Smithsonian Institution, Washington	FitzHugh (1979) micr., chem.
Western Hemisphere		
North America, late 18th–early 19th C	Spanish colonial paintings on wood New Mexico	Gettens and Turner (1951) micr., chem.
North America early 19th C	Tumacacori, Spanish mission church Arizona, painted decoration on plaster	Steen and Gettens (1962) micr., chem.

Occurrences of Indigo in Works Examined at the Doerner Institut, Munich[a]

Date	*Artist, Title or Description*	*Location*
972	German Theophanu (document)	Lower Saxony Archive Wolfenbüttel
3rd quarter 14th C	Taddeo Gaddi *St. Francis Offering Ordeal by Fire to Sultan*	BSTG,* inv. no. 10677
late 15th C	Austrian *St. Sebastian* (sculpture)	Dioces. Museum Klagenfurt
c.1560	German Murals	Moritz Chapel Freiberg Cathedral
c.1620	Jacob Jordaens *The Satyr and the Farmer*	State Art College Kassel inv. no. 102
1635	Peter Paul Rubens *Meleager and Atalanta*	BSTG, inv. no. 752
c.1654	Jan Vermeer *Christ with Mary and Martha*	National Gallery of Scotland, Edinburgh
1666	Christoph Paudiss *Wolf Tearing Lamb*	BSTG, inv. no. 3335
3rd quarter 17th C	Lucas Achtschellinck *Mountain Landscape*	BSTG, inv. no. 6515
3rd quarter 17th C	Jacob Jordaens *Moses Drawing Water from the Rock*	State Art College Kassel inv. no. 110A
3rd quarter 17th C	Adam Pynacker *Landscape with Ruin*	BSTG, inv. no. 3562
4th quarter 17th C	Abraham Storck *Marine*	BSTG, inv. no. 4569
late 17th C	Johann Baptiste Corlando *Elector Max Emanuel Hunting with Hounds*	BSTG, inv. no. 2690
c.1700	Michael Willmann *Mourning of Christ*	BSTG, inv. no. 13163
c.1709	Andrea Pozzo *Assumption of the Blessed Virgin*	Church at the Courtyard Vienna
c.1743	Jan Baptiste Govaerts *The Onion Peddler*	BSTG, inv. no. 1898
18th C	Ethiopian triptych	Ethnological Museum Zurich
late 18th/ 19th C	Ethiopian triptych	Ethnological Museum Zurich
1829/1835	Johann Christian Reinhart *Rome, View Toward South*	BSTG, WAF no. 814

*BSTG=Bayerische Staatsgemäldesammlungen, Munich

a. Identification by transmitted light microscopy and chemical microscopy.

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4
Madder and Alizarin

HELMUT SCHWEPPE and JOHN WINTER

1.0 Introduction

1.1 Pigment Definition

Madder lakes are manufactured by the conversion of the coloring substances of madder roots (*Rubia tinctorum* L. and various other plants in the Rubiaceae family) to the aluminum or other lakes. Madder lake is listed as CI Pigment Red 83, no. 58000:1, and CI Natural Red 9, nos. 75330, 75420 in the *Colour Index* (1971) and there are other listings of various madder components (see section 3.1). Ferrous madder lake is known as madder violet. The coloring substances in the madder root of *Rubia tinctorum* L. are principally alizarin (1,2-dihydroxyanthraquinone), purpurin (1,2,4-trihydroxyanthraquinone), and pseudopurpurin (1,2,4-trihydroxyanthraquinone-3-caboxylic acid). The shades of color of madder lakes vary from scarlet (stannous madder lakes), carmine red (carmine-containing madder lakes called madder carmine), pink (madder lakes with a high content of pseudopurpurin and/or purpurin called pink madder or rose madder), to red with a bluish tint (alizarin lakes). Figure 1 shows the use of madder lake.

1.2 Current Terminology

English: madder lake
German: Krapplack
French: laque de garance
Spanish: laca de rubia
Portuguese: laca de ruiva
Italian: lacca di robbia
Russian: крапплак
Chinese: qian cao (pinyin), chi'en ts'ao (Wade-Giles)
Japanese: akane (*Rubia akane*), seiyō akane (western akane, *Rubia tinctorum*)

English: alizarin
German: Alizarin
French: alizarine
Spanish: alizarina
Portuguese: alizarina
Italian: alizarina
Russian: ализарин
Chinese: qian su (pinyin), ch'ien su (Wade-Giles)
Japanese: arizarin

The Chinese name for Tibetan madder is *Zang qian cao* (pinyin) (*Tsang ch'ien ts'ao* [Wade-Giles]); *Zang* means Tibet. The Arabic name *fuwwa* is the equivalent of the Hebrew name *pua*. The Persian name is *royan*.

2.0 History

2.1 Archaic and Historical Names

The ancient Greek name given by Dioscorides in *De materica medica* (Book 6, vol. 3) was *erythrodanon* (Blümner, 1912).

The Latin name given by Pliny (Book 19, par. 47) was *rubia* (König, 1960; see also, Bailey, 1929) and also *erythrodanum* or *ereuthodanum* (Book 24, par. 94). These Latin versions of the Greek names were also given by Dioscorides and other Greek writers (Blümner, 1912).

In the Middle Ages in Europe various names were used. *Rubià* is mentioned as a component of *pandius* in the color recipes of the twelfth-century book, *Mappae Clavicula*, where *pandius* refers to a number of complex mixtures of pigments, often red, but sometimes other colors (Phillips, 1847; Smith & Hawthorne, 1974). The cultivation of *warentia* is recommended in the *Capitulare de villis*, one of Charlemagne's decrees; the terms

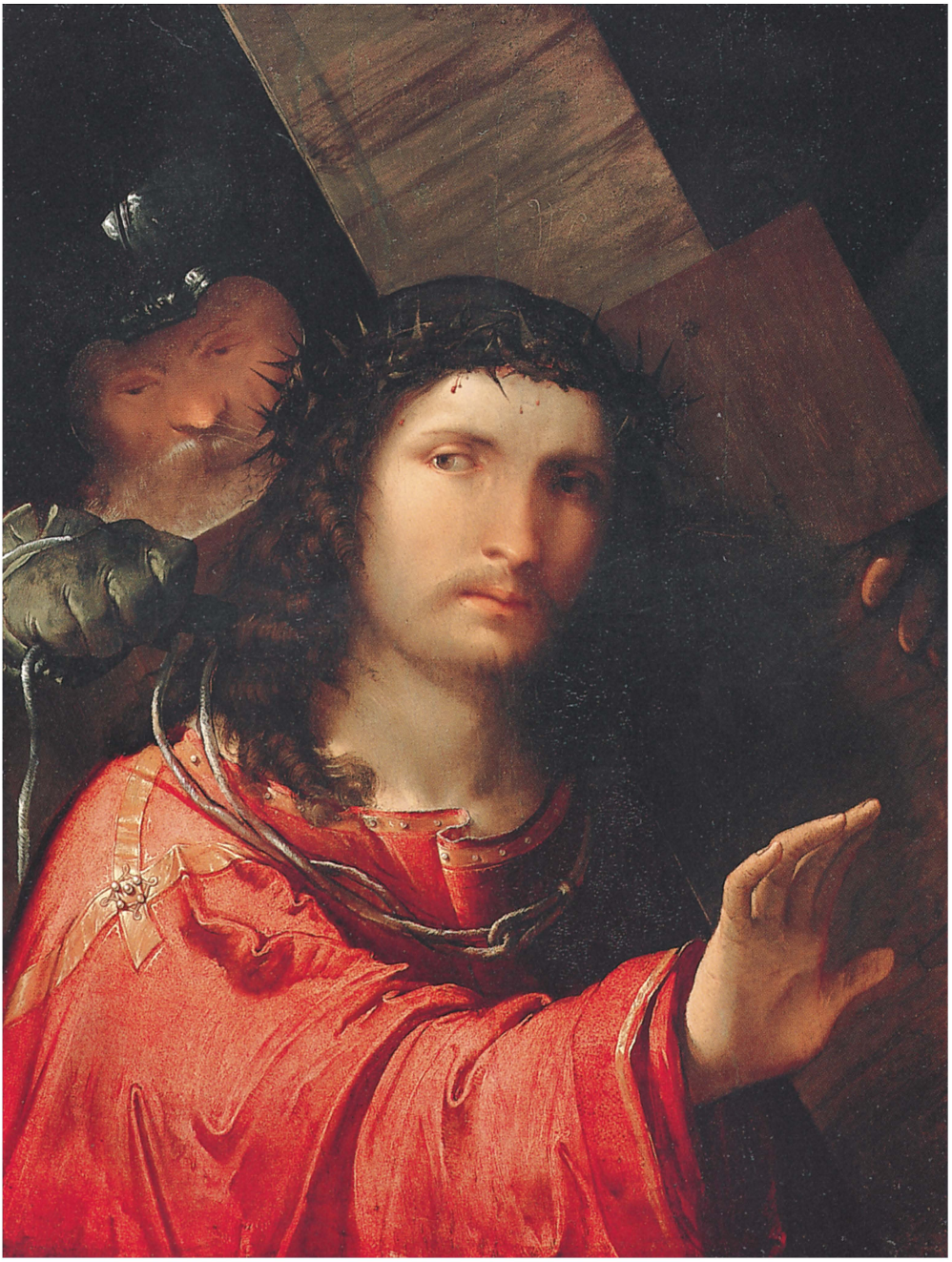

Fig. 1 Altobello Melone, *Christ Carrying the Cross*, 1520, National Gallery, London, no. 6546. Reproduced by permission of the Trustees. The area of Christ's sleeve contains madder lake and some lead-tin yellow.

warencia, *garancia*, and *rubea radix* were mentioned by Heraclius (Ilg, 1873). Jehan le Begue also used these terms in his manuscript of 1431 (Merrifield, 1967). Madder was called *rezza* in Old High German, and it is called *retzel*, *retzwurz*, *roete*, and *rubea tinctura* in formula books of the Middle Ages (Fischer, 1929; Marzell, 1937; Ploss, 1952, 1973).

In sixteenth-century Italy, madder was known by the names *robbia*, *roza*, *granzuolli*, or *ciocchi* (Rosetti, 1548). In seventeenth-century India, the common names for madder used for printing on cotton, from various *Morinda* species, were *aal* or *al*, *saranguy*, and *chiranjee* (Gittinger, 1982).

2.2 History of Use

In Asia, madder has served since ancient times for dyeing textile materials. It was described by Strabo, Dioscorides, Pliny the Elder, and in the Talmud. In the Greek and Roman period there are only vague references concerning the use of madder as a pigment in the form of madder lakes. In 1815, Humphrey Davy described a study of Roman pigments. He found a broken ceramic vase at the Baths of Titus; it was painted with a pink pigment whose organic nature he recognized, but he could not determine whether the pigment was of animal or vegetable origin (Davy, 1815).

Chaptal (1809) reported on some pigments found in a shop in the excavations at Pompeii. He decided that a pink pigment was an alumina lake. Although he gave no specific test for madder lake, the identification of the pigment, according to Chaptal's description, suggests madder lake.

Madder was identified on Egyptian textiles dated as early as the Eighteenth Dynasty (c. 1567–c. 1320 B.C.) (Vogler, 1975) and also from the Twenty-First Dynasty (1085–945 B.C.) (Wouters et al., 1990). A further example often cited is one of the pigments found at Hawara by W.M.F. Petrie (1853–1942). Lucas and Harris (1962) mentioned that Petrie's discovery was a pink pigment from a grave painting. In actuality, the discovery consisted of six paint pots of the Greco-Roman period, which are now in the British Museum. W. T. Russell (1892) examined the pigments and identified a pink pigment as madder on a substrate of calcium sulfate (gypsum). Since Russell found that the absorption spectrum was identical to that of purpurin, there is little doubt that it was a pink madder lake with purpurin as the principal constituent.

Farnsworth (1951) identified purpurin as an alumina lake in a lump of pink pigment from Corinth dated 146 B.C. The presence of purpurin was proved by comparing the visible reflectance spectrum and qualitative inorganic analysis showed the presence of aluminum, indicating that the pigment was a rose madder lake.

Al-Bīrūnī (973–1048), an Arab scholar and scientist, described dyer's madder, which was imported from Balkh and Armenia into Persia and India (Hamarneh, 1973).

It is known that textiles dyed with madder were sold at St. Denis near Paris during the seventh century A.D. and that Charlemagne promoted the cultivation of madder. Madder lake was not found in painting materials until much later. According to Götting and Kühn (1968) and Roosen-Runge (1973), it was used on the marriage certificate of Empress Theophanu in A.D. 972; it was applied on the back of the parchment and on the front as the uppermost layer in the red areas of the medallions over a base layer of red lead. Vegetative remains of madder, *Rubia tinctorum* L., were found in waterlogged deposits from the ninth to tenth century at York (Tomlinson, 1985).

Madder lakes were mentioned in workshop treatises of the early Middle Ages as components of pigment mixtures, but not as colors to be used alone for painting (Roosen-Runge, 1967). They have not been identified on miniature paintings of this date. Laurie (1913) found evidence of madder lake in a book illustration of c. 1465–1489 in the Advocates' Library, Edinburgh. In England, madder was identified by visible absorption spectra on tenth- and eleventh-century textiles from York (Taylor, 1983). Carlyle (1991) described the marketing of various madder and alizarin lakes in Great Britain in the nineteenth century. A wide variety of colors was available (Harley, 1982). According to Thompson (1956), madder lake was rarely used in European paintings of the Middle Ages, but by the seventeenth and eighteenth centuries its use had increased. Winsor and Newton first manufactured alizarin crimson as a watercolor in 1891 (Harley, 1987).

Townsend (1993) identified madder lakes in palettes used by J.M.W. Turner (active c. 1792–c. 1850). These included madder from both *Rubia tinctorum* and from other sources, and several of the substrates were reported to contain copper in addition to the more usual elements. Madder lakes were also found in oil paintings and watercolors through most of the artist's active period.

Madder is listed as a red color used for manuscript illumination in Russia, and an Armenian text lists it, along with blue, as one component of purple (Radosavijevic, 1976). The twentieth-century Chinese painter Yu Feian mentioned madder, safflower, and lac dye as having been used in traditional and modern Chinese painting practice (Yu, 1988). Feller et al. (1984) suggested that madder was available for Japanese woodblock color printing. At present these uses of madder lakes in Russia and East Asia lack corroborative identification.

Brannt (1893) indicated that madder lake was used as a colorant in sealing waxes.

2.3 Dates of Use

Madder was used as early as the sixteenth century B.C. in Egypt. Alizarin, synthetic madder, is found in artists' paints today.

3.0 General Pigment Properties

3.1 Color and Spectral Reflectance

The color of madder lakes varies greatly, depending on the organic colorants such as alizarin, purpurin, and pseudopurpurin (see section 4.2 and table 1) and on the inorganic substrates such as calcium carbonate and precipitated compounds of aluminum, tin, iron, or chromium (see section 5.3). Many madder lakes tend toward rose-red, but pink hues containing mostly purpurin or pseudopurpurin are known. Partial precipitation of an alum extract of garancine with soda or potash (see section 4.5) gives a deep-red madder lake, while complete precipitation yields a light red; the same is true for chalk precipitates. If a small amount of a tin compound is added at the end of the precipitation, the color of the resultant madder lake is more intense (Gentele, 1909). When iron(II) sulfate is added, black violet (madder violet) results, and chromium alum gives a red-brown color. For the finest of red nuances, iron-free alum must be used: brown-tinged madder lakes usually result from iron salts present in the laking agent (Cremer, 1895). Lakes of pure alizarin on alumina are generally somewhat bluer than natural madder lakes. According to Mayer (1911), obtaining alizarin lakes with a brilliant hue requires precipitation with alum together with calcium and sodium phosphates.

Paint outs illustrate the colors of typical pigments, namely madder lake, rose madder lake, alizarin lake, and purpurin lake (figs. 2–5). Spectral reflectance curves are just as variable as the

Table 1 **Naturally Occurring Hydroxyanthraquinones**

Alizarin, *1,2-dihydroxyanthraquinone,* CI 75330. Orange-red needles, 289°–290°C. UV-Vis(ethanol), 247(4.45), 278(4.13), 330(3.46), 434(3.70). IR(KBr), 3340, 1660, 1627. Very sparingly soluble boiling water (30 mg/100 ml); sparingly soluble benzene, carbon tetrachloride; soluble acetone, ethylene glycol, boiling ethanol.

Purpurin, *1,2,4-trihydroxyanthraquinone,* CI 75410. Red needles, 263°C. UV-Vis(methanol), 255(4.41), 290(shoulder, 4.09), 457(shoulder, 3.79), 485(3.92), 518(3.86), 542(shoulder, 3.58). IR(KBr), 3225, 1630, 1592. Soluble alum solution, lime water; sparingly soluble hot water, ethanol; soluble ether, benzene, glacial acetic acid.

Pseudopurpurin, *1,2,4-trihydroxyanthraquinone-3-carboxylic acid,* CI 75420. Red-brown plates, 229.5°–230.5(222–224)°C. UV-Vis(ethanol), 256.5(4.52), 285(shoulder, 4.10), 487(3.96), 520(shoulder, 3.85). IR(KBr), 3140, 1705, 1580. Insoluble cold water, ethanol; sparingly soluble boiling benzene, chloroform.

Rubiadin, *1,3-dihydroxy-2-methylanthraquinone,* CI 75350. Yellow plates, 302°C. UV-Vis(ethanol), 241(shoulder, 4.43), 245(4.48), 279(4.55), 414(3.89). IR(KBr), 3300, 1672, 1649(weak). Insoluble boiling water, lime water; readily soluble ethanol, ether, benzene.

Munjistin, *1,3-dihydroxyanthraquinone-2-carboxylic acid,* CI 75370. Orange leaflets, 232°–233(231)°C. UV-Vis(ethanol), 248.5(4.52), 288(4.31), 420(3.71). IR(KBr), 3250, 1711, 1672, 1640, 1591. Sparingly soluble cold water; fairly readily soluble boiling water; readily soluble ether, benzene, boiling glacial acetic acid.

Morindone, *1,5,6-trihydroxy-2-methylanthraquinone,* CI 75430. Orange-red needles, 275(285)°C. UV-Vis(ethanol), 232(4.50), 259.5(4.53), 292(4.16), 301(4.18), 448(4.07). IR(KBr), 3470, 1634, 1609. Insoluble water; readily soluble methanol, ethanol, ether, benzene, glacial acetic acid.

Xanthopurpurin (purpuroxanthin), *1,3-dihydroxyanthraquinone,* CI 75340. Yellow needles, 269°–270°C.

Key:
Common name in boldface type, *extended chemical name in italics* (based on substitution of anthraquinone)
CI=*Colour Index* number, if any
Color and form of crystalline solid, melting point
UV-Vis=Ultraviolet-visible absorption (solvent used) λ (log ε) values, where λ means wavelength of an absorption maximum (unless otherwise noted) in nanometers, and ε is the molar extinction coefficient
IR=Infrared absorption (form of sample) ν values, where ν is wavenumber of absorption peak in reciprocal centimeters

Table 1 Continued

UV-Vis(ethanol), 246(4.43), 284(4.36), 415(3.69). IR(Nujol), 3413, 1675, 1637. Readily soluble ethanol, benzene.

Rubiadin-1-methyl ether, *1-methoxy-2-methyl-3-hydroxyanthraquinone*. Yellow needles, 291°C. UV-Vis(ethanol), 238.5(3.98), 243(3.97), 279(4.23), 372(3.27). IR(KBr), 3300, 1672, 1649(weak).

Hystazarin-3-methyl ether, *2-hydroxy-3-methoxyanthraquinone*. Orange-yellow leaflets, 232°C. Ammonium salt readily soluble ethanol.

Anthragallol, *1,2,3-trihydroxyanthraquinone*, CI 58200. Orange needles, 312°–313°C. UV-Vis(ethanol), 245(4.21), 283(4.40), 335(shoulder, 3.21), 413(3.72). IR(KBr), 3450, 3360, 1655, 1625.

Anthragallol-2-methyl ether, *1,3-dihydroxy-2-methoxyanthraquinone*. Yellow needles, 218°C. UV-Vis(ethanol), 240(4.51), 281(4.24), 407(3.57). IR(Nujol), 3378, 1664, 1634.

Anthragallol-1, 2-dimethyl Ether, *1,2-dimethoxy-3-hydroxyanthraquinone*. Yellow plates, 238°C. UV-Vis(ethanol), 241(3.92), 281(4.30), 362(3.36).

Anthragallol-1,3-dimethyl ether, *1,3-dimethoxy-2-hydroxyanthraquinone*. Yellow needles, 212°–213°C.

Soranjidiol, *1,6-dihydroxy-2-methylanthraquinone,* CI 75390. Orange-yellow needles, 275°C. UV-Vis(ethanol), 220(4.45), 245(4.04), 271.5(4.46), 280(shoulder, 4.38), 292(shoulder, 4.18), 337.5(3.17), 395(shoulder, 3.71), 411(3.80), 425(shoulder, 3.71). IR(KBr), 3420, 1680, 1637, 1600.

6-Methylxanthopurpurin (morindanigrin), *1,3-dihydroxy-6-methylanthraquinone,* CI 75360. Yellow needles, 269°C. UV-Vis(96% ethanol), 242(4.29), 265(shoulder, 4.34), 281(4.15), 320(shoulder, 4.22), 411(3.38). IR(KBr), 3418, 1675(shoulder), 1640, 1625, 1595. (Thomson [1971] considers status of this compound as a natural product to be uncertain.)

Lucidin, *1,3-dihydroxy-2-hydroxymethylanthraquinone*. Yellow needles, >330°C. UV-Vis(ethanol), 242(4.39), 246(4.40), 280(4.38), 330(3.44), 415(3.26). IR(KBr), 3410, 1663, 1620, 1592.

Ibericin, *1,3-dihydroxy-4-ethoxymethylanthraquinone*. Lemon-yellow crystals, 129°–131°C. (Not in Thomson, 1971 or 1987). Probably an artifact of lucidin (Murti et al., 1972b).

2-Hydroxyanthraquinone. Yellow needles, 306°(312)°C. UV-Vis(ethanol), 241(4.31), 271(4.55), 283(4.46), 330(3.55), 378(3.55). IR(KBr), 1671, 1590.

1-Hydroxy-2-methylanthraquinone. Yellow needles, 185°–186°C. UV-Vis(ethanol), 255(4.51), 266(shoulder, 4.33), 270(shoulder), 325(3.51), 402(3.74). IR(KBr), 1670, 1637, 1593.

3-Hydroxy-2-methylanthraquinone. Yellow needles, 302°C. UV-Vis(ethanol), 240(4.40), 244.5(4.40), 272.5(4.50), 383(3.67). IR(KBr), 3400, 1667.

Alizarin-1-methyl ether, *1-methoxy-2-hydroxyanthraquinone*. Pale-yellow needles, 182°–184°C. UV-Vis(ethanol), 242(shoulder, 4.37), 246.5(4.38), 270(4.37), 284(4.24), 330(3.47), 385(3.64). IR(KBr), 3420, 1673.

Xanthopurpurin-1-methyl ether, *1-methoxy-3-hydroxyanthraquinone*. Yellow leaflets, 311°–313°C.

Xanthopurpurin-3-methyl ether, *1-hydroxy-3-methoxyanthraquinone*. Light-yellow needles, 193°–194°C.

2-Benzylxanthopurpurin, *1,3-dihydroxy-2-benzylanthraquinone*. Yellow crystals, 298°–299°C. UV-Vis(ethanol), 241(4.40), 246(4.45), 280(4.51), 413(3.88). IR(KBr), 1665, 1630, 1588.

6-Methylquinizarin, *1,4-dihydroxy-6-methylanthraquinone*. Red needles, 167°–168°C. UV-Vis(cyclohexane), 226(4.46), 230(4.43), 253(4.55), 260(4.57), 282(4.12), 290(4.08), 328(3.49), 460(4.02), 473(4.05), 484(4.06), 506(3.95), 520(3.91). IR(KBr), 1640, 1605, 1598.

Damnacanthol (lucidin-l-methyl ether), *1-methoxy-2-hydroxymethyl-3-hydroxyanthraquinone*. Yellow needles, 288°C. UV-Vis(ethanol), 238.5(4.35), 243.5(shoulder, 4.33), 280(4.54), 350-375(3.61). IR(KBr), 3280, 1675, 1650.

Damnacanthal, *1-methoxy-3-hydroxyanthraquinone-2-aldehyde*. Orange-yellow needles, 212°C. UV-Vis (methanol), 250(4.41), 281(4.36), 380(4.38). IR(KBr), 1677, 1661, 1650.

Nordamnacanthal, *1,3-dihydroxyanthraquinone-2-aldehyde*. Yellow needles, 220°–221°C. UV-Vis(ethanol), 219(4.56), 262(4.73), 293(4.57), 421(4.09). IR(KBr), 1683, 1651, 1634.

Physcion (parietin, parmel yellow, lichen-chrysophanic acid, rheochrysidin), *1,8-dihydroxy-3-methyl-6-methoxyanthraquinone*. Orange-yellow leaflets, 207°C. UV-Vis(ethanol), 257(shoulder, 4.35), 266(4.36), 288(4.35), 431(4.20). IR(Nujol), 1678, 1623.

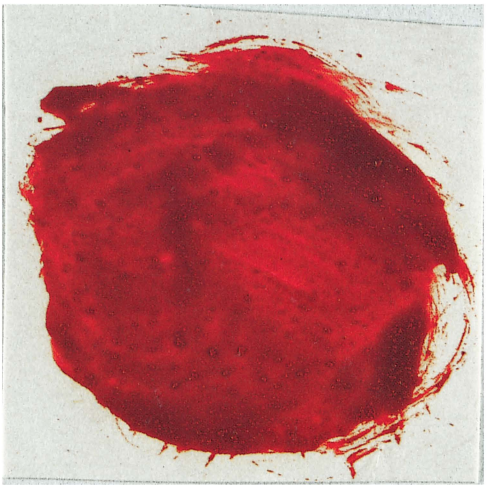

Fig. 2 Paint out of madder lake.

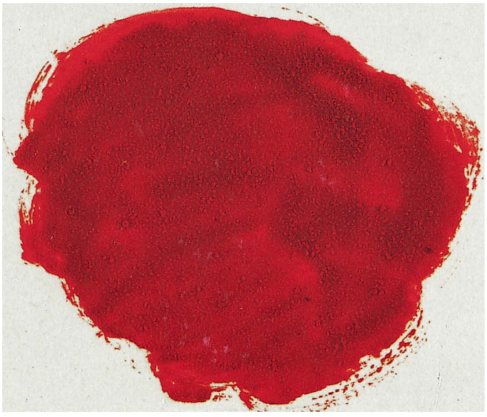

Fig. 3 Paint out of rose madder lake. Sample from Robert L. Feller, Carnegie Mellon Research Institute, Pittsburgh.

Fig. 4 Paint out of alizarin lake.

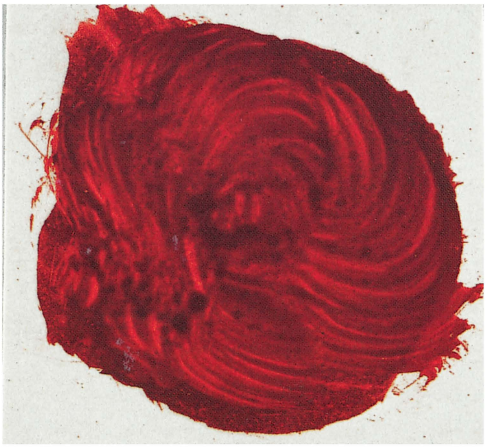

Fig. 5 Paint out of purpurin lake.

colors; examples of madder lake and alizarin crimson are shown in figure 6. Section 5.2.4 cites further examples of diffuse reflectance spectra.

3.2 **Permanence**

Madder lakes and alizarin lakes are transparent glazing lakes that have good fastness to water, alcoholic solvents, and oil. Alizarin lakes and the light-pink madder lakes that contain primarily pseudopurpurin as the color component have outstanding lightfastness grades of approximately seven (based on a scale of one to eight, with eight as the highest grade). Since madder lakes usually also contain nonlightfast purpurin lake, they are generally less lightfast than pure alizarin lakes. Pink madder lakes containing mostly purpurin lake have even less lightfastness (Täuber, 1909; Schultz, 1931–1932). Work by Saunders and Kirby (1994b) on wavelength-dependent fading of pigments confirms the good lightfastness of an alizarin lake; a madder lake faded at increasing rates as the illuminant wavelength decreased, but was overall more lightfast than kermes, lac, cochineal, or brazilwood lakes. A study of the fading rates of several red and yellow lake pigments, including the nature of the dyestuff and the method of extraction as well as the effects of substrate, support, medium, and white pigment content, confirmed that madder and alizarin lakes are among the most stable of lake pigments (Saunders & Kirby, 1994a).

Studies of the fading rate of madder lake show it to be very reactive to atmospheric ozone in the absence of light (Whitmore et al., 1987; Whitmore & Cass, 1988). The mechanism of the fad-

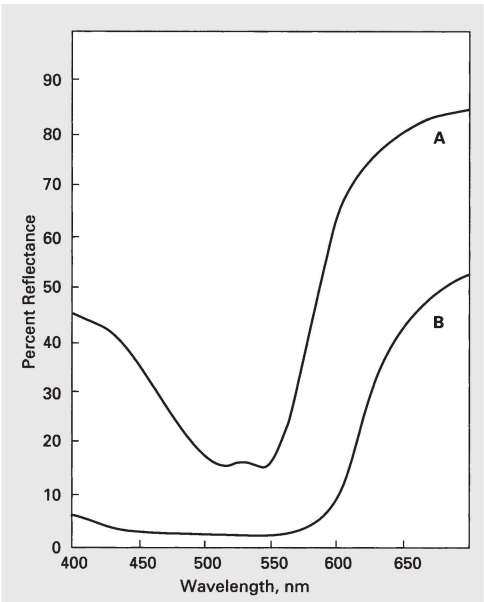

Fig. 6 Spectral reflectance of (A) madder lake and (B) alizarin crimson in parchment size. From Barnes (1939).

ing of alizarin lake when it is mixed with titanium dioxide has been studied (Johnston-Feller et al., 1984).

3.3 Compatibility

Alizarin lakes of aluminum or calcium compounds, or of sodium phosphate, can be applied to chalk. Madder lakes are, however, not resistant to chalk or waterglass (Schultz, 1931–1932). Alizarin lake cannot be used on wet lime (that is, true fresco), but it does adhere well to dry interior plaster (Doerner, 1949). Schultz (1931–1932) indicated that madder and alizarin can be used in various artists' and decorative paints, including oil, watercolor, and tempera. A characteristic of pure madder lake is that it cracks readily, especially on a white substrate. Adding a small amount of lead white or mixing it with other paints corrects this characteristic. Ruptures are sometimes observed in madder lake in oil medium and can be traced to unsuitable application (thick underpainting in madder) or to adulteration with unsuitable synthetic pigments (Doerner, 1949).

3.4 Chemical Properties

Madder lakes and alizarin lakes are completely or extensively soluble in sodium hydroxide solution because alizarin, purpurin, pseudopurpurin, and aluminum hydroxide are soluble in it. If chalk is present, it can remain undissolved, with a red coloration, but most of the dye is dissolved. When an excess of sulfuric acid is added to the sodium hydroxide filtrate, the acid-insoluble alizarin is precipitated; with madder lakes, purpurin and pseudopurpurin are also precipitated. If the liquid remains colored following acidification and filtration it is possible that the lake contained carmine or synthetic color lakes.

Madder lakes that contain purpurin or pseudopurpurin bleed red when they are boiled with sodium carbonate solution but alizarin does not. When an excess of mineral acid is added, purpurin precipitates out again; it is reported that pseudopurpurin is decarboxylated to purpurin (Gentele, 1909).

Unlike carmine, madder and alizarin lakes do not usually dissolve when boiled with ammonia. This procedure allows for differentiation between carmine and madder lakes, for example, as in madder carmine (Mayer, 1911).

3.5 Oil Absorption and Grinding Properties

The oil absorption of madder lake is approximately 70% oil (70 lb. oil per 100 lb. of pigment) and it dries poorly. For this reason it is ground with linseed oil with varnish added during the process (Doerner, 1949). Venetian artists added compounds such as manganese brown or burnt umber to improve the drying qualities in oil (Field, 1870).

3.6 Toxicity

Madder is not toxic (Wehlte, 1982).

4.0 Composition

4.1 Sources

4.1.1 ***Madder.*** Madder comes from the roots of *Rubia tinctorum* L., an herbaceous perennial plant that grows to 180 cm in height. It is indigenous to western Asia (Percival, 1917) but has long been grown in southern Europe. The Moors introduced the cultivation of madder into Spain (Martin, 1922); its use spread to Holland in the sixteenth century, and in 1666 Jean-Baptiste Colbert (1619–1683) brought it to Avignon. In Alsace the cultivation of madder began in 1729.

In Europe the madder root generally was harvested three years after planting; studies indicate that the yield of dye from the madder root is highest during its third year (Blazek & Stary, 1968).

Fig. 7 Madder plant (*Rubia tinctorum* L.). From Elisabeth Blackwell, *Sammlung der Gewächse* (Nuremburg, 1754).

Vermehrtes und verbessertes
Blackwellisches Kräuter-Buch
das ist
Elisabeth Blackwell
Sammlung
der
Gewächse
die zum Arzney-Gebrauch in den Apothecken aufbehalten werden
deren Beschreibung und Kräfften
aus dem Englischen übersetzt angezeiget
die Abbildung grossen Theils nach der Natur verbessert
mit Beyfügung
der Theile der Blume und Frucht
wie auch
des äuserlichen Ansehens eigenen Kennzeichen vermehret
und alle Arten
mit bewährten Nahmen der Kräuter-Lehrer erläutert werden
Zweytes Hundert
Mit einer Vorrede
Tit. Pl.
Herrn D. Christoph Jacob Trews
Verlegt gemachet und in Kupfer gestochen
von
Nicolaus Friederich Eisenberger
Hochfürstl. Sachsen-Hildburghausischen Hof-Mahler in Nürnberg
Nürnberg gedruckt bey Christian de Launoy. Anno 1754.

Fig. 8 Title page, *Sammlung der Gewächse*.

The peripheral areas of the madder root, approximately 8 to 10 mm in diameter, contain the dyestuff. The root bark, which contains a brown dyestuff, is removed by a crushing process and sold as mull madder, which is suitable for producing shades of low brightness. Unground madder called *lizari* or *alizari* was obtained in the form of dried and cut roots from the eastern Mediterranean area; this madder did not produce a clear red color because of the attached outer bark.

A plant of *Rubia tinctorum* L. (fig. 7) is shown in Elisabeth Blackwell's *Sammlung der Gewächse (A Curious Herbal)* (1754) (fig. 8). The ovoid lanceolate leaves arranged around the stem in whorls of four to six leaves are clearly visible.

4.1.2 ***Related dyer's plants.*** In addition to *Rubia tinctorum* L., in previous centuries another type of madder, the wild madder (*Rubia peregrina* L.), was known as a dyer's plant in the Mediterranean area. It was cultivated in Greece, Smyrna, and Aleppo (Pubetz, 1872).

Munjeet (*Rubia cordifolia* L.) was once cultivated in India and Japan and is listed in the *Colour Index* (1971) as CI Natural Red 16 (Murti et al., 1972b; Tessier et al., 1981). Madder from Japan is *Rubia akane* Nakai; its principal component is pseudopurpurin (Hayashi, 1979). The Chinese name *qian cao* is said to refer to the product from *Rubia munjista* or *R. cordifolia* (Watson, 1930). Sewell et al. (1939) suggested that *qian cao* may be from *Rubia cordifolia* L. and *Zang qian cao* (Tibetan madder) may be from *R. tinctorum* L. The plants *Rubia sikkimensis* Kurz. and *R. cordifolia* L. are botanically very similar (Perkin & Hummel, 1893a).

Oldenlandia umbellata L. (or *Hedyotis umbellata* L.), also called chay root or Indian madder (CI Natural Red 6), or by other names, grew on the sandy plains of India, Sri Lanka, and Myanmar (Burma).

The root barks of various types of *Morinda* (Rubiaceae family) have found widespread use as coloring materials in India; these are *M. citrifolia* L. (*soranjee*) (CI Natural Red 18) and *M. umbellata* L. (*mang kouda*) (CI Natural Red 19). *M. longiflora* G. Don is found in tropical locales in West Africa including the Ivory Coast (Barrowcliff & Tutin, 1907; Paris & Abiusso, 1958).

In England and some northern European countries, roots of the *Galium* species were used as a substitute for madder for dyeing, especially the roots of *G. verum* L. (yellow ladies-bedstraw) and *G. mollugo* L. (hedge bedstraw) (CI Natural Red 14) (Hill & Richter, 1937).

In South America at the time of the ancient Peruvian Paracas culture in 700 B.C., relbun roots, *chapichapi*, were in use as a red dye. They were mostly roots of *Relbunium hypocarpium* Hemsl.; *R. bigeminum*, *R. tetragonum*, *R. hirsutum*, and *R. richardianum* were also later used for dyeing purposes (Fester, 1953).

Pubetz (1872) mentioned the Russian Marenas or Derbentine madder root, which is much thicker than ordinary madder root. It is possible Pubetz was referring to roots of *Rubia iberica* C. Koch (Murti et al., 1972a).

In Australia and New Zealand there are several plants of the Rubiaceae family of the genus *Coprosma*, such as *C. lucida* Forst. (often called "orange leaf"), *C. grandiflora*, and *C. areolata* (called *karamu* by the Maori) (Mell, 1924; Briggs et al., 1948; Briggs & Nicholls, 1949; Briggs & Thomas, 1949; Briggs et al., 1952; Briggs & Taylor, 1955).

Table 1 contains a summary of the hydroxyanthraquinones occurring in the various types of madder and table 2 shows the coloring substances of the various madder plants.

4.1.3 ***Commercial types of madder.*** According to Pubetz (1872), after it is pulled from the ground the madder root is left in small heaps to dry in the fields, then it is collected into larger heaps and allowed to lie for two or three days. It is then further dried with warm air in drying houses. Finally, the dried roots are crushed and separated from the bark by sifting; the bark is used for the manufacture of mull madder. The debarked madder roots are then pulverized under vertical millstones and sifted to give a very fine powder. Various commercial types are Alsatian madder, Avignon madder, Levantine or Turkish madder (*lizari*), Dutch or Flemish madder, Schlesic, Bohemian, Steiric, and Hungarian madder.

Madder has a singularly strong odor, tastes sweet, and has a bitter aftertaste. The odor varies with the type of root used, the quality of the soil, the climate, and the method of preparation. The best type is that from the Levantine madder root.

Alsatian madder has a yellow-red color, a piercing odor, and is a medium-fine powder.

Avignon madder appears commercially as a fine powder; it takes on moisture from the air slowly and does not give off an unpleasant odor. It has a dark-red, yellow-red, or lively red color, which depends on the calcium content of the soil in which it is grown. The best Avignon madder is referred to as "root of Palut." Palut is the name of

Table 2 **Colorant Aglycones Found in Various Madder Plants**

Botanical Name (common name)	*Constituents*[a]	*References*
Rubia tinctorum L. (madder)	*Alizarin; pseudopurpurin* (decarboxylates to give purpurin); 2-hydroxyanthraquinone; xanthopurpurin-3-methyl ether; alizarin-1-methyl ether; xanthopurpurin; rubiadin; lucidin; anthragallol	Hill and Richter (1936, 1937) Schunck and Römer (1877a) Perkin and Hummel (1893a, b) Burnett and Thomson (1968a)
Rubia peregrina L. (wild madder)	*Pseudopurpurin*; alizarin	Hayashi (1979); Hager (1979)
Rubia cordifolia L. (munjeet)	Munjistin; purpurin; pseudopurpurin; nordamnacanthal; 1,4-dihydroxy-6-methylanthraquinone; 1-hydroxy-2-methylanthraquinone; 1,8-dihydroxy-3-methyl-6-methoxyanthraquinone; alizarin; xanthopurpurin	Stenhouse (1864); Perkin and Hummel (1893); Tessier et al. (1981); Murti et al. (1972b)
Rubia sikkimensis Kurz	*Munjistin*; *purpurin*; xanthopurpurin	Perkin and Hummel (1893a)
Rubia iberica C. Koch	*Alizarin*; *ibericin*; *lucidin*; nordamnacanthal	Stikhin et al. (1966); Murti et al. (1972a)

a. Major constituents, where known, are italicized. See Thomson (1971, 1987); Schweppe (1989).

Table 2 Continued

Botanical Name (common name)	*Constituents*[a]	*References*
Galium verum L. (yellow ladies-bedstraw)	*Pseudopurpurin*; 2-hydroxyanthraquinone; alizarin-1-methyl ether; alizarin; xantho-purpurin; rubiadin; purpurin; lucidin	Burnett and Thomson (1968b)
Oldenlandia umbellata L. (Indian madder; chay root)	*Anthragallol-1,3-dimethyl ether*; *anthragallol-1,2-dimethyl ether*; *alizarin*; 2-hydroxyanthraquinone; alizarin-1-methyl ether; hystazarin monomethyl ether	Perkin and Hummel (1893b 1895); Perkin (1907)
Morinda citrifolia L. (*soranjee*)	*Soranjidiol*; *morindone*; alizarin-1-methyl ether; rubiadin-1-methyl ether; alizarin; rubiadin; damnacanthol; damnacanthal; nordamnacanthal	Anderson (1849a, b, c) Simonsen (1920); Mitter and Biswas (1928)
Morinda umbellata L. (*mang kouda*)	*Morindone*; 2-hydroxyanthraquinone; alizarin-1-methyl ether; rubiadin-1-methyl ether; alizarin; xanthopurpurin; rubiadin; morindanigrin; soranjidiol; damnacanthal	Perkin and Hummel (1894) Mitter and Biswas (1928)
Morinda longiflora G. Don.	*Rubiadin-1-methyl ether*; alizarin-1-methyl ether; alizarin; rubiadin	Barrowcliff and Tutin (1907) Paris and Abiusso (1958)
South America		
(relbun roots) *Relbunium hypocarpium* Hemsl.; *R. tetragonum* Griseb.	*Purpurin*; *pseudopurpurin*; xanthopurpurin-3-methyl ether; xanthopurpurin-1-methyl ether	Fester (1953); Fester and Lexow (1942–1943); Fester et al. (1945, 1946–1947)
Australia and New Zealand		
Coprosma lucida Forst.	*Lucidin*; *anthragallol-2-methyl ether*; anthragallol-1,2-dimethyl ether; rubiadin; soranjidiol; anthragallol; 3-hydroxy-2-methylanthraquinone	Briggs and Nichols (1949)
Coprosma acerosa Cunn.	*Lucidin*; *anthragallol-2-methyl ether*; rubiadin-1-methyl ether; anthragallol-1, 2-dimethyl ether; rubiadin; soranjidiol; 3-hydroxy-2-methylanthraquinone	Briggs and Thomas (1949)
Japan		
Rubia akane Nakai	*Pseudopurpurin*	Hayashi (1979)
Damnacanthus major Sieb. and Zucc. (var. *parvifolius* Koidz.)	Damnacanthol; damnacanthal; nordamnacanthal; 2-benzylxanthopurpurin	Nonomura (1955)

a marsh on the Sorgue River, where the best French madder root is found. All madder roots grown in Avignon yield a red powder, which naturally contains a certain quantity of calcium carbonate and alkali carbonate. By reaction with alkalies, the hydroxyanthraquinones change from yellow to orange or red with the formation of calcium lakes. Avignon madder can be used immediately, but its quality is significantly increased by storage in barrels. It does not stick together and despite its slight sugar content, does not ferment.

Dutch madder forms a rough powder, which absorbs moisture from the air and becomes red. It has an extremely objectionable odor.

Alsatian and Dutch madder cannot be immediately used for dyeing; they must remain in barrels for one or two years. During its storage in the barrel, the madder undergoes fermentation, during which the glycosides are hydrolyzed to yield the free anthraquinones. The powder particles stick together as a result of this process and after a while form a solid mass.

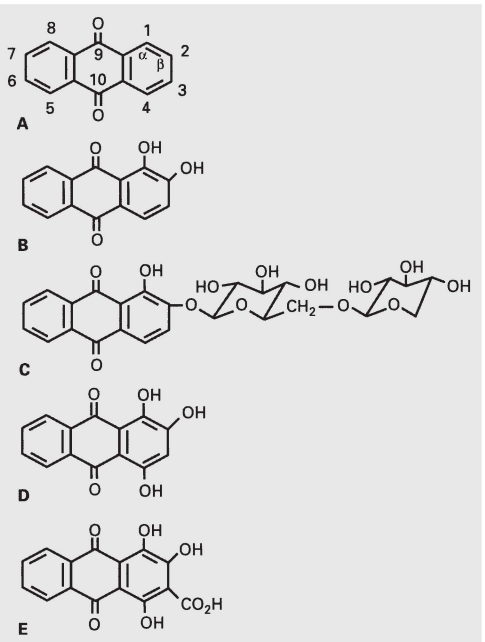

Fig. 9 Formulas for typical madder constituents; (A) anthraquinone (B) alizarin (C) ruberythric acid (alizarin-2-β-primeveroside) (D) purpurin (E) pseudopurpurin.

4.2 Coloring Constituents of the Various Madder Plants

The main anthraquinone colorants found in madder and related plants are given in table 1 and their occurrence in the different botanical species are in table 2. The formulas for anthraquinone and for typical madder constituents are shown in figure 9. The following comments on individual compounds supplement the two tables. Many compounds are from plants other than *Rubia tinctorum* L. and are used for textile dyeing, but could also possibly appear in painting materials.

Alizarin (see fig. 9B) is the main coloring matter in the roots of *Rubia tinctorum* L., but it is found also in other types of madder in varying amounts. It dissolves in strong alkali to give a violet-blue color and in concentrated sulfuric acid to give a yellowish red; the latter forms an orange precipitate on dilution with water. The alumina lake is rose red, or bluish red if calcium is present; the tin lake is red-violet, the iron lake is black-violet, and the chrome lake is brown-violet or red-brown (Springer, 1918). Chemical studies of alizarin began in 1826 when it was isolated in impure form from madder root (Colin & Robiquet, 1826). Graebe and Liebermann (1869, 1870) later determined the constitution of alizarin and achieved an early synthesis.

Ruberythric acid, which forms as yellow needles, with a melting point of 258°C to 260°C, is the form in which alizarin occurs in fresh madder roots. Its constitution was determined as alizarin-2-β-primeveroside (see fig. 9C) (Richter, 1936). Ruberythric acid is easily soluble in hot water, sparingly so in cold water and in ethanol. On heating with acids and alkalies, it is decomposed into alizarin and two molecules of glucose; if it is pure, it can withstand prolonged heating in water or ethanol without decomposition. Ruberythric acid does not ferment with yeast. Fibers stained with metal-salt mordants are not dyed at all. On addition of a hot alcoholic solution to alcoholic potassium hydroxide, the potassium salt forms as a deep red precipitate. Barium and calcium hydroxide solutions produce cherry-red precipitates from an aqueous solution.

To obtain ruberythric acid from madder, powdered madder roots are extracted by boiling ethanol (9 liter/kg) for two to three hours. The solution is evaporated to about one-quarter volume and allowed to cool; the glycoside is precipitated and the aglycone (the noncarbohydrate part of the molecule) remains in the solution (Bergami, 1887). According to Rochleder (1851), ruberythric acid can be purified via the vermilion-colored lead lake, which is easily decomposed by hydrogen sulfide.

Purpurin (see fig. 9D), after alizarin, is the most significant coloring material of madder, although in fresh madder roots no noticeable quantity of it can be detected (Hill & Richter, 1936). Apparently, the large proportion of purpurin in commercial madder is formed during the manufacturing process and storage by decarboxylation of pseudopurpurin. Purpurin is found in madder plants other than *Rubia tinctorum* L. (see table 2). It dissolves to give a red color in alkali and a rose color in concentrated sulfuric acid. The alumina lake is scarlet red. Purpurin can be separated from alizarin by recrystallizing from hot alum solution because of its better solubility (Schunck & Römer, 1877a, b). The same separation can be achieved if the mixture is dissolved in sodium hydroxide solution and carbon dioxide is introduced when alizarin is precipitated (Auerbach, 1871). Purpurin can be manufactured by oxidation of alizarin (Lalande, 1874), xanthopurpurin

(Rosenstiehl, 1874), or quinizarin (1,4-dihydroxyanthraquinone) (Baeyer & Caro, 1875).

Pseudopurpurin (see fig. 9E), dissolves slightly in alum solution but simultaneously gives rise to an insoluble alumina lake. With alkaline earth carbonates it forms insoluble alkaline earth lakes, so that dyeing with pseudopurpurin can only be done in distilled water. This behavior can also lead to decomposition during thin-layer chromatography if the silica gel plates used contain gypsum as a binding material. Pseudopurpurin dissolves to give an orange-red color in alkali and in concentrated sulfuric acid. On heating at 180°C to 195°C, it undergoes quantitative separation of carbon dioxide to give purpurin; this reaction also proceeds on brief heating with potassium hydroxide solution or prolonged heating with water or alcohol. Pseudopurpurin can be made by oxidation of 1,2- or 1,4-dihydroxyanthraquinone-3-carboxylic acid with manganese dioxide and sulfuric acid (Bayer, 1911, 1913). Another synthesis given is based on the condensation of purpurin and formaldehyde with associated oxidation of the resulting hydroxymethyl compound (Hill & Richter, 1936); however, further research (Ayyangar, 1967) indicated that the product is not pseudopurpurin.

Galiosin, which forms as yellow needles that decompose above 100°C, is the 1-β-primeveroside of pseudopurpurin, occurring in madder in some *Galium* species, in *Rubia peregrina* L., and in *R. cordifolia* L. In the relbun root (see table 2) pseudopurpurin appears principally as the calcium salt. Galiosin is much less stable than ruberythric acid and is easily hydrolyzed. The Kopp process (1864) for the production of Kopp's purpurin (a mixture of purpurin, pseudopurpurin, xanthopurpurin, and munjistin) from madder is based on this property. In this process, the madder is treated with cold dilute sulfurous acid, filtered, and the extract is warmed to 60°C. The glycosides galiosin and rubiadin-3-glucoside are hydrolyzed, Kopp's purpurin is precipitated, and it can be separated by filtration from the more stable ruberythric acid.

Rubiadin dissolves in alkalies to give a red color and in concentrated sulfuric acid to give a yellow color. Schunck (1853) isolated rubiadin initially from madder and later established that it occurred as the glucoside (Schunck & Marchlewski, 1893). Its constitution is rubiadin-3-β-D-glucoside, which forms as yellow spikes, with a melting point of 270°C to 271°C and was demonstrated by synthesis (Jones & Robertson, 1930). It is notable for its great stability.

Rubiadin-3-β-primeveroside forms as pale yellow sheets, with a melting point of 248°C to 250°C, when isolated from the roots of *Galium verum* L. (Hill & Richter, 1936) and of *Galium mollugo* L. (Hill & Richter, 1937).

Munjistin dissolves in alkalies to give a carmine red color, in boiling alum solution to give intense orange-yellow, and in concentrated sulfuric acid to give intense yellow. Wool is colored orange when munjistin is used with an alum mordant. There are several possible methods for manufacturing munjistin synthetically; among them are reduction of pseudopurpurin with alkaline sodium dithionite solution (Thomson, 1971) and oxidation of lucidin with alkaline silver oxide (Ayyangar & Venkataraman, 1956).

Morindone dissolves in alkalies and in concentrated sulfuric acid to give a blue-violet color. The alumina lake is orange-red. Anderson (1849a, b, c) discovered morindone in 1849 in the roots of *Morinda citrifolia* L. (*soranjee*) as a glycoside that was named morindin. Morindone and the same morindin glycoside were also isolated from the roots of *Morinda persicaefolia* Bich.-Ham. (Paris & Ba Tuoc, 1954) and from *M. umbellata* L. (Perkin & Hummel, 1894). Morindone and a glycoside also named morindin, together with rubiadin-1-methyl ether, constitute up to 17% of the bark of the New Zealand bush *Coprosma australis* Robinson (Briggs & Dacre, 1948). The barks of various types of *Coprosma* species were used by the Maoris in New Zealand to dye flax. In fact, the two glycosides of morindone are different. Morindin from *Coprosma australis*, which forms as orange-red needles, with a melting point of 264.5°C (decomposition), $\alpha_D^{25} = -90°C$ (dioxan), is morindone-6-rhamnoglucoside (Briggs & Dacre, 1948) while the morindin isolated from *Morinda persicaefolia*, which forms as golden-yellow needles, with a melting point reported as 264°C to 265°C, is morindone-6-primeveroside (morindone-6-xyloglucoside). The constitution of morindone was determined by Bhattacharya and Simonsen (1927).

Xanthopurpurin (or purpuroxanthin) dissolves giving a red color in alkali and a yellow color in concentrated sulfuric acid. Xanthopurpurin was first isolated from impure "madder-purpurin," that is, purpurin from true madder (Schützenberger & Schiffert, 1865). The constitution was

determined by Noah (1886), who simultaneously demonstrated the possibility of synthesis from benzoic acid and 3,5-dihydroxybenzoic acid.

Rubiadin-1-methyl ether, in addition to the occurrences listed, is a secondary component of the root bark of: *Coprosma rhamnoides* A. Cunn. (Briggs & Taylor, 1955), *C. australis* Robinson (Briggs & Dacre, 1948), and *C. areolata* Cheesem (Briggs et al., 1948).

Hystazarin-3-methyl ether dissolves in alkalies giving a red color and may be purified by recrystallization from ethanol. It does not color mordanted wool. The compound can be manufactured synthetically through partial demethylation of hystazarin dimethyl ether, which can be obtained by cyclization of 2-(3,4-dimethoxybenzoyl)-benzoic acid (Lagodzinski, 1905).

Anthragallol dissolves in concentrated sulfuric acid giving a brownish red color; brown flakes precipitate upon dilution with water. It can be synthesized by heating together gallic and benzoic acids in sulfuric acid (Seuberlich, 1877).

Anthragallol-2-methyl ether has been synthesized from anthragallol (Kubota & Perkin, 1925).

Anthragallol-1,3-dimethyl ether and *anthragallol-1,2-dimethyl ether* were the first anthragallol ethers to be found in plants, having been isolated as noted in table 2, as well as in the root bark of *Coprosma lucida* Forst. and *C. acerosa* Cunn. (Briggs & Taylor, 1955).

Soranjidiol dissolves in alkali giving a blue-violet color; in concentrated sulfuric acid it gives a cherry-red color. It was isolated from *Coprosma australis* (Briggs et al., 1952) in addition to other *Coprosma* and *Morinda* species (see table 2). Synthesis of 1,6-dihydroxy-2-methylanthraquinone was in a two-step condensation from anisole and 3-methoxy-4-methylphthalic anhydride (Simonsen & Rau, 1921).

6-Methylxanthopurpurin dissolves in alkali giving a yellowish red color. It can be manufactured by condensation of *p*-toluic and 3,5-dihydroxybenzoic acids (Marchlewski, 1893).

Lucidin dissolves giving a red color in alkali, and an orange-red color in concentrated sulfuric acid; it has a brown color reaction with ferric chloride solution. Its structure was determined by Briggs and Nicholls (1953). A direct synthesis of lucidin, proceeding from xanthopurpurin, is possible through hydroxymethylation with formaldehyde (Ayyangar & Venkataraman, 1956). Lucidin occurs in *Rubia iberica* as the primeveroside (Stikhin et al., 1968).

Ibericin occurs in the roots of *Rubia iberica* C. Koch (Stikhin et al., 1966).

4.3 Madder Extracts and Madder Preparations

Numerous madder treatments were carried out in the nineteenth century for brightening the color and enriching and refining the coloring material.

Madder flowers (fleurs de garance), introduced in 1852 by Messrs. Julian and Roquer in France (Schlumberger, 1852) were derived by treatment of ground madder roots with twelve parts of water containing 0.5% sulfuric acid; the mixture was allowed to stand for a few days until fermentation began, then the madder was filtered off and rinsed with water until it was neutral. It was then packed in cloth sacks, pressed in a hydraulic press, dried in a room at 50°C to 70°C, ground, and packed in barrels. Through this treatment with dilute sulfuric acid, the madder was cleansed of the various acids and salts, lime, magnesia, pectin, and sugar. The color of the madder was not much changed, but its coloring strength doubled.

Madder flowers were used for dyeing by adding them to the dye liquor. The color exchange required less time than dyeing with madder, and the madder flowers were removed after each exhaustion of the dye liquor. Madder flowers can be used for the production of beautiful pink and violet shades. By treatment with sulfuric acid, the residue of dyeing with madder flowers or madder can be converted into *garancée* (*garanceux*), which means spent garancine.

Garancine was obtained from madder by boiling the root with dilute sulfuric acid. The ground madder was washed with cold water and then cooked with a mixture of water (one part, equal in weight to the madder) and sulfuric acid (one-sixth part) for approximately one hour, after which the liquid was filtered and the residue washed to neutrality and dried.

One hundred parts of madder yield thirty to forty parts of garancine with about four or five times the coloring strength of the original madder. The garancine manufacturing process was introduced by Robiquet and Colin (1828). Concentrated sulfuric acid in place of dilute sulfuric acid can also be used. Garancine is a chocolate-brown powder, which dissolves giving a yellow color in cold water, reddish yellow in hot water, greenish

yellow in mineral acids, and brownish red to red in alkalies. It has no odor or taste.

Pincoffin (commercial alizarin) was manufactured from carefully washed and neutralized garancine by treatment with superheated steam at 150°C. It no longer contained purpurin; its coloring strength was less than that of the raw material, but it gave especially pure colors, notably a beautiful violet. For coloring ability, one part of pincoffin was equivalent to four parts of madder. The pincoffin manufacturing process was introduced in 1854 by Pincoff and traded by the company Pincoff, Schunck, and Company, Manchester, England.

Kopp's purpurin was manufactured from ground madder that had been thoroughly soaked with water, saturated with sulfurous acid, and then allowed to stand for twelve hours (Kopp, 1864). The residue was then filtered off and it was once again treated with cold sulfurous acid. The combined filtrates were acidified to about 2% with sulfuric acid and heated with steam to 40°C. Kopp's purpurin then formed in large flakes. It was filtered off, and finally the filtrate was heated, causing green alizarin (alizarin with resinous impurities) to precipitate. Rubiadin was found in the filtrate. Green alizarin supplied good color and had eighteen to twenty times the color strength of madder, while Kopp's purpurin possessed fifty to fifty-five times the coloring strength of madder.

Madder extract Pernod. According to Pernod (1867), in Avignon the garancine was treated with boiling dilute sulfuric acid (5 g/liter) until all the coloring matter was dissolved; the extract was allowed to cool and a reddish orange sediment formed. The sediment was filtered off, washed to neutrality, and after the addition of a thickener, it was used directly for textile printing. Pernod madder extract is said to have produced brilliant and beautiful shades (Schäffer, 1887).

4.4 Manufacture of Madder Lakes

Pubetz (1872) described the manufacture of madder lakes. Madder lakes can be manufactured either from madder or a madder preparation such as garancine or Kopp's purpurin. The madder or the garancine is extracted by boiling it with an alum solution and precipitating with a soda, potassium arsenate, or borax solution. Before extraction, sugar can be removed from the madder by an alcoholic fermentation.

The quality of the color of a madder lake depends significantly on the alum extract being precipitated hot; otherwise the free alizarin, which separates as a brown material from the alum solution during cooling, will color the madder lake brown. Madder lakes, according to the type of manufacture, possess various red colors.

In order to obtain an intense and beautiful color in a madder lake, care must be taken not to overcook the madder or garancine, otherwise decomposition products will form and the lakes will have a dull color. The alum solution must be kept hot during the laking process, but should not be boiled. Likewise a large excess of alum solution produces a dull and lusterless madder lake. The optimum combination is one part madder to one part alum.

Since alizarin and purpurin, the two main components of the madder, are insoluble in cold alkali sulfates, 1 kg of madder or garancine is treated for removal of water-soluble products for twelve hours at room temperature with a solution of 1 kg sodium sulfate in 12 liters of water before the manufacture of madder lake. The residue is pressed on a filter cloth and washed with cold water until no sulfate ions are present in the water. Finally, a boiling solution of 1 kg of alum in 12 liters of water is added to the madder or garancine, allowed to stand for twenty minutes, and then filtered or decanted. The residue is washed with hot water. To the combined filtrates is added 1 kg of lead acetate at a temperature of 50°C and the mixture is agitated intensively until all the sulfate is changed into lead sulfate. The deep-red liquid is then removed from the lead sulfate deposit and later decanted. The lead sulfate is washed with hot water and this wash solution is used instead of pure water in the next madder preparation. The washed garancine residue can be extracted a second or third time, but about 240 g less of alum and lead acetate must be used.

The entire deep red solution is now heated to boiling, until a purple-red sediment separates (boiling of the solution at this stage must be carefully avoided). After cooling, a madder lake superior to the product of other methods in color and intensity is obtained.

Purpurin madder lake is prepared from one part purpurin (or Kopp's purpurin) combined with one part alum; the product is finely pulverized and washed with cold water. A yellowish red liquid runs off, which yields a rose-red lake at 80°C with the addition of a small amount of soda. The extracted residue is treated with a 5% alum solution, the solution is filtered boiling and is then sat-

urated with magnesium carbonate until red flakes appear. In this fashion a beautiful red lake is obtained (Pubetz, 1872).

Rose madder (pink madder) is prepared by extracting powdered madder for one day with cold 3% to 4% sulfurous acid. Sulfuric acid, about 2%, is added to the extract, which is heated to 55°C. The purpurin carboxylic acid (pseudopurpurin), which precipitates in flakes, is redissolved in alum solution. The lake is precipitated from the liquid, warmed to 70°C, by the addition of soda (4.5–5 kg to 30 kg of alum). If the precipitation of rose madder is performed on chalk (calcium carbonate) a brighter shade of color is obtained. Concentrated color lakes can be obtained by dissolving the pseudopurpurin in sodium hydroxide solutions and precipitating with aluminum sulfate (Cohn, 1930). Although purpurin lakes are not very lightfast, pseudopurpurin lakes display excellent lightfastness (Täuber, 1909).

De Puyster (1920) gave three examples of the preparation of madder lakes:

(a) For a fine quality product ground madder is allowed to stand for twenty-four hours in water at 27°C to 38°C; then an alum solution is added that contains approximately the same amount of alum as the madder used. The mixture is heated to 71°C, the liquid is filtered, and the madder lake is precipitated with sodium carbonate. Exceeding the temperatures given above should be avoided as undesirable products, which may influence the color and brilliance of the madder lake, will otherwise be dissolved by the alum solution.

(b) For a madder lake of moderate quality, the manufacturing process can be changed as follows: 100 lbs. of ground madder is put into a fine-mesh cloth bag in a tank to which 250 gallons of water is added in small portions until the coloring matter is completely extracted. The solution is filtered, brought to a boil, and a solution of 100 lbs. alum in 150 gallons of water is added, followed by 75 lbs. of potassium carbonate in 60 gallons of water under constant agitation. The solution is allowed to stand for twelve hours and the precipitated madder lake filtered off to avoid the extraction of brown products and tannins, which are produced upon longer cooking. The lake is dried at a moderate temperature.

(c) To prepare madder lake from garancine: 100 lbs. of garancine is boiled for three hours with 250 gallons of water; 100 lbs. of alum dissolved in water is then added and the combined solution is boiled for two hours. It is then filtered hot through a flannel cloth, and a solution of 1¾ lbs. of tin(II) chloride in water is added to the filtrate. A solution of 75 lbs. of soda crystals in water is added, using only enough to ensure complete precipitation of the alumina lake; the alumina lake is filtered off using a flannel cloth, the residue is rinsed well with water and dried at a moderate temperature.

Inexpensive madder lakes such as Steiner lake and Van Dyck red are manufactured from inferior quality madder; thus, they are less brilliant in color (Seufert, 1955).

The brilliance of madder lake is frequently improved by adding an ammonia alkali solution of cochineal carmine during the precipitation of the madder lake with soda crystals. This product is called madder carmine.

Mixtures of madder and brazilwood can be extracted with aqueous solution of soda crystals and then precipitated with alum and/or tin(II) chloride (De Puyster, 1920).

The so-called crystallized madder lake forms dark red, shiny platelets. Burnt madder lake has lost its water by heating to about 150°C and is thus darkened (Wagner, 1939).

4.5 Manufacture of Alizarin Lakes

4.5.1 ***Alizarin lake.*** According to Wagner (1939), aluminum sulfate (100 g) is dissolved in 1,000 ml of water at 60°C; it is treated with a solution of 50 g of anhydrous soda in 100 ml of water and the precipitated aluminum hydroxide is rinsed once with water. To this hydroxide is added in sequence 20 g sodium phosphate dissolved in 200 ml of water, 30 g calcium chloride dissolved in 300 ml of water, and a paste of 200 g alizarin mixed with 40 g of Turkey red oil (sulfated castor oil, a surfactant), and 200 ml of water. The mixture is diluted to 5,000 ml and boiled for six hours with replenishment of the water. After cooling, the alizarin–alumina–calcium lake is filtered off and dried at the lowest possible temperature.

4.5.2 ***Pink alizarin lakes*** can be manufactured by mixing water containing aluminum hydroxide, aluminum phosphate, calcium salts, sulfated castor oil, and alizarin. The mixture is boiled at a pH of 3.2 to 5.5. The pink alizarin lake thus obtained is reported to be very lightfast (Murometsev & Ivanova, 1940).

4.6 Adulteration and Sophistication

4.6.1 ***Contaminants, adulterants, and their detection.*** Madder can be contaminated with inorganic as well as organic substances. Inorganic contaminants include brick powder, ocher, yellow clay, and yellow sand. Burnt sienna and copper ferrocyanide have been reported in samples of madder brown. The inorganic content is determined by incinerating a sample; a madder that yields more than 6% ash is definitely contaminated with inorganic substances.

Among organic contaminants are oak shavings, logwood, redwood, old fustic wood, sandalwood, almond shells, mahogany shavings, and clover.

These contaminants can be determined by a comparative dyeing test with a known sample of madder. The dyed textile samples are drawn through a weak solution of bleach and then through a soap solution. They are then treated with a tin(II) chloride solution. In this way all the wood dyes are destroyed except for the madder dyes. By comparing samples treated in this way, the quality of the madder can be determined with relative accuracy. To determine the type of wood with which the madder is contaminated, Pernod gave the following method: a piece of paper is impregnated with a tin chloride solution of one part tin dissolved in 2.5 parts nitric acid and 5.5 parts hydrochloric acid diluted by twenty parts water, and the madder powder to be tested is sprinkled on the surface of the paper. After approximately thirty minutes, all places where a wood particle came to rest will be indicated by the following: redwood by carmine red, logwood by violet, and old fustic wood by yellow dots. Pure, uncontaminated madder displays only a light yellow color (Pubetz, 1872).

Samples containing tannic substances can be identified in a similar way, except that the paper must be impregnated with iron(III) chloride solution in ethanol. In the presence of tannic substances, the paper will display randomly spaced black dots (Pubetz, 1872).

4.6.2 ***Substitutes.*** With the advent of synthetic dyes, attempts were made to replace madder lakes with synthetic organic pigments because of the laborious preparation necessary for madder lakes and the resulting cost and the lack of lightfastness observed in rose madder lakes containing purpurin.

Soon after the synthesis of alizarin became possible, lakes based on the synthetic product were used as substitutes for those based on alizarin extracted from madder (see section 4.5). The alum lake made with Alizarin Red W (1,2-dihydroxyanthraquinone-3-sulfonic acid, CI no. 58005) can also substitute for madder lake, as can a number of azo dyestuffs in the form of calcium, barium, strontium, or manganese lakes used alone or mixed with other pigments; examples are: Permanent Red 6B (CI no. 15610), Lake Red C (CI no. 15585), Lithol Red RS (CI no. 15630), Lithol Rubine brands (CI nos. 15825, 15850, 15865), and Litholbordotoner TR. The alum lake of Helio Fast Rubine RL (purpurin-3-sulfonic acid, CI no. 58210) has been especially recommended as a substitute for pink madder lakes (Wagner, 1939). Madder carmine is a madder lake improved with carmine; it may be detected using thin-layer chromatography by comparison with carminic acid, alizarin, purpurin, and pseudopurpurin (Schweppe, 1976, 1977, 1985) (fig. 10).

5.0 Identification and Characterization

5.1 Optical and Chemical Microscopy

Microscopy will not identify madder definitively, but can give an indication of its presence. Its appearance, when mounted on a microscope slide, is crimson red in color, sometimes seen as fine particles, but more often as a stain, depending on the presence or properties of the substrate. Refractive indices, which are normally those of the substrate, are variable and have been given as >1.66 for alizarin lake and <1.66 for madder lake (McCrone, 1982). Alizarin alone is also said to have a refractive index of about 1.70 (Merwin, 1917).

Tests for madder by chemical microscopy depend on the production of an orange solution of flocculent precipitate with acid and a purple color with alkali (Weber, 1923; Plesters, 1956). Such tests have been supplanted by other identification methods.

5.2 Identification of Organic Colorants

5.2.1 ***Color and fluorescent reactions.*** In ultraviolet radiation, cochineal carmine and kermes carmine fluoresce bright pink and madder lakes fluoresce dull orange, while alizarin lakes and lac lakes display no fluorescence.

The results of color test reactions for the major compounds are given in table 3. These tests, described by Pfister (1935), Schweppe (1977), and in the *Colour Index* (1977), are carried out as follows:

Sulfuric acid: In a small porcelain vessel, two to ten drops of concentrated sulfuric acid are added to 0.1 to 1 mg of sample; large particles of pigment may be crushed with a glass rod. The color and ultraviolet fluorescence are observed after about one minute. The solution is then diluted with water and the color as well as the possible appearance of flakes are observed.

Sulfuric/boric acid: The same procedure as above is carried out using a 10% solution of boric acid in concentrated sulfuric acid.

Dilute hydrochloric acid, ammonia, and sodium hydroxide: Each small sample is boiled with hydrochloric acid (1:10), dilute ammonia (1:10), and 2% sodium hydroxide solution.

Alum solution: This test is intended to distinguish between madder lakes and synthetic alizarin lakes. A

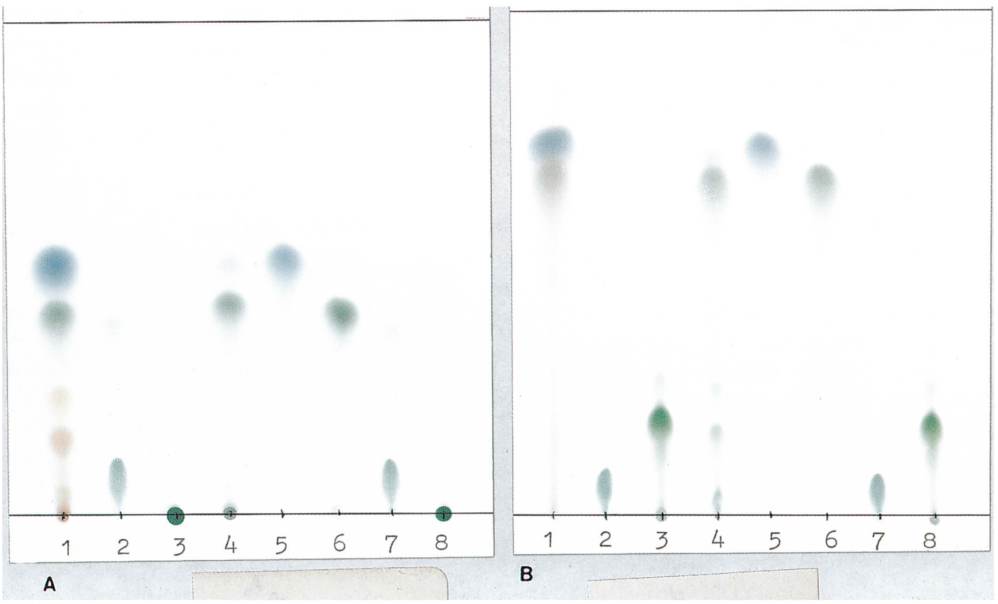

Fig. 10 Thin-layer chromatography.
Layer: polyamide powder (Mikropolyamid F1700, manufactured by Schleicher and Schüll).
Solvents: (A) toluene-acetic acid (9:1) (B) methyl ethyl ketone-methanol-formic acid (65:30:5).
Color reaction: uranyl acetate (1% in water) + methanol (1:1).
(1) madder lake (hydrolyzed) (2) rose madder lake (hydrolyzed) (3) carmine (hydrolyzed) (4) madder carmine (hydrolyzed) (5) alizarin (6) purpurin (7) pseudopurpurin (8) carminic acid.

small sample is boiled with 2% aqueous alum solution. Any purpurin present dissolves to give a faint yellowish red solution with an orange ultraviolet fluorescence. Alizarin does not react.

Madder carmine preparations (see section 4.8) may sometimes be recognized through color tests. Following treatment with sulfuric acid and dilution with water, the resulting solution is shaken with ether. Madder colors the ethereal layer yellow (from alizarin) to orange (purpurin or pseudopurpurin). Kermesic acid colors it orange-red and must be distinguished from madder by chromatographic or spectroscopic methods. If the aqueous layer is orange, carminic acid from cochineal may be present, as may lac dye or synthetic pigments with sulfonic acid groups. In this case, the ethereal and aqueous layers are separated and the aqueous layer reextracted with isoamyl alcohol. If cochineal carmine is present, the isoamyl alcohol layer is colored orange-red, the aqueous layer being left faintly red. Results such as these are best confirmed by chromatographic methods.

5.2.2 ***Chromatographic methods.*** Techniques that have been used to separate and identify hydroxyanthraquinones include paper chromatography (Shibata et al., 1950; Paris & Rousselet, 1958), thin-layer chromatography (Masschelein-Kleiner, 1967; Masschelein-Kleiner & Heylen, 1968; Masschelein-Kleiner et al., 1969; Boutrop, 1970; Masschelein-Kleiner & Maes, 1970; Hofenk de Graaff & Roelofs, 1972), and gas-liquid chromatography (Furuya et al., 1966). High-performance liquid chromatography has also been used; here, identities are confirmed by ultraviolet-visible spectroscopy and by addition of reference materials to the samples (Wouters, 1985).

For identifying artists' pigments, thin-layer chromatography has the advantage of being simple, inexpensive, and requiring small samples, micrograms or less. Madder and alizarin lakes must first be hydrolyzed with mineral acids and the free hydroxyanthraquinones separated by extraction with organic solvents. Several procedures are:

(a) Hydrolysis is performed with a mixture of acetone, hydrochloric acid, and water (1:1:3) for a maximum of forty-eight hours at 50°C; the dyestuffs are extracted with hexane or amyl alcohol (carminic acid is insoluble

Table 3 **Color Reactions of Alum Lakes of Madder and Related Colorants**[a]

	Madder	*Pink Madder*	*Alizarin*	*Purpurin*	*Pseudopurpurin*
Sulfuric acid (98%)					
Color	Dull red	Magenta red	Brownish red	Magenta red	Magenta red
Ultraviolet fluorescence	Orange	Reddish orange	—	Orange	Reddish orange
Diluted by water	Brown flakes	Brownish red	Yellow-orange flakes	Brown-orange	Brown-red flakes
Sulfuric/boric acid					
Color	Magenta red	Magenta red	Brown-violet	Magenta red	Bright magenta
Ultraviolet fluorescence	Faint orange	Intense orange	—	Orange	Bright orange
Dilute hydrochloric acid (1:10)					
Color	Orange	Orange	Yellow	Orange	Orange
Dilute ammonia (1:10)					
Color	Faint pink	Faint pink	—	Faint pink	—
Sodium hydroxide (2%)					
Color	Violet	Magenta	Violet	Faint magenta	—
Alum solution (2%)					
Color	Faint red	—	—	Faint red	Faint red

a. See section 5.2.1.

Table 4 **Thin-Layer Chromatography of Some Hydroxyanthraquinones**[a]

	Rf-Values		*Detection*		
Compound	*A*[b]	*B*[c]	*Color of Spot*	*Ultraviolet Fluorescence*	*Uranyl Acetate Reaction**
1,2-Dihydroxyanthraquinone (alizarin)	0.42	0.74	Yellow	None	Violet-blue
1,3-Dihydroxyanthraquinone (xanthopurpurin)	0.14	0.72	Yellow	Orange-yellow	Orange-red
1,2,4-Trihydroxyanthra-quinone (purpurin)	0.33	0.67	Scarlet	Intense pink	Gray
1,2,4-Trihydroxyanthra-quinone-3-carboxylic acid (pseudopurpurin)	0.06	0.06	Scarlet	Intense pink	Gray
1,3-Dihydroxyanthraquinone-2-carboxylic acid (munjistin)	0.02	0.49	Yellow	Intense yellow	Red

*Plate dipped in a reagent prepared by diluting 1% aqueous uranyl acetate with an equal volume of methanol

a. Carried out under conditions of chamber saturation on layers of Mikropolyamid F1600, manufactured by Schleicher and Schull, Dassel, Kreis Einbeck, Germany.

b. Solvent: toluene-acetic acid (9:1).

c. Solvent: methyl ethyl ketone–methanol–formic acid (65:30:5)

in hexane). The organic phase is separated and washed free of mineral acid with water (Masschelein-Kleiner, 1967; Masschelein-Kleiner & Heylen, 1968).

(b) A small sample of the lake is heated in a test tube with one drop of concentrated hydrochloric acid, two drops of methanol are added, the tube is reheated, and the solution is used for thin-layer chromatography (Roelofs, 1972).

(c) Hofenk de Graaff and Roelofs (1972) boil a sample of the lake for a few minutes with 10% hydrochloric acid and extract it with methanol in a microextraction apparatus.

(d) Schweppe (1975, 1977) adds two to ten drops of 98% sulfuric acid to 0.1 to 1 mg of the lake in a small porcelain vessel, crushing the larger particles with a glass rod (see also section 5.2.1). After the lake has dissolved, the solution is diluted with 5 ml water, allowed to cool, and extracted with 10 ml ether. The lower, aqueous layer may be used for the detection of inorganic components (see section 5.3). The ethereal layer containing the dyestuffs is washed to neutrality with water, evaporated to dryness, the residue is dissolved in one to three drops of acetone and the solution is used for thin-layer chromatography.

Naturally occurring hydroxyquinones, such as those in madder, cochineal, alkanna, sandalwood, and others, may be separated on layers of acetylcellulose powder (10% acetyl content) without binder (suitable precoated plates are type MN-300 AC produced by Macherey, Nagel and Company, Düren, Germany). With the solvent mixture of ethyl acetate:tetrahydrofuran:water (6:35:47), the following Rf-values were obtained: alizarin, 0.32; purpurin, 0.31; carminic acid, 0.94 (Masschelein-Kleiner, 1967; Masschelein-Kleiner & Heylen, 1968).

Schweppe (1986, 1989) achieved good separations of madder constituents on polyamide plates with mixtures of 9:1 toluene:acetic acid or 65:30:5 ethyl methyl ketone:methanol:formic acid (table 4). This method requires only short separation times, usually twenty to thirty minutes. The reliability of identification can be increased by using the following detection methods in combination: (a) natural color of the spots, (b) fluorescence in ultraviolet radiation, and/or (c) colors produced with uranyl acetate reagent (1% aqueous uranyl acetate diluted 1:1 with methanol). Table 4 summarizes the Rf-values for the above solvent mixtures and the colors observed for various hydroxyanthraquinones found in madders. See figure 10 for typical chromatograms on polyamide plates under these same conditions.

Thin-layer chromatography has been used for the analysis of natural red dyes in early Indian textiles (Kharbade & Agrawal, 1988) and of a series of synthetic organic pigments, including alizarin, from artists' commercial oil paints (Strauss, 1984).

5.2.3 ***Infrared spectroscopy.*** Identifications of natural organic pigments by comparison of infrared spectra have been published (Flieder, 1968; Masschelein-Kleiner & Heylen, 1968) and the use of infrared microspectroscopy for the analysis of early paint materials has been reported (Van't Hul-Ehrnreich, 1970). Low and Baer (1977) give infrared spectra of madder lakes, alizarin, and purpurin obtained by the Fourier transform method. Abrahams and Edelstein (1964, 1967) identified coloring materials on ancient textiles from the Bar Kochba find in Israel (A.D. 135) by comparison of their infrared spectra with those of known natural dyestuffs. Kühn (1968) described the identification by infrared spectroscopy of madder lakes in paintings.

Bloom et al. (1959) evaluated the infrared spectra of sixty hydroxyanthraquinone derivatives, and described relationships between the position of the absorption bands and their constitution. The location of the O—H stretching band of a hydroxyl group and the C==O stretching band of the anthraquinone nuclear carbonyls is affected by whether the hydroxyl group is in one of the α (1, 4, 5, or 8) positions adjacent to a carbonyl group, or one of the β (2, 3, 6, or 7), nonadjacent positions (see fig. 9A). Therefore, Bloom et al. proposed the following generalizations:

Hydroxyl-group absorption. Beta-hydroxyl groups can be recognized by a sharp band between 3600 and 3150 cm^{-1}. If more than one such band is present, the anthraquinone possesses two or more β-hydroxyl groups with different molecular environments.

Carbonyl-group absorption.

(a) Derivatives without α-hydroxyl groups have a strong C==O stretching band in the region of 1678 to 1653 cm^{-1}.

(b) Derivatives with one α-hydroxyl group have two carbonyl frequencies, one in the region of 1675 to 1647 cm^{-1}, and a stronger band between 1637 and 1621 cm^{-1}; the separation is 24 to 38 cm^{-1}.

(c) Two hydroxyl groups in the 1, 4 or 1, 5 positions (both carbonyls are hydrogen bonded) give a single C==O band between 1645 and 1608 cm^{-1}.

(d) Derivatives with two hydroxyl groups in the 1, 8 positions (one carbonyl hydrogen bonded) have two C==O bands, one at 1678 to 1661 cm^{-1} and another stronger one between 1626 and 1616 cm^{-1}; the separation is 40 to 57 cm^{-1}.

(e) 1,4,5-trihydroxy compounds show a single C==O band between 1616 and 1592 cm^{-1}.

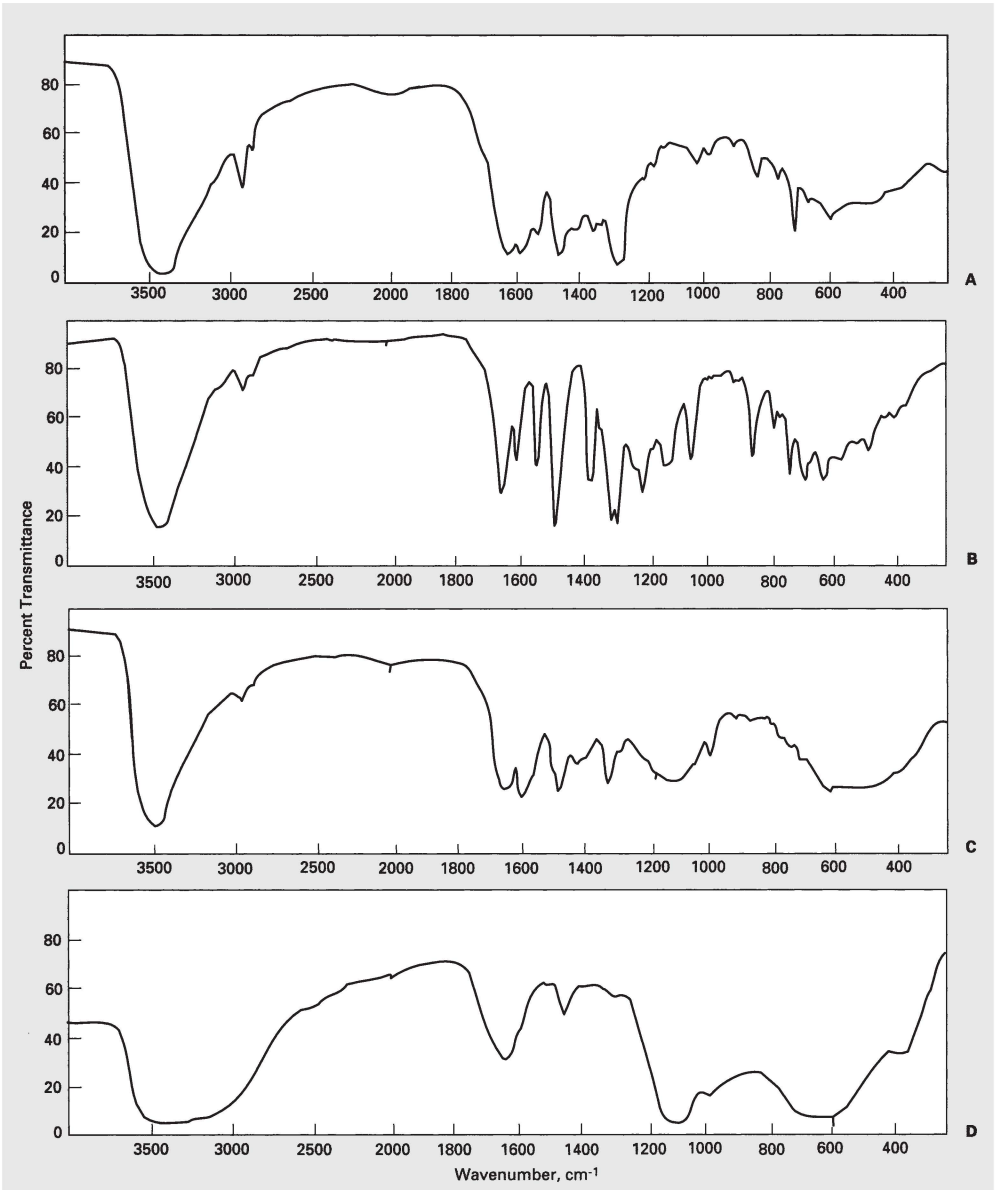

Fig. 11 Infrared spectra.
A. Madder lake from garancine, on aluminum-containing substrate.
B. Infrared spectrum of an alizarin lake.
C. Infrared spectrum of a purpurin lake on aluminum phosphate substrate.
D. Infrared spectrum of a rose madder lake.

(f) 1,4,5,8-tetrahydroxyanthraquinone derivatives have a single C==O band between 1592 and 1575 cm^{-1}.

In some cases, where a pure pigment sample without binding medium is available, it may be possible to obtain a useful infrared spectrum without pretreatment (Ziegler, 1974). However, if the lake contains a high proportion of inorganic substrate, as for example with pink madder lakes, the quality of such a spectrum is usually not good enough for identification. In such cases, the spectrum may be obtained after hydrolysis of the lake followed by concentration and purification of the

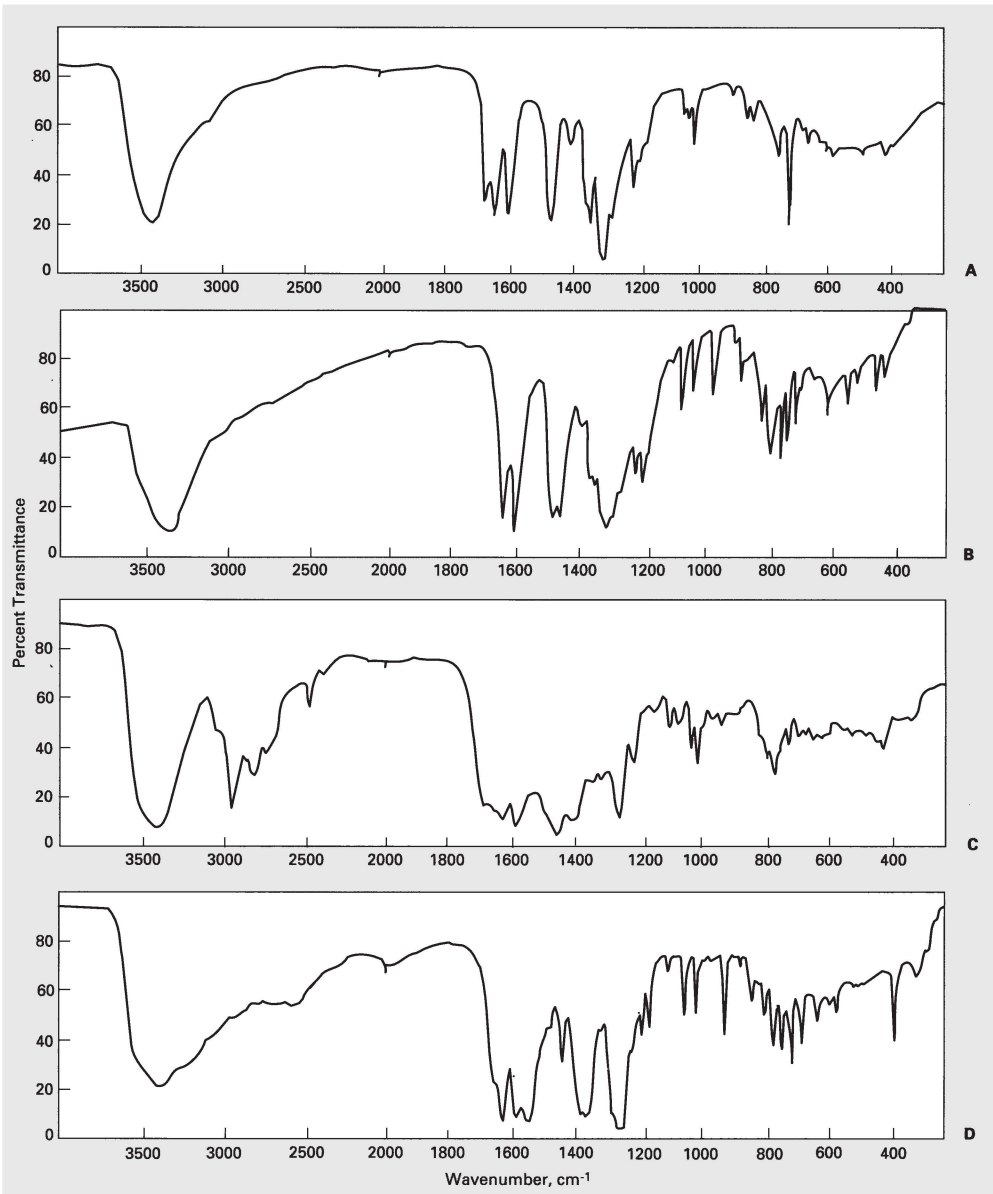

Fig. 12 Infrared spectra.
A. Alizarin.
B. Infrared spectrum of purpurin.
C. Infrared spectrum of pseudopurpurin.
D. Infrared spectrum of munjistin.

colorant. A similar hydrolysis may be needed to obtain a useful spectrum from madder lake samples taken from actual paints containing binders in addition to the pigment.

Infrared spectra of a madder lake, an alizarin lake, a purpurin lake, and a rose madder lake (fig. 11) were all taken without preceding hydrolysis. Acid hydrolysis of madder lakes to obtain free hydroxyanthraquinones may be performed in the same way as for thin-layer chromatography (see section 5.2.2). Figures 12 and 13 show the infrared spectra of typical pure hydroxyan-

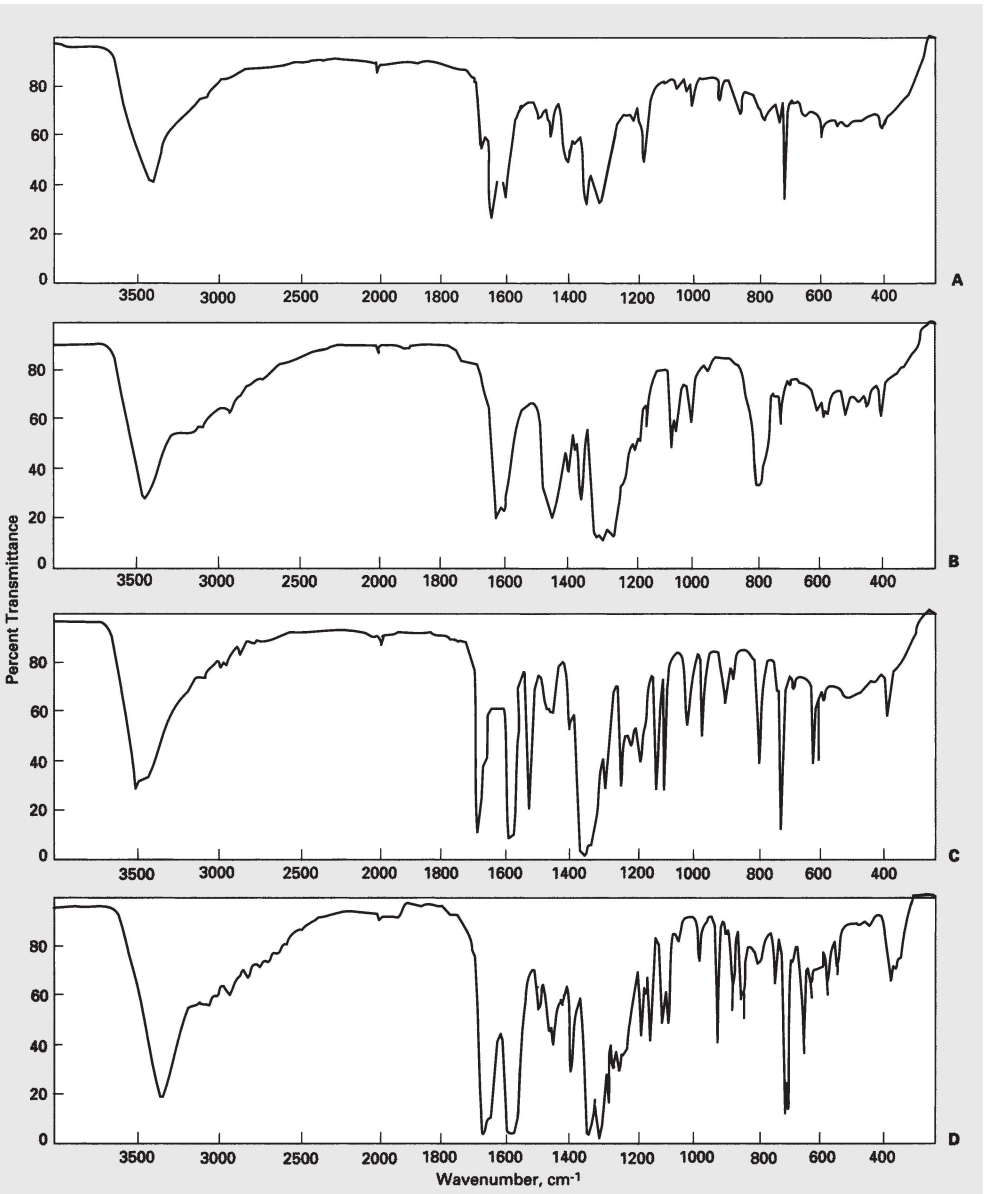

Fig. 13 A. Infrared spectrum of xanthopurpurin.
B. Infrared spectrum of morindone.
C. Infrared spectrum of hystazarin monomethyl ether.
D. Infrared spectrum of 2-hydroxyanthraquinone.

thraquinones. Figure 14 shows the infrared spectra of madder lake and rose madder lake after hydrolysis. Because of the small amounts of material usually available, micropotassium bromide (KBr) pellets with a diameter of 2 mm or less are useful for infrared spectroscopy. With 2 mm pellets, about 10^{-5} g (10 µg) of pure substance are required. See table 1 for values given in the literature for the main infrared absorption peaks of various hydroxyanthraquinones.

5.2.4 ***Visible and ultraviolet spectroscopy.*** Absorption spectroscopy of colored materials in the visible range has the advantage over other spectroscopic methods of avoiding interference by colorless compounds. Saltzman et al. (1963)

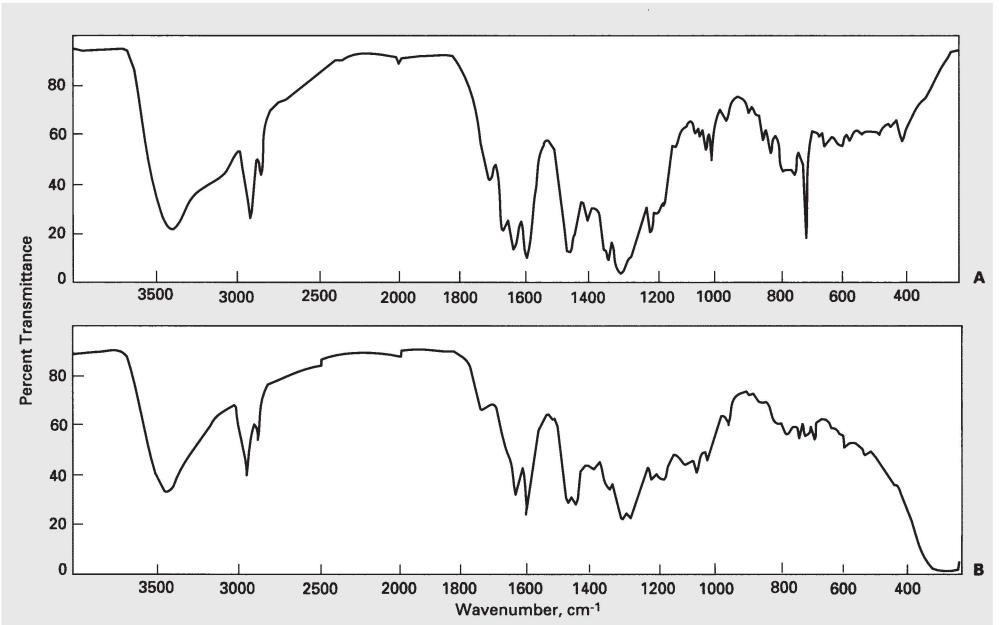

Fig. 14 A. Infrared spectrum of ether extract of hydrolyzed madder lake. B. Infrared spectrum of toluene extract of hydrolyzed rose madder lake.

used this method principally for the identification of natural dyestuffs on early Peruvian textiles. Care should be taken with spectroscopy on extremely dilute solutions of hydroxyanthraquinones in ethanol, where bathochromic peak shifts have been observed similar to those seen upon the addition of alkali (J. Winter, M. Deemer, unpublished). The effect may be suppressed by the addition of small amounts of acid or by the use of a non-protonic solvent such as acetonitrile and may be a result of alkali leaching from the glass walls of vessels used during analysis. Visible spectra may also be obtained nondestructively from the diffusely reflected light. Johnston and Feller (1963) and Kirby (1977) described this approach.

Absorption spectra of hydroxyanthraquinones have been recorded in solutions ranging from concentrated sulfuric acid to aqueous or alcoholic caustic alkali. Fierz-David (1926) published some early data. Schultz (1931–1932) published absorption maxima for alizarin lake in alcoholic potassium hydroxide of 624.0, 577.0, and 536.0 nm. Figure 15 shows the absorption curves in the visible region of solutions of alizarin at various pH values. Figure 16 shows those for purpurin; a precipitate appears at about pH 6.5 when titrating with acid and fluorescence appears between pH 6.3 and 7.5. Conventional visible-ultraviolet spectra in ethanol down to 200 nm for alizarin (fig. 17) and purpurin (fig. 18) are shown for both neutral solutions and after the addition of an excess of potassium hydroxide. Table 1 also gives the locations and intensities of absorption maxima for various hydroxyanthraquinones.

Figure 19 shows fluorescence spectra of natural madder. The fluorescence spectra of various madder samples have been studied by De la Rie (1982); he believes the fluorescence probably originates from purpurin chelates. Larson and Zink (1991) reported on the absorption and fluorescence spectra of alizarin, its potassium salt, and its aluminum(III), cobalt(II), nickel(II), copper(II), and zinc(II) complexes.

5.3 Identification of Inorganic Substrates

5.3.1 ***Chemical methods.*** The most common inorganic substrate for lake pigments is precipitated aluminum hydroxide, also called alumina gel. From the accounts of methods of manufacture (see section 4.6), other metals that may be encountered are tin, calcium, iron, chromium, and possibly magnesium or lead. Among acid radicals, phosphate or sulfate could be present. In ad-

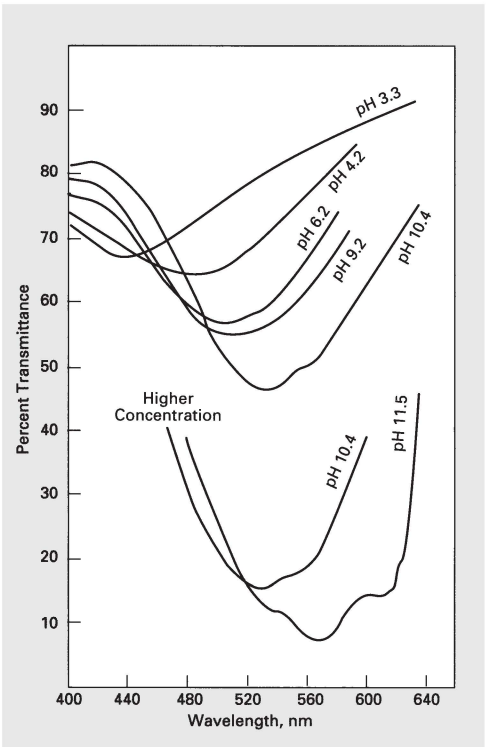

Fig. 15 Spectral absorption curve of solutions of alizarin at various pH values.

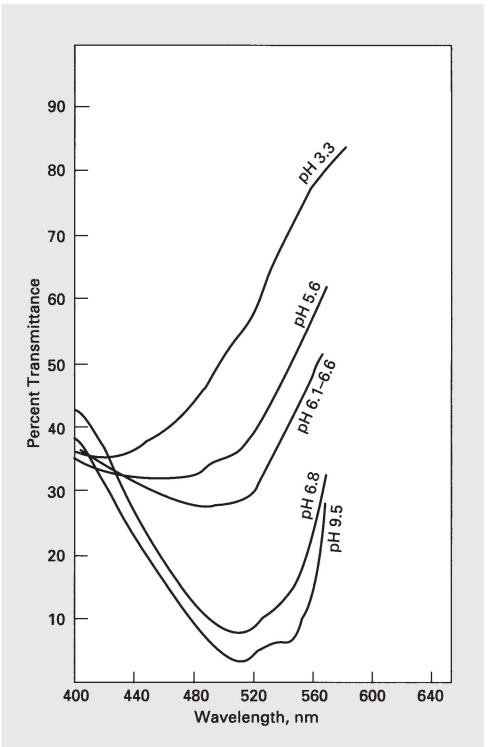

Fig. 16 Spectral absorption curve of solutions of purpurin at various pH values.

dition, Mayer (1981) suggests the use of barium sulfate (barytes or blanc fixe) and clay as substrates, while Gettens and Stout (1966) include zinc oxide, explaining that "the true lake is a transparent color precipitated on a transparent base like aluminum hydrate, but the word has been extended to include those colors struck on barytes, tin oxide, zinc oxide, and a number of other materials." Previous chapters in volumes in this series have described barium sulfate (Feller, 1986), zinc oxide (Kühn, 1986), calcium carbonate (Gettens et al., 1993a), and the lead carbonate group (Gettens et al., 1993b) in terms of their use as white pigments.

When a sample of the lake is hydrolyzed with mineral acid and extracted with an organic solvent to free the colorants for chromatographic separation (see section 5.2.2), it may often be convenient to use the aqueous phase for identification of the inorganic species. A suggested procedure based on the traditional qualitative separation scheme (see, for example, Vogel, 1954) was published in a chapter in this series (Schweppe & Roosen-Runge, 1986). The latter account describes a preliminary sample treatment involving digestion with perchloric acid to destroy any residual traces of organic material. Following this treatment, most residues may be taken up in a small amount of 20% hydrochloric acid, with any traces of insoluble material being removed by filtration or centrifugation. A problem may arise with barium sulfate, if present, as this is notoriously insoluble, and best identified by instrumental methods. Barium sulfate can, however, be dealt with by fusing the sample with pure sodium carbonate on a platinum foil until a colorless, clear melt is obtained. After cooling, this melt is extracted with drops of water to remove sodium sulfate and leave a residue of barium carbonate, which is then taken up in a little dilute hydrochloric acid and tested for barium.

True micromethods for inorganic ions may be divided into those performed on the microscope stage (chemical microscopy) and spot tests usually done on filter paper or spot plates. An extended scheme for the former is given in Chamot and Mason (1940) and chemical microscopic tests are also described by Plesters (1956)

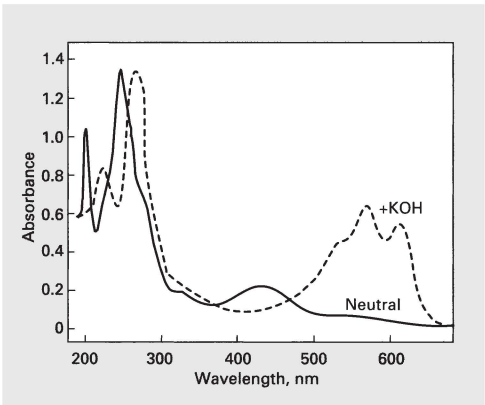

Fig. 17 Ultraviolet-visible absorption spectrum of alizarin, 0.001% in ethanol.

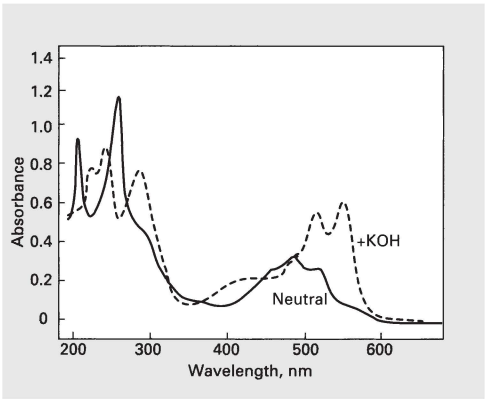

Fig. 18 Ultraviolet-visible absorption spectrum of purpurin, 0.001% in ethanol.

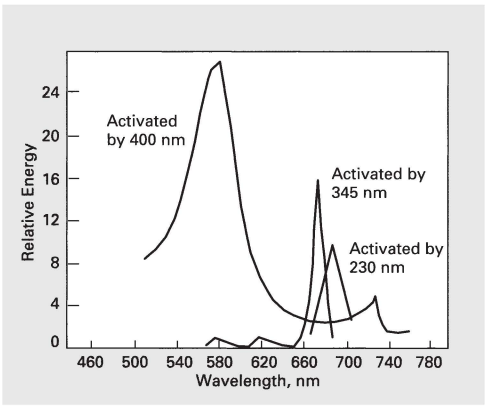

Fig. 19 Fluorescence of natural madder. Sample from Winsor and Newton.

and Short (1964). These tests are perhaps less useful than others for the ions usually found in madder and alizarin lakes.

A standard source for information on spot tests for metals and acid radicals present in lake substrates is Feigl and Anger (1972).

Two problems that are pervasive with both micromethods are that a species has to be suspected before it can be tested for and the problem of possible interferences between different species. Schweppe and Roosen-Runge (1986) describe several relevant spot tests, including the morin test for aluminum, the chlorindazon C test for calcium (Schweppe, 1969), and the cacotheline test for divalent tin (Gutzeit, 1929).

5.3.2 ***Thin-layer chromatography.*** This method can be used for the separation and identification of inorganic ions, although it is much less widely used for this purpose than in the organic field. On cellulose layers *n*-butanol:concentrated hydrochloric acid:water (10:2:3) will separate aluminum, iron, and tin ions applied from hydrochloric acid solution. Visualization may be done with 0.5% carmine solution in ethanol followed by exposure to ammonia vapor (Boutrop, 1970).

5.3.3 ***Instrumental methods of analysis.*** Various instrumental methods are available, a number of which should be well adapted to identifying inorganic substrates, although in fact few such results seem to have been published. Ziegler (1974) reported on the use of emission spectroscopy, x-ray fluorescence, and atomic absorption for the analysis of early artists' pigments. The account below is confined to some general remarks.

X-ray diffraction. In our experience, aluminum hydroxide rarely gives a well-defined diffraction pattern, and consequently most lakes rarely do so either. Some of the more nontraditional substrates, such as barium sulfate or zinc oxide are readily identified by this method.

Atomic spectroscopy. Emission spectroscopy is a long-standing method for element identification and quantitation; in recent years it has been made more powerful by the development of inductively coupled plasma techniques. It is mostly applied to metallic elements. Comprehensive listings of the wavelengths of emission lines are available in standard works (for example, Goldstein et al., 1992). The converse method of atomic absorption spectroscopy is usually adapted to the quantitative

Table 5 **Characteristic X-ray Lines* for Madder Substrates**

Element	*Atomic Number*	$K\alpha$	$K\beta_1$	$L\alpha_1$	$L\beta_1$
Aluminum	13	1.486	1.557	—	—
Barium	56	32.062	36.372	4.465	4.827
Calcium	20	3.690	4.012	—	—
Chromium	24	5.411	5.946	—	—
Iron	26	6.398	7.057	—	—
Magnesium	12	1.253	1.302	—	—
Phosphorus	15	2.013	2.137	—	—
Lead	82	—	—	10.550	12.612
Sulfur	16	2.307	2.465	—	—
Tin	50	25.191	28.481	3.443	3.662
Zinc	30	8.630	9.570	1.012	1.034

*Line positions expressed as characteristic quantum energies in keV. From Leyden (1984). Only lines likely to be in the range of, and resolved by, conventional energy-dispersive spectrometers are listed. For more comprehensive listings at higher resolutions see standard works such as Goldstein et al. (1992)

analysis of one element at a time, which appears less applicable to work in the pigment field.

X-ray spectroscopy. X-ray spectra may be obtained via electron microscopy, usually scanning electron microscopy, x-ray fluorescence, or in other ways such as proton-induced x-ray emission. The x-ray lines usually of interest are given in table 5. Elements in the first and second periods of the periodic table are accessible by methods operating under high vacuum, such as scanning electron microscopy, but most of these elements are difficult to detect when an air path is involved. This is the case when x-ray fluorescence is used directly on the surface of a painting (or other object). More of the second-period elements can be detected by replacement of the air path by helium, but this can be difficult to arrange for a painting or large object. In most cases, a removed sample is likely to be necessary especially in the case of an important element like aluminum.

5.4 Criteria for Identification

The best methods available for the positive identification of anthraquinone colorants are most likely those based on absorption spectroscopy. The infrared spectrum of a pure compound can in most cases be regarded as definitive; unfortunately the size of a sample usually available coupled with the complexity of mixtures often found frequently make this approach unrealizable since infrared spectroscopy rapidly loses its "fingerprinting" value in mixtures. Ultraviolet-visible spectroscopy has the advantages of great sensitivity and good selectivity for colorants, but, again, mixtures can be difficult to interpret.

Reflectance spectroscopy performed on the surface of a work of art has the obvious attraction of being nondestructive. However, this method has been largely limited thus far to the visible region, making it difficult to produce a reliable identification.

Thin-layer chromatography has been refined to the point that it will probably solve a great many identification problems, particularly in view of its simplicity and sensitivity. High-performance liquid chromatography has considerable potential, possibly best realized by the use of a diode-array detection system that will yield spectral information on the separated constituents. Microspectrophotometry on paint cross sections gives a good indication of the presence of madder or other dyes, but following up by chromatography or other methods is needed for positive identification (Kirby, 1977).

Most lake substrates may be identified by a determination of the elements present using the methods described in section 5.3.

6.0 Occurrences

In addition to the evidence relating to historical aspects described in section 2.2, a number of identifications of madder and alizarin lakes on paintings are available and are here tabulated. These have all been published over the past twenty to twenty-five years; the identification of these pigments was difficult before the widespread adoption of chromatographic and spectrometric methods.

Occurrences of Madder

Date, Country or School	*Artist, Title or Description Collection or Location*	*Analyst and Method of Identification*
Russian, 6th–7th C	Icon, encaustic on wood panel *The Martyrs*, Museum of Eastern and Western Art, Kiev	Birstein et al. (1978) IR
Tibet, 15th–19th C	*Thang-ka* paintings on cotton Private collection, The Netherlands	Mehra (1970) micr., TLC
Italian, 1456	Manuscript illumination in a Missale Romanum (location not given)	Wallert (1986) spec.
German, 1466	Herlin Altarpiece, Church of St. James, Rothenberg	Broekman-Bokstijn et al. (1970) GLC, micr., IR, TLC
German, c.1485–1490	Studio of "The Master of the Life of the Virgin," *The Mass of St. Hubert* National Gallery, London NG253	Kirby (1977) spec., TLC
Italian, 15th C	Leonardo da Vinci, *Last Supper* Santa Maria delle Grazie, Milan	Kühn (1985) micr., chem.
Italian, 1520	Altobello Melone, *Christ Carrying the Cross*, National Gallery London NG6546 (see fig. 1)	J. Kirby, 1994* HPLC
Swiss, early 16th C	Niklaus Manuel, panel paintings Kunstmuseum, Bern; Kunstmuseum Basel; Kunsthaus, Zurich; and Private collection, Bern	Kühn (1977) micr.
Dutch, 1654–1655	Jan Vermeer, *Christ in the House of Mary and Martha*, National Gallery of Scotland, Edinburgh	Kühn (1968) IR
French, 19th C	Henri Fantin-Latour, *Chrysanthemums* John G. Johnson Collection Philadelphia, cat. no. 990	Mark Tucker, 1984* micr., UV fluorescence
Dutch, 19th C	Hafkenscheid Collection of Pigments Technical University of Delft The Netherlands	Pey (1989) HPLC

*Personal communication
chem.=Microchemical tests
ESA=Emission spectrography
GLC=Gas-liquid chromatography
HPLC=High-performance liquid chromatography
IR=Infrared spectroscopy
micr.=Light microscopy
spec.=Spectrophotometry
TLC=Thin-layer chromatography
UV=Ultraviolet

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5
Gamboge

JOHN WINTER

1.0 **Introduction**

1.1 **Pigment Definition**

Gamboge is a yellow vegetable pigment produced in south and southeast Asia from various trees of the genus *Garcinia*, the most important being *Garcinia hanburyi*. It is a gum resin formed from a latex that exudes from incisions made in the tree bark that is collected and allowed to harden. The resinous portion, soluble in organic solvents such as ethanol, forms the major component and is responsible for the yellow color; the water-soluble gum is composed of colorless carbohydrates. Raw gamboge is usually in the form of hard, brittle lumps of a dull brownish yellow color, which may be pulverized to a bright yellow powder (fig. 1). The *Colour Index* (1971) lists gamboge as CI Natural Yellow 24.

Fig. 1 *Left*, lumps of raw gamboge collected in Japan in 1970; *center*, pulverized gum resin; *right*, gamboge painted on Japanese paper.

1.2 **Current Terminology**

English: gamboge (pronounced either -ōj or -ōōzh)
French: gomme-gutte
German: Gummigutt
Italian: gomma gutta
Spanish: gomaguta or gutagamba
Russian: гуммигут
Chinese: teng huang (pinyin), t'eng huang (Wade-Giles)
Japanese: tō-ō or gambōji; sometimes shiō (see below)

The Chinese *teng huang* has the literal meaning "rattan yellow," a name that occasionally arises in translations and commentary. The Japanese *tō-ō* is that language's reading of the same pair of characters, imported from China. However, the first

character, *tō* designates wisteria, rather than rattan in Japanese, and the translation "wisteria yellow" has occurred, though rarely. There is no connection between gamboge and either wisteria or the rattan family. Other Japanese names that have been used are *dō-ō*, which could be written in two different ways, and *shiō* (Oguchi, 1969; Taguchi & Taguchi, 1977; Uyemura, 1931). The two *dō-ō* compounds are now mainly of historical interest. *Shiō* appears to have been used originally for orpiment, but during the Edo period (seventeenth to nineteenth centuries) it came gradually to be adopted for gamboge, for which it is still sometimes used. It has been suggested by Uyemura (1931) and Oguchi (1969) that *shiō* was used essentially to designate a particular yellow color, and the material most commonly used to achieve this changed over the years.

2.0 History

2.1 Archaic and Historical Names

A number of variants on the English name may be found; they include gambogium (Weber, 1923), gumboge, gumbooge (Harley, 1982), and gumbouch (Dow, 1927). The word gamboge appears to be derived from the same linguistic origin as Cambodia (earlier Camboja) in southeast Asia, an area that has been a major source of the material. Gamboge was called cambodiam in the early records of the British India Office (Yule & Burnell, 1903) and camboge has been used. Other names include cadie gum, *gummi gambogia*, *gummi gutti* (Thorpe, 1922), *gamma gitta* (Harley, 1982), and *gom guttae* (Pey, 1989).

2.2 History of Use

It is not known when gamboge first began to be used as a pigment. The earliest evidence comes from the countries of East Asia and refers to use in the eighth century A.D. However, a difficulty with many of the technical studies (see sections 5 and 6) is that only in a few instances does the evidence show more than the presence of an organic yellow colorant, and the use of gamboge—rather than of some other yellow organic material—is a conclusion of probability rather than from experimental results. Investigation has implied that gamboge was used on certain Japanese painted objects in the Shōsōin repository established in Nara during the eighth century (Yamasaki, 1968), as well as on an eighth-century illustrated scroll of the Ingakyō, a Buddhist sutra (Yamasaki, 1954). Oguchi and Hayashi (1981) noted an organic yellow, which they thought was most probably gamboge, on a Tang dynasty (seventh to ninth centuries) painting from Turfan in Xinjiang province, China. There is evidence that the pigment continued to be used until modern times, particularly on scroll paintings, in Japan and China.

The importation of gamboge into Europe in the seventeenth century has been well established and it may have occurred, at least occasionally, even earlier. Eastlake (1847) suggested that a reference in the fifteenth-century Strasburg Manuscript may be to gamboge (Borradaile & Borradaile, 1966); while this may be a possible interpretation, the evidence seems inconclusive. Laurie (1914) thought gamboge may have been used in the green area of a fifteenth- to sixteenth-century European illuminated manuscript. Harley (1982) indicated it was regarded as a novelty item when the East India Company imported a quantity into England in 1615, and Turquet de Mayerne recommended its use for a yellow varnish in his seventeenth-century manuscript (Faidutti & Versini, n.d.). By the eighteenth century, it was imported to the American colonies, as a 1738 Boston newspaper referred to "gumbouch" being offered for sale (Dow, 1927).

Curiously, there is little historical evidence relating to gamboge as a pigment in its areas of origin—south and southeast Asia. Agrawal (1984) mentioned its presence on Indian miniatures, Burkill (1935) and Howes (1949) noted its use for the yellow ink found in writings on black (*khoi*) paper in Thailand, and a handbook to the flora of Sri Lanka (Dassanayake, 1980) refers to its use for painting there. None of these authorities gave dates, however, or an indication of whether this information only refers to observed contemporary practice. It seems likely that if gamboge had been exported to China and Japan as a pigment as early as the eighth century, the people from the countries of origin would have been familiar with that particular application. Knowledge about gamboge in China, however, does not necessarily imply its use as a pigment (see section 3.6).

2.3 Dates of Use

In China and Japan gamboge was probably in use in the eighth century and is still available.

In Europe it was rare or unknown before the seventeenth century. Although it is still available and appears in the catalogues of some artists' suppliers for use as a watercolor, it is infrequently used.

3.0 General Pigment Properties

3.1 Applications

Gamboge is best known as a watercolor pigment, and in the countries of Asia where it originated it appears to be used mostly in aqueous medium (fig. 2). After its arrival in Europe it found other applications.

The gamboge chromophore resides in the resin component, which is insoluble in water but can form a finely divided dispersion. This dispersive ability is undoubtedly helped by the presence of approximately 20% carbohydrate gum. While it is possible that aqueous media such as gums or animal glue have been added to gamboge preparations, apparently this is not necessary to form a watercolor paint dispersion. March (1935) recorded of Chinese practice that "if any glue is added it is very little." Uniform gamboge particles of colloidal size, prepared by fractional centrifugation, were used by Perrin (1910) for a study of Brownian motion and to derive a value for Avogadro's number.

After its introduction into Europe, gamboge was used as a transparent oil color by Flemish painters (Church, 1890; Weber, 1923). Doerner (1949) denounced this application because "as an oil color it strikes through and so is absolutely unusable," whereas Church (1890) and Weber (1923) referred to the necessity of adding small amounts of resin (such as copal) or wax to enhance its permanence and durability. *Field's Chromatography* (Taylor, 1885) stated that gamboge alone was employed in oil only with difficulty, but that it was more easily usable as a mixture with lemon yellow or, better, with alumina, in the latter form being known as "Extract of Gamboge." Weber noted that it is very difficult to restore paintings containing gamboge as the pigment is soluble in most organic solvents.

Many sources refer to gamboge being used to make a transparent yellow varnish for decorative applications such as coloring of metals, wood, or leather. This reference originates from the Turquet de Mayerne manuscript (see section 2.2), which cited the use of such a varnish to color silver or tin, and for the decorated leathers then made in Amsterdam. In the nineteenth century it appears to have been a common constituent of varnishes for metals, including those for "philosophical instruments" (that is, scientific instruments) (Brannt, 1893), and a twentieth-century account (Mell, 1922) described its use in improving the appearance of brass, as well as for coloring leather, wood, fabrics, and other items. A compendium of traditional recipes revised in 1956 by Hiscox and Sloane continued to mention gamboge as a varnish colorant, although widespread use as late as this seems unlikely.

Other accounts (Howes, 1949; Dassanayake, 1980) refer to gamboge used for dyeing textiles, although this has not been confirmed by technical evidence. This application would, of course, imply dyeing from a dispersion rather than from a solution.

Hooker's green is the name given to a mixture of gamboge and Prussian blue (or indigo [Weber, 1923]) intended for watercolor (Gettens & Stout, 1966; Mayer, 1970). However, the relative impermanence of the gamboge component led to a decline in its popularity. Although the history of Hooker's green will not be considered further here, clearly its chemical and physical properties reflect those of its two constituents.

According to Wehlte (1975) "the only [present day] admissible application" for gamboge is in leaf gilding on paper or parchment by precoating the support, then breathing on it to render it tacky enough to receive gold leaf.

3.2 Color and Spectral Reflectance

Gamboge is a transparent yellow. Its use in tinting varnishes has been noted, and, where it has been made up in an oil medium, it has the properties of a glaze (see section 3.1). East Asian paintings often show an organic yellow, presumed to be gamboge, over another pigment, usually white.

It follows that the perceived color depends considerably on how heavily the gamboge is painted and on what is underneath. An experimental paint out by the author on a thick ground of precipitated chalk in gelatin to a Munsell value of 8.5 gave a hue from 3.4 to 3.8Y and a chroma of 10.0 to 10.5 when measured with a Minolta chromameter CR100 using D-65 illuminant. On white paper it appears at times by visual comparison to be rather toward the orange end of yellow, even as far as Munsell 10YR and still exhibits a fairly high chroma of 10 or above.

Figure 3 shows spectral reflectance curves in the visible region for gamboge mixed with titanium dioxide and as a glaze over barium sulfate.

3.3 Permanence

The lightfastness of gamboge is not high; indeed, this has led most contemporary references, for example Mayer (1970) and Wehlte (1975), to re-

Fig. 2 Utagawa Kuniyuki, *An* Oiran *Standing by a Plum Tree*, Japan, Edo period, mid-nineteenth century, Ukiyo-e School; painting, color and gold on silk. Yellow areas in the woman's clothing are gamboge over shell white. Freer Gallery of Art, Smithsonian Institution, Washington 98.420.

gard it as obsolete for modern watercolor use. Feller and Johnston-Feller (1981) and Feller et al. (1984) found an ISO R105 blue-wool lightfastness grade of two to three with "some" protection being afforded by ultraviolet filtration. It follows that Hooker's green (see section 3.1) may change to blue after prolonged exposure because the Prussian blue present is more lightfast. Other mixtures may show changes based on the same principle. Bailie et al. (1988) found that the rate of fading of gamboge on titanium dioxide (rutile) was fairly insensitive to variations in relative humidity, no change being found with poly(vinyl acetate) as the medium, and relatively small changes with either hydroxypropylcellulose or carboxymethylcellulose as the medium. Authorities such as Weber (1923) and the *Colour Index* (1971) have claimed that to some extent the color of faded gamboge returns in the dark. Whitmore et al. (1987) showed that ozone, an atmospheric pollutant in certain areas, will induce fading in the dark.

Since the colorant of gamboge is an organic resin, migration of this color over time is also possible and apparently has been observed. It is for this reason that Doerner (1949) and Wehlte (1975) considered it unsuitable as an oil color. Staining may sometimes be seen behind yellow areas on the reverse of East Asian scroll paintings; this may be from gamboge, but there is little definite evidence to support this suggestion.

3.4 **Chemical Properties**

The yellow resin of gamboge is more or less soluble in many organic solvents including most of those commonly used by conservators for cleaning. Several closely related compounds may constitute the resin (see section 4.3), but all have the same chromophore, which contains a phenolic grouping. The presence of this group leads to a marked color change to orange when an alkali hydroxide is added (see section 5.1); an intense greenish blue color is produced with ferric chloride solution. The reader is reminded that since phenols are common in the world of natural organic colorants, similar reactions may be observed with unrelated compounds. Gambogic acid, the major resin constituent found by many authors (see section 4.3), contains a carboxylic acid group, leading to its being soluble in alkali carbonates. This grouping is not, however, conjugated with the visible chromophore and thus has little effect on the color changes noted above.

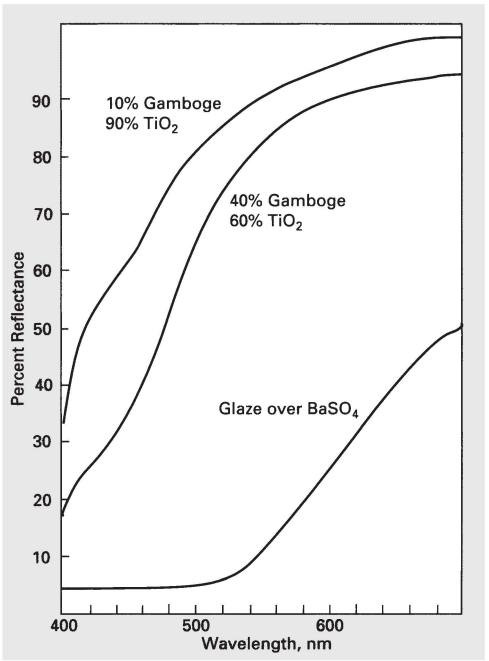

Fig. 3 Spectral reflectance for gamboge in the visible region. From Robert L. Feller and Catherine Bailie, Carnegie Mellon Research Institute, Pittsburgh.

According to Church (1890) and Weber (1923) gamboge is darkened by ammoniacal fumes and bleached by strong heat but is unaffected by sulfur compounds.

3.5 **Compatibility**

The chemical properties given above suggest that gamboge may change color if it is mixed with a substance containing lime or other alkali. It may be partly for this reason that no record has been found of its use in fresco painting. Church (1890) and Weber (1923) suggested it is incompatible with lead white; if this is true, it is presumably connected with a reaction of the resinous components of gamboge with lead carbonate. Other carbonate pigments therefore would also be suspect. However, gamboge is present in a yellow glaze over a calcium carbonate white on certain Japanese paintings and the gamboge appeared to be unaffected (Winter, 1987). On the whole gamboge seems to tolerate being mixed with other pigments.

3.6 **Toxicity**

Schafer (1963) cited evidence for the use of gamboge in Chinese alchemy. Generally, however, the

Chinese seem to have regarded it, perhaps supererogatorily, as a dangerous poison, and limited its medicinal use to external application (Stuart, 1911). Various accounts warn against licking brushes containing gamboge. The scholar and writer Van Gulik (1957) described gamboge being used in an attempted murder in a detective story set in Tang dynasty China. Wehlte (1975) noted that it is poisonous and has a toxicity rating of two. Modern literature (Merck & Co., 1983) records it as a drastic purgative for veterinary application.

4.0 **Composition**

4.1 **Chemical Composition**

Gamboge usually contains about 70% to 80% yellow resin, and 15% to 25% water-soluble gum (Burkill, 1935; Howes, 1949). There have been reports of esters and hydrocarbons (Amorosa et al., 1969) and of wax, vegetable detritus, and an ash residue (Dieterich, 1901). Precise analyses will vary with the source and quality of the product.

There have been several investigations of the resin's chemical constitution. A number of closely related compounds based on an unusual hydroxanthone skeleton (fig. 4) are involved, and those found can depend somewhat on the particular plant species (Venkataraman, 1973). Most investigations of commercial gamboge have found gambogic acid (fig. 4A) as the major constituent. Gambogic acid was first isolated by Furrer (1934) as the monoacetyl derivative; other subsequent studies on the structure were by Land and Katz (1949), Amorosa and Lipparini (1955), Auterhoff et al. (1962), and Dyson and Rigby (1963). Resin extracted from *G. morella* grown in India yielded morellic (fig. 4C) and isomorellic (fig. 4D) acids, rather than gambogic acid. Morellin (fig. 4E) was found in the seed pericarp of the same species and was the subject of extensive studies by researchers in India (Venkataraman, 1973). The structure of morellin (fig. 4E) was determined from an x-ray diffraction analysis of the crystalline *p*-bromobenzenesulfonyl ester (Kartha et al., 1963). The molecular formula of gambogic acid (Dyson & Rigby, 1963), along with its spectral and other properties, strongly suggests that it and morellin are closely related. Yates et al. (1963) suggested a structure for acetylgambogic acid based on figure 4A; Ollis et al. (1965) confirmed this structure for gambogic acid itself.

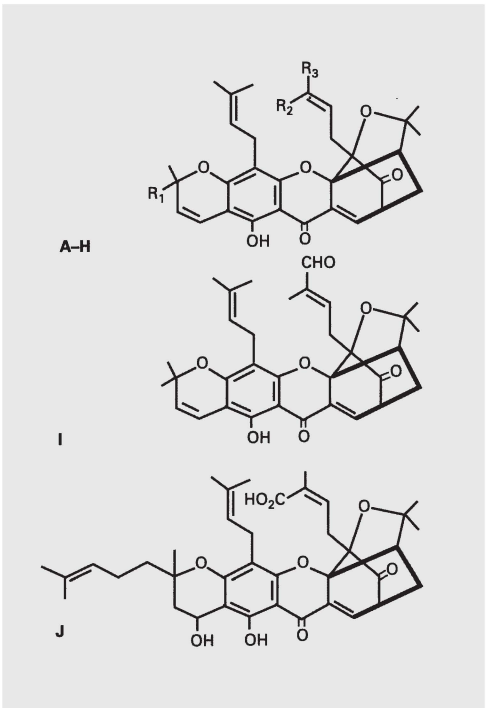

Fig. 4 Chemical structures of resin components of *Garcinia* species.

A. Gambogic acid: $R_1=(CH_2)_2C=CH(CH_2)_2$, $R_2=CO_2H$, $R_3=CH_3$.

B. Isogambogic acid: $R_1=(CH_2)_2C=CH(CH_2)_2$, $R_2=CH_3$, $R_3=CO_2H$.

C. Morellic acid: $R_1=R_3=CH_3$, $R_2=CO_2H$.

D. Isomorellic acid: $R_1=R_2=CH_3$, $R_3=CO_2H$.

E. Morellin: $R_1=R_3=CH_3$, $R_2=CHO$.

F. Morellinol: $R_1=R_3=CH_3$, $R_2=CH_2OH$.

G. Isomorellinol: $R_1=R_2=CH_3$, $R_3=CH_2OH$.

H. Desoxymorellinol: $R_1=R_2=R_3=CH_3$.

I. Dihydroisomorellin.

J. Neogambogic acid.

Several other related compounds have been found in extracts from various *Garcinia* species; figure 4 summarizes those known to date. Isogambogic acid and isomorellinol have been isolated from *Garcinia hanburyi* (Lin et al., 1993) as has neogambogic acid (fig. 4J; Lu et al., 1984). All of these compounds are of the same structural type, and most (fig. 4A–H) have the same conjugated π-electron system and therefore the same absorption in the visible region, that is, the same

color. Dihydroisomorellin from *G. morella* (fig. 4I; Venkataraman, 1973) and neogambogic acid from *G. hanburyi* (fig. 4J) have this chromophore slightly modified, but such variants probably have little overall importance. Compounds of the structural type represented in figure 4 can be regarded as diagnostic for gamboge.

The literature on *Garcinia* products has in the past caused confusion by the application of various names to the same compound. Gambogic acid, for example, is synonymous with β-guttiferin (Gupta et al., 1962) and it has also been known as β-guttic acid and later as α-guttic acid. Other names are α-, β-, and γ-garcinolic acids, which are likely to refer to impure preparations (Ahmad et al., 1966). The nomenclature used here is that adopted by researchers who produced definitive structures for the compounds concerned.

There has been less investigation of the gum component of gamboge. It is clearly carbohydrate based; acid hydrolysates have yielded arabinose, galactose, rhamnose, and glucuronic acid (Pinkas & Bézanger-Beauquesne, 1963; Auterhoff & Liesenklas, 1965; Amorosa & Guarnieri, 1968).

Amorosa et al. (1969) found straight-chain alkanes of sixteen to thirty-one carbon atoms among minor components and identified the presence of α-amyrin and lupeol (colorless triterpene resin alcohols).

4.2 Sources

Gamboge is a gum resin produced by a number of *Garcinia* species in the family Guttiferae (Clusiaceae). *Garcinia hanburyi* Hook.f. yields "Siam gamboge," which appears to have formed most of the commercial product during the last hundred years or so (Church, 1890; Mell, 1922; Uphof, 1968). *G. morella* Desrouss. is usually given as the source of gamboge in India (Venkataraman, 1973). "Ceylon gamboge" is likely to have come from Sri Lanka (Dassanayake, 1980). Various other *Garcinia* species can produce very similar yellow gum resins. Among those cited are *G. cambogia* Desrouss. and *G. elliptica* Wall., from India, and *G. heterandra* Wall. from Myanmar (Burma).

Most of the exported product seems to have been Siam gamboge from southeast Asia, especially Cambodia and Thailand; Ceylon gamboge appears to have been less important in trade. Mell (1922) referred to a minor production in the Philippines.

The trees producing gamboge can grow to a height of perhaps sixty feet. In the rainy season these trees are tapped by making spiral incisions in the bark approximately ten feet above the ground and the exuded latex is collected, traditionally in sections of bamboo; when it hardens there it forms cylindrical, often hollow, lumps of gum resin (*Kew Bulletin*, 1895). Other parts of the plants yield resin constituents of this general type (Venkataraman, 1973); collection is by methods such as boiling branches or other tree parts with water and collecting the product that rises to the surface (De Puyster, 1920).

4.3 Preparation

It is not clear how often gamboge used as a watercolor paint was mixed with any of the usual media, but it appears such compounding was not necessary and may have been minimal. Harley (1982) quoted an early eighteenth-century author who described how to add water to a hole made in the lump of gamboge and stir it until the required depth of color was reached. As noted in section 3.1, the presence of a gum component enables an aqueous dispersion of the resin to be easily obtained.

When gamboge was used as an oil color, it was evidently necessary to add either resin or wax to it to ensure its durability and to prevent "striking through" (see section 3.1). When used for tinting varnish, it was added to the other varnish resins in the required proportion.

4.4 Adulteration and Sophistication

Early twentieth-century accounts reveal that, at least at that time, gamboge was often adulterated. Starch and/or colophony, and sometimes sand, were often present (Taylor, 1910); in one case, lead chromate had been added to correct the color after starch adulteration. Dieterich (1901) also found starch, colophony, and sand, along with rice meal and dextrin; dirt and vegetable impurities were also sometimes present, but they may not have been deliberate adulteration.

5.0 Identification and Characterization

5.1 Optical and Chemical Microscopy

Dispersions of gamboge in water are finely divided, and the usual major constituent, gambogic acid, is noncrystalline; as a result, samples of gamboge from a watercolor application are difficult to characterize by optical microscopy. Usually, the pigment is seen as an amorphous yellow resin or as a yellow stain on, for example, paper

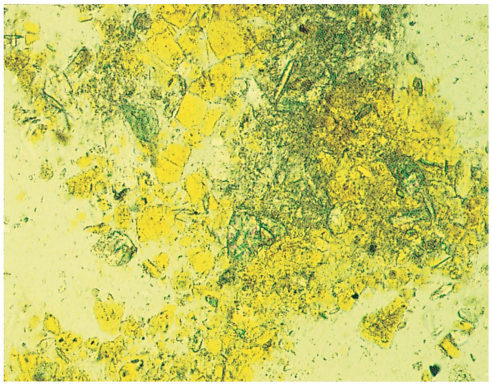

Fig. 5 Photomicrograph of gamboge in partially crossed polars, seen as a yellow stain on crystalline particles of shell white (calcium carbonate). Mounted in Canada balsam, n=1.53. From a seventeenth-century Japanese screen by an unknown Ukiyo-e School artist. Freer Gallery of Art, Smithsonian Institution, Washington 03.208. 130x.

fibers from the support, or on another pigment (fig. 5). Addition of aqueous sodium or potassium hydroxide changes the gamboge color from yellow to orange. The change in absorption spectrum after caustic alkali is added is described in section 5.3.3. Townsend (1993) has used fluorescence microscopy, describing a yellow-gold fluorescence best seen with blue excitation.

5.2 **Chemical Identification**

Chromatographic methods are among the most practical for identifying gamboge, although there is little available published information. Winter (1987) conducted thin-layer chromatography on the gamboge sample shown in figure 1 on silica gel plates with development using a solution of cyclohexane:ethyl acetate:acetic acid in a 50:50:1 ratio. Gambogic acid has an Rf-value of approximately 0.64 under these conditions and appears to be readily distinguishable from many other yellow natural products. Visualization may be done in several ways. The strong ultraviolet absorption of the gamboge-resin chromophore enables the resin components to be located either by the use of fluorescent plates, which contain a phosphor that fluoresces strongly under shortwave (254 nm wavelength) ultraviolet, or by spraying the plates with a fluorescent dye such as rhodamine B; with either method, dark spots can be seen against a fluorescent background under ultraviolet radiation. Spraying the plates with a solution of 5%

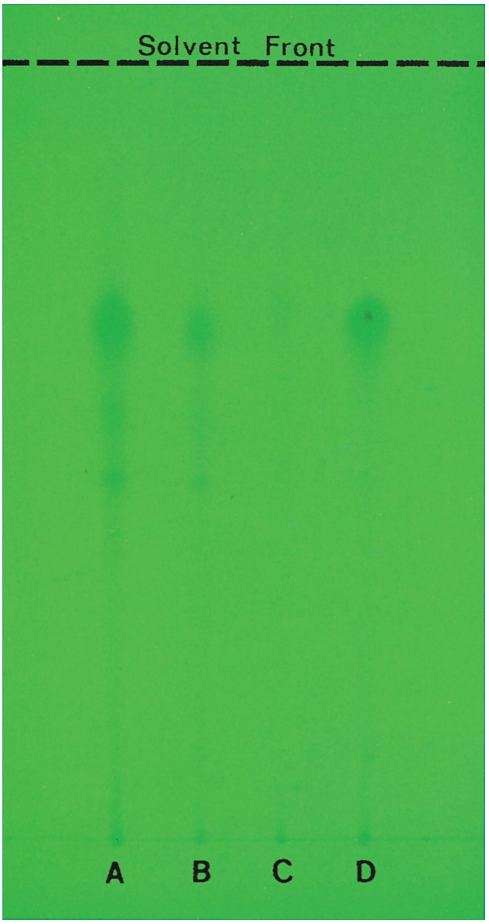

Fig. 6 Thin-layer chromatography of gamboge; 10 x 5 cm fluorescent plate seen under 254 nm ultraviolet illumination. Sample shown in fig. 1.

A. Gamboge, 10 µg.
B. Gamboge, 3 µg.
C. Gamboge, 1 µg.
D. Gambogic acid.

ferric chloride causes the phenolic components to appear as blackish spots. A standard method used for resins (Stahl & Jork, 1969) is to spray the plate with antimony trichloride in chloroform, followed by heating the plate at 100°C for ten minutes, the phenols will become blackish and, in our gamboge sample, a number of other spots became ultraviolet fluorescent. Winter (1987) experimented with a method based on spraying the plate with a 2% N-bromoacetamide solution in acetic acid, followed by heating at 100°C. Gambogic acid and its congeners developed characteristic fluorescence in long-wave ultraviolet without interference with the shortwave ultraviolet "quenching" effect on fluorescent plates (fig. 6).

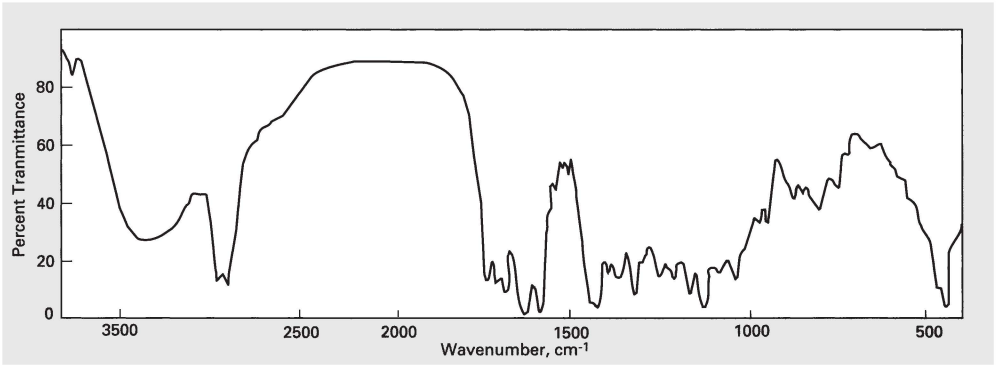

Fig. 7 Infrared absorption spectrum of gamboge sample (fig. 1) (film cast out from acetone). From Walter R. Hopwood, Conservation Analytical Laboratory, Smithsonian Institution, Washington.

Pey (1989) used high-performance liquid chromatography to identify gamboge in a nineteenth-century pigment collection.

5.3 Instrumental Methods of Analysis

5.3.1 ***X-ray diffraction.*** Gamboge is a noncrystalline resin and its most common major component, gambogic acid, has apparently never been crystallized. Various derivatives are, of course, crystalline, and the structure of morellin (see fig. 4E) was determined by x-ray diffraction studies (Kartha et al., 1963), but to date x-ray diffraction has not been found useful for identification.

5.3.2 ***Infrared spectroscopy.*** This technique contributed to studies on the structure of gamboge constituents (section 4.3). An infrared spectrum for total gamboge has been published in a standard compendium (Sadtler, 1964), and a spectrum of our sample is shown in figure 7.

5.3.3 ***Ultraviolet and visible spectroscopy.*** Ultraviolet absorption peaks from the literature for gambogic acid are given in table 1. Our gamboge sample gave the ultraviolet-visible spectrum shown in figure 8. Also shown is the spectrum after the addition of a few drops of ethanolic potassium hydroxide. This procedure has the effect of ionizing the phenolic group, as well as the carboxylic acid group, thereby placing a negative charge in the conjugated electronic chromophore, with shifts in the spectrum as shown. The relatively high extinction coefficients mean that an ultraviolet-visible spectrum can be obtained on a very dilute solution of approximately 0.001%, making the method fairly sensitive and discriminating against other materials present in a mixture.

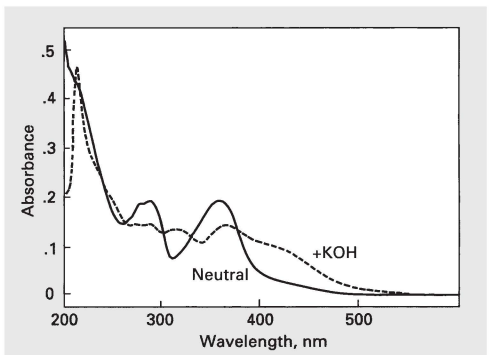

Fig. 8 Ultraviolet–visible absorption spectra of gamboge sample (fig. 1), 0.0012% in ethanol, before and after adding several drops of 20% ethanolic potassium hydroxide solution.

Table 1 **Ultraviolet Absorption Maxima for Gambogic Acid**[a]

Wavelength	*Extinction Coefficient*
217 nm	26,000
280 nm	16,700
291 nm	17,800
362 nm	14,900

a. From Ollis et al. (1965).

5.3.4 ***Nuclear magnetic resonance spectroscopy.*** Ollis et al. (1965) published details and interpretation of the nuclear magnetic resonance spectra of gambogic acid and some of its derivatives. Lin et al. (1993) extended these interpretations and used magnetic resonance

methods to identify isogambogic acid (see fig. 4B) and isomorellinol (see fig. 4G).

5.4 **Criteria for Identification**

Few "identifications" of gamboge in historical paintings (or similar examples of use) are adequately supported by the technical evidence. In these circumstances, criteria for identification are more a matter of presenting proposals than an established methodology.

Thin-layer chromatography offers potentially two kinds of evidence for identifications: the correspondence of rates of migration on the plate (Rf-values) with those for a known material, and the production of characteristic colors or fluorescent reactions by the spots once separation has been achieved. Rf-values of the usual gamboge constituents seem to be fairly characteristic and distinguishable from those of most alternative colorants. However, the possible presence of different hydroxanthones exemplified by figure 4A–J (see section 4.3), coupled with known differences between gamboge samples of different botanical origins, should compel an attitude of caution. The identification is enhanced somewhat by the use of fluorescent plates, which show that the spots concerned absorb shortwave (254 nm) ultraviolet radiation fairly strongly. Spray reagents are currently not as specific as one might wish; some possibilities are discussed in section 5.2, and the question of identification by thin-layer chromatography is discussed further in Winter (1987). Overall, thin-layer chromatography should render an identification as very probable and has fairly good sensitivity.

The spectroscopic properties of gamboge are characteristic; however, unless a separation method is also used, many of these methods suffer acutely from interferences. This is true of infrared spectroscopy, particularly where other resins or drying oils and waxes may be present, as is the case for gamboge in oil painting or varnish (see section 3.1). A separation method such as high-performance liquid chromatography combined with mass spectrometry would be very powerful, but does not yet appear to have been published for this application.

Ultraviolet–visible absorption spectroscopy (see section 5.3.3), a method not widely used in the analysis of works of art may be useful as it combines specificity—in the sense that many other substances likely to be present have much weaker ultraviolet absorption—with a characteristic spectrum. Spectra can easily be obtained on the neutral molecules and also on the phenolate anions by adding caustic alkali to the cuvette, giving stronger evidence.

Taguchi and Taguchi (1977) used reflectance spectroscopy to give evidence of gamboge on a Japanese painting. Spectra in the visible region only might be considered insufficient as many yellow colorants tend to look fairly similar; however, the extension of the spectrum sufficiently far into the ultraviolet range to include the 360 nm peak gave more confidence in this identification.

A further problem with reflectance spectroscopy on gamboge in works of art lies in its transparency. This transparency can be a drawback with reflectance infrared spectroscopy since the spectrum obtained is likely to be a combination of spectra for the medium, underlying pigments, and perhaps support material, as well as for the gamboge.

Most attributions of yellow colorants as gamboge in the literature seem to be supported, if at all, only by simple chemical tests such as the change in color to orange upon addition of caustic alkali, a procedure typically used in chemical microscopy. While such tests may be useful, they lack adequate specificity.

6.0 **Occurrences**

The difficulty with listing historical occurrences of gamboge lies mainly in their incomplete substantiation in many cases. Indeed, some accounts claim only an "organic yellow" along with the suggestion that it might be gamboge. Other sources simply do not state their basis for identification. For these reasons, the following should be regarded as tentative, except where technical evidence is noted.

Yamasaki and co-workers (see Yamasaki & Emoto, 1979) have found an organic yellow, apparently gamboge, in some early Japanese art. In addition to the paintings and decorated objects cited in section 2.2, it was noted on an early twelfth-century hand scroll depicting the *Tale of Genji* (Yamasaki, 1954; Yamasaki & Nakayama, 1954). As noted earlier, a possible occurrence of gamboge has been recorded on a Chinese Tang dynasty (seventh to ninth centuries) painting (Oguchi & Hayashi, 1981). A seventeenth-century hand scroll of the *Tale of Genji* contained a yellow with a reflectance spectrum from 350 to 700 nm, corresponding to that of gamboge (Taguchi & Taguchi, 1977). Since this includes the first gam-

boge absorption maximum (c. 362 nm), the identification appears to be firmer than most others. FitzHugh (1979, and personal communication), in an extensive pigment census of seventeenth- to nineteenth-century Japanese paintings of the Ukiyo-e School, in the Freer Gallery of Art, Washington, found thirty-four examples of an organic yellow that had turned orange with caustic alkali (see section 5.1). In three of these examples, plus one more not on FitzHugh's list, thin-layer chromatography confirmed the presence of gamboge (Winter, 1987). One example, a late eighteenth- or early nineteenth-century hanging scroll by Shunman, was actually gamboge mixed with indigo to form a green color that might be regarded as a Japanese version of Hooker's green (see section 3.1).

In Europe, Kühn (1977) noted a gamboge occurrence in a 1641 Rembrandt van Rijn painting in the Staatliche Kunstsammlungen, Dresden; however, no identification method was given. Hanson (1954) used chromatography to identify gamboge in a paint box owned by John Mallord William Turner (1775–1851) and Townsend (1993), using fluorescence microscopy and infrared spectroscopy, found it in Turner's studio pigments and in a watercolor palette, as well as reporting its use in oil and watercolor paintings. Richter and Härlin (1974) noted the presence of gamboge, confirmed by thin-layer chromatography, in a nineteenth-century collection of painting materials from Germany. Pey (1989) identified it by high-performance liquid chromatography in a Dutch nineteenth-century pigment collection.

A historically interesting case is the tentative identification of gamboge in an Armenian gospel dated to c. 1300 (Orna & Mathews, 1981). If confirmed, this would, of course, indicate the availability of the pigment in Asia Minor at that period.

Acknowledgments

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6
Vandyke Brown
Cassel Earth, Cologne Earth

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1.0 **Introduction**

The primary purpose of this chapter is to discuss the properties of the humic-earth material called Vandyke brown that historically seems to have come initially from the Cologne region and, later, primarily from the Kassel region of Germany. These environs are not, however, the exclusive sources in the world. Similar pigments from other sources, as well as pigments of different composition with names that have sometimes been considered synonyms of Vandyke brown, are discussed in sections 2.1.1 through 2.1.8.

1.1 **Pigment Definition**

Vandyke brown is comprised chiefly of the humic substances found in soil, peat, and brown coal. It is listed in the *Colour Index* (1956) as CI Natural Brown 8, no. 77727. This translucent pigment of low refractive index is principally organic in composition and has a long history, beginning possibly as early as the late sixteenth century in England and the Netherlands. Under certain circumstances the raw material may have been roasted or "calcined" and designated as "burnt" Vandyke brown (see section 2.1.7).

1.2 **Current Terminology**

English: Vandyke brown, Cologne earth, Cassel earth
French: terre de Cologne, terre de Cassel
Italian: terra di Colonia, terra di Cassel
German: Van Dyck Braun, Kasslerbraun
Spanish: carmelita Van Dyck, moreno de Van Dyck, tierra de Cassel, marrón de Cassel

In early literature the pigment appears under the names of its principal sources in Germany, Kassel (alternatively spelled Cassel) earth and Cologne earth. Today, however, it is generally referred to as Vandyke brown. Although the name refers to the seventeenth-century Flemish painter, Anthony van Dyck, it is customarily anglicized and spelled as one word, Vandyke.

The three names, Vandyke brown, Cassel earth, and Cologne earth can be considered practically synonymous. When reading the older literature considerable care must be given to interpreting exactly what type of pigment is being referred to because a variety of substances were available under these names (see section 2.1). In particular, the French have long regarded Vandyke brown to be of iron oxide or calcined ocher composition. Church (1915) designated this type as Vandyke brown A (see section 2.1.6). To refer unambiguously to the pigment of humic-earth composition it may be useful in the future to establish a compound term such as Vandyke brown-Cassel brown, or perhaps introduce something such as Church's term, Vandyke brown B.

By the end of the eighteenth century, the two names, Cologne earth and Cassel earth, were frequently used. Nonetheless, there is little reliable data to justify an opinion as to whether there were significant differences between pigments from the two different areas of Germany. The material from one locale may possibly have had a higher iron or ocherous content than pigment from another. Without authenticated samples it is presently impossible to determine any differences. Because the earliest literature refers to Cologne (or Cullens, see section 2.1.3) earth, this was probably the initial locale from which pigment of excellent quality came. Unfortunately, the sources in the Cologne region were long ago

replaced by those in the vicinity of Kassel. As a consequence, the authors have been unable to analyze a well-documented sample known to derive from the Cologne region.

2.0 History

2.1 Archaic and Historical Names

As mentioned, the names Vandyke brown (with various capitalizations), Cologne earth, and Cassel (Kassel) earth are generally accepted as the proper synonyms for the brown organic pigment based on humic-earth ingredients (Gettens & Stout, 1966). Unfortunately, considerable confusion existed in the past concerning the actual composition of pigments with these names. It should be realized that some older literature indeed describes the properties of the humic-earth pigment. It soon becomes apparent, however, that some authors—knowingly or unknowingly—were actually describing the properties of an ocherous or iron oxide-based pigment.

Hurst (1896) in England, followed by Holley and Ladd (1908) in the United States, recognized and described three types of Vandyke browns: (1) the natural humic earth, (2) a synthetic organic material made by calcining cork cuttings and the twigs and bark of trees, and (3) mixtures of lamp or vegetable black with red oxide and a small amount of yellow ocher. Three types were also described by Church (1915), different from those of Hurst, Holley, and Ladd:

> The first is made by calcining certain very ferrugenous earths or brown ochres [(2), above]; the second is nothing more than a dark brown variety of colcothar [iron oxide] [(3), above]; and the third is a kind of brown earth containing, along with some iron oxide and hydrate, a good deal of organic substance in the form of humus or bituminous matter [(1), above].

As a consequence of this confusing but nonetheless very definite state of affairs, some writers have declared Vandyke brown to be permanent while many others have stated that it is relatively fugitive. Church insightfully suggested that many of those declaring Vandyke brown to be permanent were commenting on the properties of the iron oxide and ocherous types and those declaring the pigments to be prone to fading were referring to the organic types.

To further complicate matters, the word bituminous has for many years been used to describe the characteristics of the earth pigment of lignite or humic-earth composition. Today, however, bitumen is understood to be a distinctly different substance from the components of humic earth. The black material called asphaltum or native bitumen is primarily used in the manufacture of black varnishes and japan finishes and is associated with natural deposits of oil and tar. Bitumen is soluble in petroleum naphtha (Hurst, 1896) whereas humic earth is not. Because of the difference in properties, it is not likely that the practicing artist would have confused the humic-earth substance with bitumen. The latter was well recognized and at times was even called an entirely different name, Antwerp brown (Williams, 1787; Eastlake, 1847; Fielding, 1852). It is not surprising nonetheless to find early writers describing these natural materials using imprecise terms such as bituminous and ferruginous as, over time, definitions and usages changed. Even today, the detailed chemistry of humic earth and the concise definition of these highly complex substances pose a challenge (White, 1986; Mills & White, 1987).

Other names used were coal brown (Condit, 1883) or *Braun Kohl* (Doerner, 1949).

In the English-speaking world, the name Vandyke brown apparently was not applied to the pigment formerly known as Cologne or Cassel earth until at least one hundred years after its introduction in the painter's palette (see section 2.2). Harley (1982) wrote that the name first appeared in late-eighteenth-century books such as Ibbetson's 1794 *Process of Tinted Drawing*. Payne (1798) was also an early author to write that Cassel earth was named Vandyke brown because of the high esteem Anthony van Dyck (1599–1641) held for the pigment.

The following survey of the many names given the brown humic-earth colorant over the past three hundred years reveals that care must be taken when assuming that a pigment named Vandyke brown, or Cassel or Cologne earth in an early reference is actually the humic-earth substance rather than an ocherous- or iron oxide-based material. It is prudent to remember the basic confusion that has long surrounded pigment names; that is, there has often been little firm connection between the name of a color—that which the eye perceives—and that of the particular chemical substance used to produce it.

2.1.1 ***Kassel umber.*** In eighteenth-century Germany *Kollnische Erde* was considered to be a form of umber (*Der Staffirmaler*, 1779; *Praktisches Handbuch*, 1795). However, by the mid-nineteenth century, most sources recognized that

the artists' pigment *Cassler Umbra* came from a brown coal source and was synonymous with Cologne earth (Blumenbach, 1846; Seubert & Seubert, 1866; Geith, 1886). Nevertheless, the pigment is frequently found listed under umber or *terra umbracea*, a practice that continued into the twentieth century (Hanausek, 1901; *Merck's Warenlexikon*, 1919).

In his study of early American house paints, Candee (1966–1967) noted that "somewhere between the eighteenth and nineteenth century, it was called umber, while the natural pigment today known as umber was often called brown ocher." Tingry (1816) referred to Cologne earth as umber earth with a comment that it was sometimes called brown ocher. Thus, brown ocher and umber were names used at various times in history to refer to two entirely different materials, the brown humic earth and an essentially ocherous or iron oxide type of pigment (see section 2.1.6).

2.1.2 ***Rubens' brown.*** This name is a synonym encountered in the older literature (Hurst, 1896; Wehlte, 1982). The *Handbook of Young Artists and Amateurs in Oil Painting* (1879) states that Cassel earth is probably "the earth used by Vandyke . . . Vandyke Brown, Rubens' Brown (used by the Belgians, as Americans and the English use Vandyke), Cassel earth, Cologne earth, are of a similar generic character and differ but in shade or in greater or less warmth of tone." Fielding (1852) considered Rubens' brown to be "an excellent colour in working, rather more opaque than Vandyke Brown and of a yellower tint, and is equally permanent." Field (1877) wrote that Cassel earth "does not differ essentially from Rubens' and Vandyke browns." He further commented:

> The pigment still in use in the Netherlands under this appellation is an earth of a lighter colour and more ochrous texture than the Vandyke brown of the London shops; it is also of a warmer or more tawny hue than the latter pigment [Cologne earth], and is a beautiful and durable brown, which works well both in water and oil, and much resembles the brown used by Teniers.

Because Van Dyck studied with Rubens and continued to be closely associated with him, it is not unexpected that brown pigments would be used similarly in the work of both artists. Doerner (1949) wrote that Cassel brown, Cologne earth, or Vandyke brown, is "found on the pictures of the old masters, among them Rubens, who used it mixed with gold ocher as a warm transparent brown which held up well, particularly in resin varnish." However Doerner gave no chemical test data to prove his statement. Von Sonnenberg (1979) reported that Rubens used *Kasslerbraun*.

2.1.3 ***Corruptions of names for Cologne and Cassel earth.*** References to Cullens earth, Colens earth (Salmon, 1675), or in Italian *terra di colonia*, were based on modifications or corruptions of the word Cologne and began to appear in the literature at the beginning of the seventeenth century (Harley, 1982). Müntz (1760) recommended Collens earth as "a very good colour and of singular use" for painting in encaustic. Dossie (1764) cited *Cologn* or Collen's earth for use as a watercolor. Later, *Mackenzie's Five Thousand Receipts* (1829) recommended Cullens earth for crayon painting and listed Cologne earth for miniature paintings on ivory and for oil and watercolors.

Fielding (1852) listed Castile earth. Field (1870) listed Castle earth and his remarks were copied verbatim in *The Painter, Gilder, and Varnisher's Companion* (1881). Weber (1923) listed *bruno* and *pardo Vandyke* as synonyms.

2.1.4 ***Campania and Nocera earths, Cappagh brown.*** Although Field (1870) wrote that the Campania brown of the Italian painters was a similar pigment, the authors believe this pigment was closer to umber. Lomazzo (1598) recommended earth of Campania for the shadows in carnations (a pinkish color).

In comparing the earth mined near Cologne to that from Nocera in the Umbria district of Italy, Tingry (1816) wrote:

> The earth of Nocera is light, subtle, argillaceous, and flammable; it emits a fetid odour of coals when exposed to a strong heat. [And also that] the bishopric of Cologne produces a kind of umber earth which is heavier, as well as browner, and which has a stronger and more disagreeable smell than that of Nocera. It is also more bituminous and contains more iron; in a word, it is inferior to it [the Nocera product] in quality.

The described flammability and odor seem to relate to humic earth. Leuchs (1829) also mentioned Nocera "in the vicinity of Spoleto," but it is evident that the pigment he described is essentially umberlike.

Field (1835, 1877) wrote that Cappagh brown, found on the estate of Lord Audley near Cork, was "a bog-earth or peat, mixed or mineralized by manganese in various proportions." It was said by Field that there was a peaty and also a more mineral variety. An analysis by Church (1915) of Cappagh brown reported 34.4% ferric oxide and

27.2% manganese dioxide; it was certainly not a peatlike material.

The precise character of these three pigments remains uncertain. Some varieties may not have been much like the essentially humic-earth material under discussion.

2.1.5 ***Spanish brown.*** Spanish brown was occasionally referred to as a humic earth, adding considerable confusion to the nomenclature.

Candee (1966–1967) wrote that Spanish brown "has been one of the most elusive pigments with which the architectural historian has had to deal." He assumed that it was always considered an iron oxide pigment whether it was of natural origin or of synthetic manufacture, imported from Europe or obtained from American sources. For example, Candee cited an English patent of 1796 to John Atkinson in which Spanish brown, along with Venetian red and "colcothar of vitriol," was made from crocus martis, saffron of Mars, or iron oxide. This conforms to the terminology used in France (see section 2.1.6). Dossie (1764) wrote that "Spanish brown or brown-red is a native earth" and that "they [painters] may depend on its standing equally with any other pigment whatever, being native ochrous earth, of which kind none are ever known to fail." Davidson (1900) described Spanish brown or majolica as an "individual pigment belonging to the class of red ochres."

Consideration of the early literature suggests another possibility. Le Pileur d'Apligny (1779) is one of the earliest sources to indicate that Spanish brown is *terre Cologne*, "que les Peintres en bâtimens donnent une premiere impression pour peindre en couleur de bois . . ." [that building Painters apply as a first impression paint (undercoat) in order to imitate the color of wood]. Tschelnitz (1857), Mierzinski (1881), Geith (1886), and Fischer (1930) also stated that Spanish brown is Cologne earth. In America, Condit (1883) wrote in the *Railroad Gazette* that "Spanish brown is a pulverized and washed brown coal inferior in color and coloring capacity to umber, but of lasting value for roofs." In France, Lemoine and du Manoir (1893) listed *brun d'Espagne* as a synonym for *ombre de Cologne*. Other early sources, however, were less definite. Sanderson (1658) listed Spanish brown and Cullins earth separately. He describes "Colens-earth" and "Spanish brown" as colors to be washed and ground, and, in another passage, describes "Terra-Colen" and "brown of Spaine" as "colors to be grinded." Smith (1738) simply wrote of Spanish brown: "'tis an Earth, it being dug out of the ground."

In Germany, Cremer (1895) assumed Spanish brown was the same pigment as Cologne earth and provided an interesting explanation for the name. In an extensive discussion he suggested that the name Spanish brown might have been given to Cologne earth owing to the extended presence of Spaniards in the Cologne district during the sixteenth and seventeenth centuries.

Just what Spanish brown consisted of remains an intriguing question. Reference to the matter has been briefly presented here because of the possibility that it is one of the names used in the past for the brown humic earth, a circumstance not often considered by writers today.

2.1.6 ***Nomenclature in France.*** In France, a clear distinction seems to have been made between Vandyke brown and Cologne (or Cassel) earth. Pernety (1757) listed *terre de Cologne* in his dictionary but made no reference to Cassel earth or Vandyke brown. By the mid- to late-nineteenth century, however, French texts commonly identified Vandyke brown as an iron oxide pigment and *terre de Cologne* and *terre de Cassel* as of lignite origin, coming from the environs of Cologne. Lemoine and du Manoir (1893) cited *brun d'Eisenach* and *brun d'Espagne* as synonyms for *ombre de Cologne*, which they identified as a lignite-based pigment. Eisenach is a city about thirty-five miles from Kassel.

In contrast, Lemoine and du Manoir, as well as their contemporary, Halphen (1895), described *brun* Van Dyck as being obtained by calcining either iron sulfate or yellow ochers. Other contemporary references (Riffault & Vergnaud, 1851; Fink, 1981) list "Van-Dyck" brown as "provient" [coming or arising from] iron, and as being very stable.

Instructions for preparing one type of Vandyke brown required repeatedly calcining "certain yellow ochres found in the Midi" or calcining iron sulfate. At an exposition in 1900, pigment made from the calcination of natural iron oxides was designated as "bruns Van Dyck O" and pigment made from pyrite was designated as "bruns Van Dyck M" (Guédy, 1901). The descriptions of Vandyke browns given later by Coffignier (1924) agree with the characteristics of an iron oxide pigment. An iron oxide-based pigment was also known in France in the 1880s as Vandyke red (Blockx, 1926). Thus, to the French the name

Vandyke brown appears to have clearly signified an iron oxide- or calcined ocher-based pigment by the late nineteenth and early twentieth centuries. The *Encyclopedie-Roret* (Thomas, 1902) mentions various iron oxide-ocherous "Van Dick" browns: English, foncé, Swedish, violet (Brun Van Dick violet)." The "English" type, "was reinforced with aniline colors."

In 1883 Condit summed up the situation: "The German Vandyke brown is still Cassel brown, as in Vandyke's day; the French is burnt umber, the English uncertain but some bituminous substance." There are references to English sources of a humic-earth brown in the literature. For example, Fielding (1852) wrote that these earths were found in England in the Mendip hills and other regions and "possess nearly all the qualities of Vandyke brown; the small differences that exist is in favour of the latter [Vandyke brown] as a glazing colour and the former [the English earth] for body."

2.1.7 ***Calcined pigment.*** To add further confusion to interpreting some of the remarks made in the early literature, it is found that from the days of initial usage, humic earths were sometimes "calcined." Undoubtedly this meant only brief treatment at moderate temperatures or possibly heating in a closed vessel, that is, in the absence of air. In the presence of air, an organic material would tend to burn away. For example, Coffignier (1924) clearly indicated that *terre de Cassel*, when calcined, will lose 79% to 80% of its weight and become a dull red. This procedure apparently altered the lightfastness of the pigment (Church, 1915; Blockx, 1926, footnote p. 71). In the American publication *Handbook of Young Artists* (1879), a quote from *Vergnaud's Manual of 1834* refers to "Burnt Cologne earth" and "Burnt Cassel earth" as the second class of lightfastness: "sufficiently though not perfectly solid." "Burnt" probably refers to the calcined (or roasted) version as compared to Vandyke brown that Vergnaud considered "of but little solidity," and apparently not roasted; "solidity" refers to the pigment's fastness (Riffault & Vergnaud, 1851 [this reference is apparently a later edition of Vergnaud's manual]).

Several authors have described the change in hue and chroma as well as permanency following the "calcining" process. Church (1915) attempted to state the case with some precision: "When slightly roasted, a part of the brown organic matter in these [humic] earths is charred or carbonized, and the substance becomes darker, duller, and decidedly less alterable by exposure." As mentioned, Church classified materials marketed at the time as either Vandyke brown A, prepared by calcining brown ochers or perhaps a dark brown variety of colcothar (iron oxide), or as Vandyke brown B, the organic brown earth. He continued, "Some of the so-called Cologne earth now sold is merely Vandyke brown B, slightly changed by gentle roasting; it is then rather less alterable. We have met with some specimens of Cassel earth which proved practically permanent in oil, but even these faded quite distinctly when exposed to strong light after having been mixed with flake-white." The pigment's widest use, of course, was not in mixture with white, but rather as a glaze in oil or as a watercolor.

In Winsor and Newton's booklet that contained samples of washes of their watercolor pigments (Taylor, c. 1887), Cologne earth is referred to as "Originally a native bituminous earth; but the modern pigment is obtained by calcining Vandyke brown." The booklet says of Vandyke brown that "the most celebrated variety comes from Cassel." These points have also been stressed by Carlyle (1991) and it may be that in the late nineteenth century many pigments labeled Cologne earth in the English market were indeed the calcined product.

The booklet further indicates that Vandyke brown "varies a great deal in hue and in reputation for permanence. It is probably durable under ordinary conditions, but fades in sunlight." The graduated washes of watercolor prepared by J. S. Taylor and mounted in front of the booklet (see fig. 4) reveal hue and chroma differences between the Vandyke brown (possibly unroasted) and the Cologne earth (possibly roasted); the Cologne earth is blacker in appearance suggesting the presence of carbonized material. Measurement of the color of these materials is discussed in section 3.1.

Thus, throughout much of the history of its use, humic-earth pigment was sold variously as an untreated natural pigment and as a roasted or "calcined" version. When reading the early literature, however, it must be recalled that the French also prepared iron oxide- and ocher-based "Vandyke browns" by calcination (see section 2.1.6).

2.1.8 ***Cassel yellow, Cologne yellow, Cologne black, and alkali-extracted stain.*** The names Cassel yellow, Cologne yellow, and Cologne black need cause little confusion. Cassel yellow is an inorganic pigment, $PbCl_2.7PbO$; the

name would not have been associated very long with the properties of Cassel earth. The term Cologne yellow, used at one time for an inferior chrome yellow containing lime and sulfate of lead (Condit, 1883), also refers to a pigment distinctly different in composition from Cologne earth.

Although Cologne earth or Cassel earth may be considered by certain early sources as appearing more black than brown, the organic humic earth is unlikely to be confused with Cologne black (or Cassel black), a pigment said to have been made by heating fragments or turnings of ivory and similar osseous parts of animals in closed vessels until they are reduced to a char (Davidson, 1900; Thomas, 1925).

A brown stain is prepared by extracting humic earth using an alkali solution, and is still manufactured under such names as *Nuss beize*, *Maserierbraun*, Vandyke crystals, walnut stain (Zerr & Rübencamp, 1908), walnut crystals, or sap brown (Dove, 1941). This material was even occasionally sold as a form of bistre (bister) (Wagner, 1928; Kittel, 1960).

2.2 History of Use

Technical analyses documenting the presence of Vandyke brown in paintings and historical artifacts are relatively rare. Because the pigment is primarily organic, it does not yield to many of the conventional analytical methods used in the examination of paintings, such as polarized-light microscopy, x-ray diffraction, or emission spectroscopy. Infrared spectroscopy, the analytical instrumental method recommended for its identification (see section 5.3.2), was not widely available until the late 1940s and has not been used to identify Vandyke brown except by the authors at Carnegie Mellon Research Institute on a group of early American paintings undergoing conservation treatment (Quandt, 1971) (fig. 1).

As a consequence of the difficulty in obtaining positive identification of the pigment, the principal documentation concerning the history of its use comes from written European sources. As mentioned, relying on old books and manuscripts for references to the use of Vandyke brown contributes to the considerable confusion between the names employed and the actual chemical composition of the pigment being referred to. The authors can say nothing of the use of such a substance in Asia; nonetheless, that possibility must not be overlooked.

Interestingly, the several eighteenth-century German texts known to the authors provide little clear information regarding the use of the humic-earth pigment; at most, the sources gave only a brief citation to a Cologne brown in a list of colorants. The English as well as Americans seem to have been much more concerned with its properties and uses and appear to have written about it to a greater extent. The French, as noted, distinguished between the humic-earth pigment, deriving its name from the German region of origin, and Vandyke brown, which they considered an iron oxide pigment. As one may deduce from Forni's text (1866), the Italians came to accept the usage of French terms for the pigment, designating the *terra di Cologne* or *terra di Cassel* as the fossil lignite pigment and the *bruno Vandick* as a pigment either based on iron oxide (colcothar) or made by calcining yellow ocher, also an iron oxide pigment.

2.2.1 *Sixteenth and seventeenth century.*

A number of references to the pigment are found in early seventeenth-century manuscripts. The Turquet de Mayerne manuscript of 1620 to 1637 refers to *la terra de Cologne* (Berger, 1901). Sanderson (1658) listed Cullins earth, Colens-earth, and terra-Colen for use in limning. Harley (1982) mentioned that earth of Cullen is listed with black pigments in the British Museum's early seventeenth-century Sloane Manuscript 6284 (f. 109v); Marshall Smith, an English author whose work was published in 1692, was also cited. The presence of a pigment resembling Vandyke brown in paintings by the seventeenth-century artists Peter Paul Rubens, Rembrandt van Rijn, and Diego Velázquez has been reported (see section 6.0).

There is apparently a significant reference that occurs earlier in the seventeenth century. Following the 1598 publication of the translation of Lomazzo's, *Trattato dell' arte de la pittura*, which contained no reference to the pigment Cologne earth, Richard Haydocke (the physician who was the translator of Lomazzo) requested that Nicholas Hilliard, an English miniaturist, write a treatise on the art of limning (Williamson & Buckman, 1926). Hilliard's manuscript (exact date unknown) refers to the use of earth of Cullen as a color suitable for shading browns and blacks. Since Hilliard died in 1619, it seems likely that the reference to Cullen earth in his manuscript is earlier than that of De Mayerne, particularly since, according to Williamson and Buckman, the manuscript contains a reference to an interview with Queen Elizabeth, who died in 1603.

Fig. 1 The ground and the shadows in the proper right hand are pigmented with Vandyke brown in *Mr. Van Vechten*, attributed to The Schuyler Limner (possibly Nehemiah Partridge), c. 1719, oil on canvas, National Gallery of Art, Washington, Andrew W. Mellon Collection 1947.17.14.

Eastlake (1847) stated that Van Mander in *Het Schilder-Boeck* (1604) recommended Cologne earth for the shadows of the flesh and that Willem Beurs also mentioned Cologne earth in *De Groote Waerelt* of 1692.

Wehlte (1982) wrote that Hieronymi (1932) claimed that the pigment dated from the sixteenth century. From the apparent dates of Hilliard and Van Mander, this seems possible, but Wehlte remarked further that "Raehlmann had not confirmed this" (Raehlmann, 1914).

2.2.2 ***Eighteenth century.*** In the eighteenth century there are many references to the pigment.

However, although the term Cologne earth is used, it is often unclear what sort of pigment is being described (Crokern, 1743; *Der Staffirmaler*, 1779; *Praktisches Handbuch*, 1795; Stöckels, 1808). Interestingly, many old German sources did not mention the pigment. A contemporary book, *Kunst-Stücke* (1768), made no mention of it. Likewise, in the *Bewährte Vorschriften* (1798) there is no reference to Cologne, Cassel, or Vandyke brown in the discussion of brown pigments. As late as 1826 the German author Rumbenius only briefly noted that *Köllnische Erde* was one of the brown pigments in use.

In *The Dictionarium Polygraphicum* (1758), the English editor J. Barrow listed the "chief brown pigments" as "umber, Spanish brown, Cologn earth, gall-stone, rust of iron, and mummy." Müntz (1760), also English, recommended using Collens earth for painting in encaustic: "Collens earth, a dark blackish brown and somewhat bituminous earth, inclining a little towards purple is a very good colour and of singular use where extraordinary strength is required in fore grounds." References to the use of the pigment in America are found in import documents. Candee (1966–1967) indicated "Collin's Earth" was imported to Philadelphia as early as 1747, citing the June 25 issue of the *Pennsylvania Gazette* of that year.

In London, Dossie (1764) described "Cologn or Collen's earth" as "a fossile substance. . . . It is of a dark blackish brown colour, a little inclining towards purple. The principal use of it is as a water colour." Payne (1798) referred to "Terra de Cassel, or Vandyke brown, so-called from the great estimation the inimitable painter of that name held it in, is the finest rich brown in the world, in itself. It is in general use amongst the Oil and Water Painters in London." Payne used two names, Cassel earth and Vandyke brown, not commonly encountered before that date.

As mentioned, Ibbetson (1794) may have been the first writer to introduce the idea of associating the pigment with Anthony van Dyck. However, the authors have found no documented technical studies to support the view that particular use of the pigment is to be found in paintings by that artist. A questionable reference to the fact that Van Dyck may have used the pigment occurs in the following comment in Birren (1965): "According to [René] Piot [1931], around 1845 one Baroness de Meyendorf acquainted Delacroix with the palette of Van Dyck and the Frenchman made an adaptation of it for certain paintings in the library of the Luxembourg palace." Van Dyck brown is one of ten base colors cited in Birren (1965) in a Van Dyck palette of Eugène Delacroix (1798–1863). It is possible that the brown of Delacroix's palette was the French-designated iron oxide or ocherous brown rather than the classic humic earth. A second Delacroix palette of twenty-three base colors, given in Birren (1965), includes Cassel earth, the name the French applied to the humic-earth pigment, but not Van Dyck brown. Harley (1982) noted that since Van Dyck lived from 1599 to 1641, he would certainly not have been the earliest to use the pigment. However, because Van Dyck spent a considerable amount of time in England where the pigment was being used, he could have included it in his palette.

Using infrared spectroscopy, Feller identified the humic-earth pigment in early American eighteenth-century paintings by unidentified artists of the Upper Hudson Valley region (Quandt, 1971) (see fig. 1). The presence of a humic-earth pigment of the Vandyke brown type was identified in the grounds of six portraits (see section 6.0).

2.2.3 ***Nineteenth century.*** By the end of the eighteenth century, three names were common: Cologne earth (or its corrupted names, Collens and Cullens earth), Cassel earth, and Vandyke brown. The first two names are often listed separately, yet there are few references to confirm that there were distinct differences between the earth from the Cologne region and the Kassel region. In the *Handbook of Young Artists* (1879), Cassel earth is considered excellent, "one may obtain tones of such vigor as no other color can give . . . but being quite bituminous, it must never be mixed with white, nor with gray and light color; it would attack them." The author further indicated that Cologne earth is "less transparent than Cassel earth." Condit (1883) also referred to Cologne earth as "untransparent."

Thus the humic-earth pigment was recommended for artists' use in watercolor, oil, encaustic, and—well into the nineteenth century—for crayons and miniatures on ivory (Mackenzie, 1829). Because of its sensitivity to alkalies, it was not recommended for *buon fresco* (Doerner, 1949).

In addition to its use by artists, the humic-earth substance has found other applications. According to the Dutch author Simis (1801), *Keulsche Aarde* was "mostly used to paint rooms in such a manner

that one puts a little under the white color; it is also used for greyish-looking sculptures, as for instance in the gardens, also on smooth [well-sanded] wood for painting." Davidson (1900) and Dove (1941) reported its use as a stain for grainers in woodworking applications. Fielding (1852) reported that "the snuff-makers on the Continent use much more of this substance for colouring and adulterating their snuffs than is consumed by artists." The pigment has been used in wallpaper and in decorative papers (*Gentele's Lehrbuch*, 1906). Harrison (1930) wrote that it was used in confectionery, as well as for staining leather and paper.

Because of the confusion resulting from the variations in the chemical constitution of pigments called Vandyke brown, it is not possible to state for certain how extensively the humic-earth pigment was used by specific artists in the past. The limited information available is noted in section 6. More extensive analysis of samples from works of art is needed to ascertain its use by particular artists.

2.3 **Dates of Use**

Vandyke brown was first used in the seventeenth, and possibly as early as the sixteenth century. It is still in use. A brown pigment of the humic-earth type is currently available for use in artists' and industrial paints. In 1968 the American company Reichard-Coulston, listed "Van Dyke" brown no. 1373 as "an organic substance of peat moss type" and included an analysis typical of humic earth. To date the material is still principally derived from the environs of Kassel where at least one source remains active (Josef Riederer, personal communication). The pigment has also been exported from Czechoslovakia (now Czech Republic and Slovakia).

3.0 **General Pigment Properties**

3.1 **Color and Spectral Reflectance**

Differing descriptions of hue and relative transparency of the color of Vandyke brown (Cassel earth or Cologne earth) are encountered in historical accounts (see section 2.2). Dossie (1764) described it as "a blackish brown colour, a little inclining towards purple." In *Handbook of Young Artists* (1879), *Vergnaud's Manual of 1834* is quoted to the effect that "Cologne earth is more violaceous than Cassel earth and less transparent." Undoubtedly differences in color and transparency existed but whether any such statements can provide reliable information today remains in question.

The Vandyke brown swatches of Rowney watercolors in Seward's (1889) little booklet, *Manual of Colours*, are a redder brown than the sample of Cologne earth but not as red as the burnt umber sample. The swatches in Winsor and Newton's booklet (Taylor, c. 1887) are similar. Other than these swatches, we do not have authenticated samples of the old pigments (see fig. 6 and associated discussion).

Although historical descriptions of the color of Vandyke brown can vary, the color of the modern humic-earth pigment can be described. Glazes were prepared from samples obtained in 1968 from three sources: G. and E. Habich's Farbenfabrik GmbH and Wilhelm Urban Company, both in Germany, and from Czechoslovakia, by way of W. Hawley and Son Ltd., England. The term glaze indicates a transparent or semitransparent layer applied at incomplete hiding so that the substrate remains partially visible. Using this definition, watercolors, as generally applied, are essentially glazes (Preston, 1985). From the literature it is known that the pigment was recommended primarily as a glaze for oil painting and as a watercolor, implying that it had transparent qualities.

Because the three samples proved to be similar in hue and chroma, all of the detailed spectrophotometric measurements are not given; the spectral reflectance curves for the two samples from Germany are illustrative. As can be seen in figure 2, the curves are not distinctive. Humic acids extracted from various soils exhibit no character-

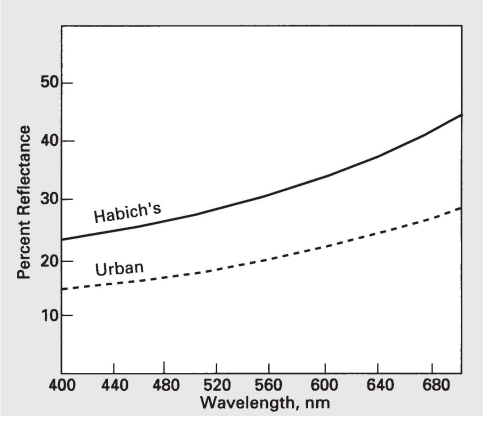


Fig. 2 Spectral reflectance of Vandyke brown glazes over white gesso board. Prepared from G. and E. Habich's Farbenfabrik and Wilhelm Urban and Company samples in Acryloid B-72 acrylic vehicle.

Table 1 **Color of Vandyke Brown Glazes**[a]

Sample Number	*Munsell Notation*		*ISCC–NBS Universal Color Name*[b]
	Hue	*Value/ Chroma*	
1 (Darkest)	2.27RP	2.35/0.20	Dark Gray or Black
2	9.71R	2.61/0.63	Dark Reddish Gray
3	5.40YR	3.6/2.0	Grayish Brown
4	7.04YR	4.86/2.37	Light Grayish Brown
5 (Lightest)	7.93YR	6.40/2.05	Light Grayish Brown

a. G. and E. Habich's Farbenfabrik GmbH Vandyke brown in Acryloid B-72 over white gesso board.
b. From Kelly and Judd (1976).

istic absorption bands in the visible and ultraviolet regions that would provide positive identification (Mortensen & Himes, 1964). Because the curves are nearly flat, reflecting all wavelengths of light, the colors are nearly neutral and are very low in chroma or saturation.

To illustrate the color range more completely, the glazes prepared at five concentrations are described (table 1), using material from Habich's dispersed in Acryloid B-72, which is a thermoplastic copolymer based on methylacrylate and ethylmethacrylate. (In considering the "optics" of glazes, that is, the reflectances obtained, the intensity of the color depends on the product of the thickness, X, as well as the concentration, C. Thus, when the term concentration is used here, it describes this product, CX, concentration times thickness.) The glazes were applied over white gesso board and the spectral reflectances were measured in the visible spectral region. The glazes were not glossy, exhibiting a relatively matte surface characteristic of the substrate gesso board; therefore the total reflectance was measured using an integrating sphere spectrophotometer. The measured reflectance values were then integrated to obtain the CIE (*Commission Internationale de l'Eclairage*) color coordinates, the tristimulus values X, Y, Z, and the chromacity coordinates x, y, for illuminant type C and the 1931 Standard Observer. From these coordinates a Munsell notation was determined. Had the glazes been very glossy, the most concentrated sample (no. 1), would have been darker and more saturated. The effect of the included scattered surface reflectance in reducing the saturation or purity of the measurements becomes less important as the lightness increases. The data shown represent the color as perceived on these particular samples. The data would be slightly but not radically different in samples prepared in a different medium over a different white substrate.

From an examination of the Munsell data in table 1, it is evident that the chroma (corresponding approximately to the saturation or color purity) increases from the darkest sample (1) to a maximum in sample 4 and then decreases with the increasing lightness of hue in sample 5. Thus, there is a certain lightness at which a Vandyke brown pigment applied as a glaze exhibits its maximum chroma, a phenomenon exhibited by all chromatic colorants applied as glazes (Johnston-Feller & Bailie, 1982). The particular pigment concentration at which the maximum chroma is achieved depends on the color underneath (the substrate color) as well as on the spectral and optical characteristics of the pigments in the glaze layer.

Note in table 1 that at the highest concentration level (1) (darkest) the hue designation is a red purple (RP), thus supporting old references to the pigment as "violaceous." As the concentration becomes lower, however, the hue shifts quickly through the red to the yellow-red (YR) (or brown) region, justifying its classification as a brown. Standard color names are given by Kelly and Judd (1955, 1976).

The logical sequence of these changes in hue can be understood by consulting figure 3. Here, the locus of chromaticity coordinates, x and y, for the five glazes made with the Habich's sample is plotted on a CIE chromaticity diagram (Johnston-Feller & Bailie, 1982). The dominant wavelength lines on this diagram indicate the hue. It can be seen that the darkest sample is in the purple region with a dominant wavelength of about 530c (a purple complementary to a green of 530 nm dominant wavelength). The next-lighter sample has a dominant wavelength of about 600 nm, bordering on the orange-red. Further dilution finds the color moving into the orange region (brown) with a change of only a few nanometers in dominant wavelength, about 587 to 584 nm; it then continues as an increasingly lighter brown of fairly constant hue.

Figure 3 also reveals the increase in excitation purity, P_e, which approximately corresponds to chroma or saturation. The lines of constant P_e parallel the spectrum locus of purest colors as a per-

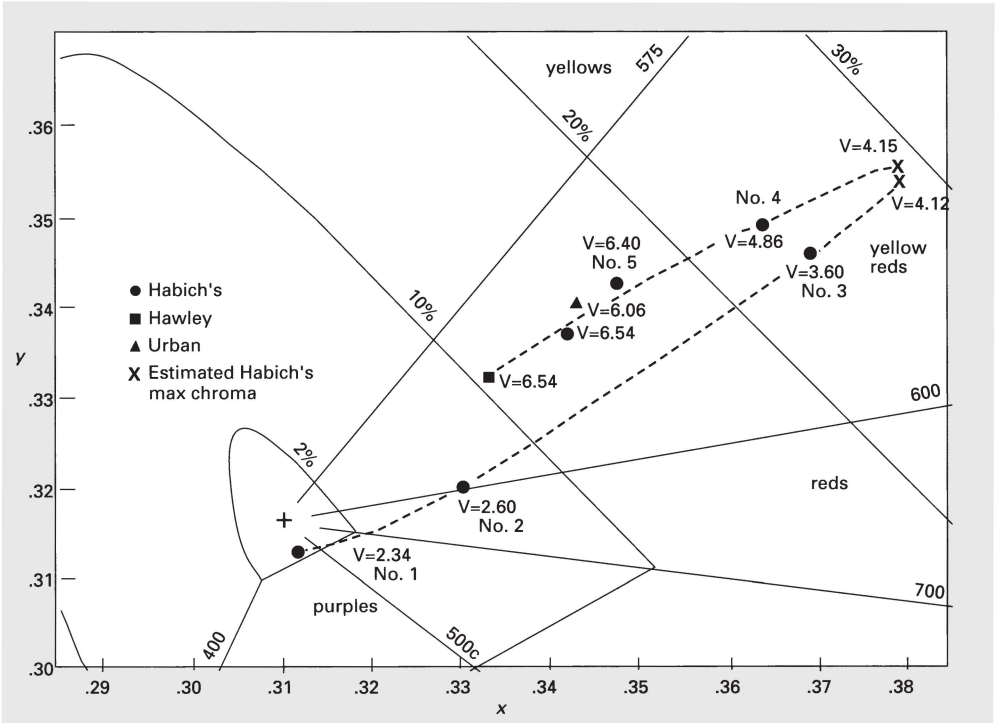


Fig. 3 Locus of CIE chromaticity coordinates (*x, y*) of a series of Vandyke brown glazes, prepared from the Habich's sample, of increasing lightness from Munsell value, V, of 2.34 to 6.54 (illuminant type C, 1931 Standard Observer). X =calculated data points. Glazes prepared from a Hawley and an Urban sample are included for reference (Johnston & Bailie, 1982, with permission).

centage of the distance from the neutral point, here designated as +, and the perpendicular to the spectrum locus. From the dark sample at about 1% to 2% P_e, the purity increases up to 23% to 24% for samples no. 3 and 4. Thereafter the purity decreases. To indicate the lightness, the Munsell value, V, for each sample is noted in the figure beside each data point (Munsell value is a scale from 0 for black to the highest value of 10 for white).

Applying the Kubelka-Munk equation for incomplete hiding layers, the point of maximum purity (chroma) for the sample of Habich's Vandyke brown can be calculated. (For details of this calculation, see Johnston-Feller & Bailie, 1982.) The two points marked X indicate the results. Thus, it is estimated that the maximum achievable purity of Vandyke brown glazes over the particular white gesso board would be about 29%, corresponding to a Munsell chroma of 2.8, achieved at a Munsell value of about 5.0 or luminous reflectance, *Y*, of about 20%. The significance of this hue and chroma shift behavior cannot be overstated, particularly as it concerns the exposure (fading) data described in section 3.3.

After these extensive studies of the coloristic behavior of currently available Vandyke brown pigments were completed, the authors' attention returned to the swatches of watercolors that appeared in the previously noted booklets issued by Winsor and Newton (Taylor, c. 1887). Specimens labeled Vandyke brown and Cologne earth (characterized therein as being prepared "by calcining Vandyke brown") differed in chroma and, possibly, hue. Three different editions of the book were located: printing nos. 13,000; 14,000; and 22,000. Swatches were also found in a similar booklet by Rowney (Seward, 1889). A fourth color-swatch booklet by Winsor and Newton, bound in buckram without text (fig. 4A), contained specimens in both watercolor and oil. The oil specimens, illustrated in figure 4B, offered an unusual opportunity to measure the color of samples of Vandyke brown and Cologne earth as well

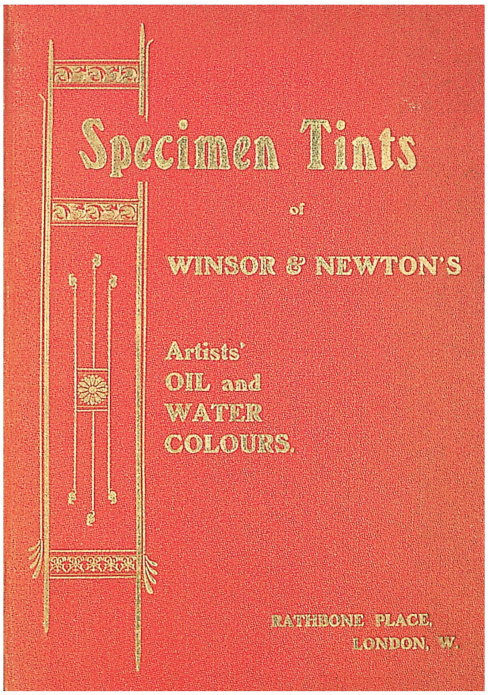
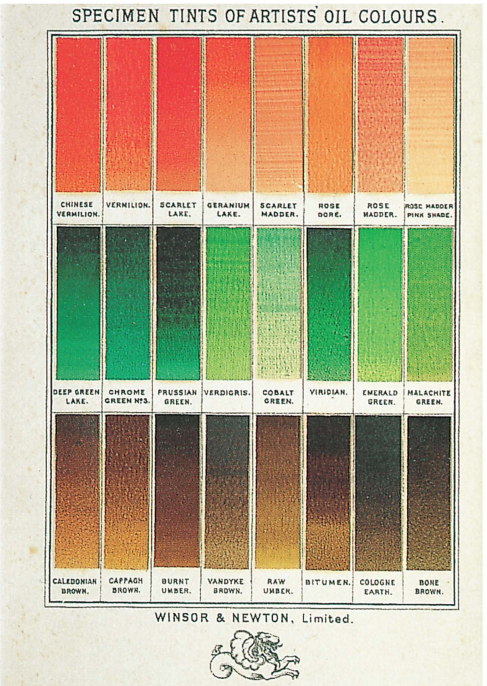


Fig. 4 A. Cover of Winsor and Newton catalogue, undated and without text, that contained swatches of watercolors and oils.



B. Catalogue page includes a sample of Caledonian brown, Cappagh brown, Vandyke brown, and Cologne earth in oil.

as samples labeled Caledonian brown and Cappagh brown.

The dimensions of the swatches were 10 x 37.5 mm and the paints, applied at incomplete hiding, were usually tapered from a dark to a lighter application, as can be seen in figure 4B. Figure 5 illustrates spectral reflectance of the four swatches made with oil. The Cologne earth swatch is much darker than the Vandyke brown. The curves of Caledonian and Cappagh brown differ from the other two in that, while having similar reflectances in the short wavelengths, they have higher reflectances in the yellow, orange, and red wavelength regions. The spectral reflectance curves are more similar to those of iron oxide pigments than to the humic-earth pigments.

Two measurements were made on each of five swatches of watercolor, one in the lighter area and one in the darker area: three samples from Taylor (c. 1887), one from Seward (1889), and one from the color-swatch booklet (fig. 4B). The results are shown in the chromaticity diagram seen in figure 6. The locus of chromaticity points for a series of paints of increasing lightness tends to pass through a point of maximum color purity, as seen in the behavior of the Vandyke brown glazes (see fig. 3), the locus of which is superimposed in figure 6. The hues of the Cologne earth and Vandyke brown, as represented by the dominant wavelength close to 585 nm, prove to be very similar, with the Vandyke brown perhaps very slightly redder. The Cappagh and Caledonian browns have a distinctly higher color purity and are perhaps slightly redder.

Although Vandyke brown is perhaps less commonly used in mixtures with white pigments, its chameleonlike behavior when used in this way is noteworthy. Because of its transparency and low chroma, the light-scattering characteristics of the white pigment play a major role in determining the hue of the mixture. Figure 7 shows the spectral reflectance of the Urban sample in a mixture with three white pigments. The spectral curves of the other two Vandyke brown samples were similar. As can be seen from these nearly flat spectral curves, the colors are practically gray. In table 2 the Munsell notations are given for the three pigment samples, each mixed with the three white pigments. The concentration of the Vandyke

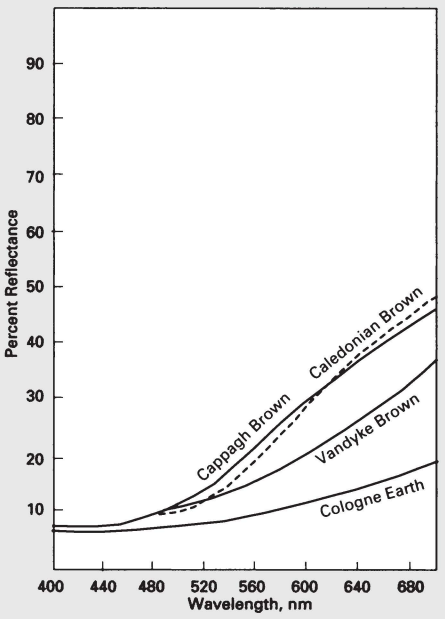


Fig. 5 Representative spectral reflectance of the specimen tints in oil on the swatches on the catalogue page shown in figure 4B.

brown has been adjusted to give about the same Munsell value (related to luminous reflectance) for each sample. The order of the white pigments in the table corresponds to their history of use from lead white, the earliest, to titanium dioxide, the latest (after 1920). As a guide to interpreting Munsell hue letters and numbers, it may be helpful to remember that the progression is as follows: ten purple-blue, 10PB, is the same as zero purple, 0P; ten red-purple, 10RP, is the same as zero red, 0R; ten red, 10R, is the same as zero yellow-red, 0YR; and ten yellow-red, 10YR, is the same as zero yellow, 0Y.

From the hue notations in table 2 it can be seen that the mixture with the oldest white pigment, lead white, is the reddest hue, with zinc oxide in the middle range toward purple, and with rutile titanium dioxide, the most bluish. Note that the chroma is extremely low, less than 1.0 in all cases

Fig. 6 Locus of CIE chromaticity coordinates (x, y) measured on swatches of pigments in watercolor found in five samples, three from Taylor (c. 1887), one from Seward (1889), and one from the color swatch booklet shown in figure 4B. (● Vandyke brown ○ Cologne earth). Also noted are the chromaticities of the four samples in oil referred to in figures 4B and 5, which are designated by ⊕, ⧋, or ⧁. Data regarding the behavior of Vandyke brown (VDB) glazes were obtained from figure 3.

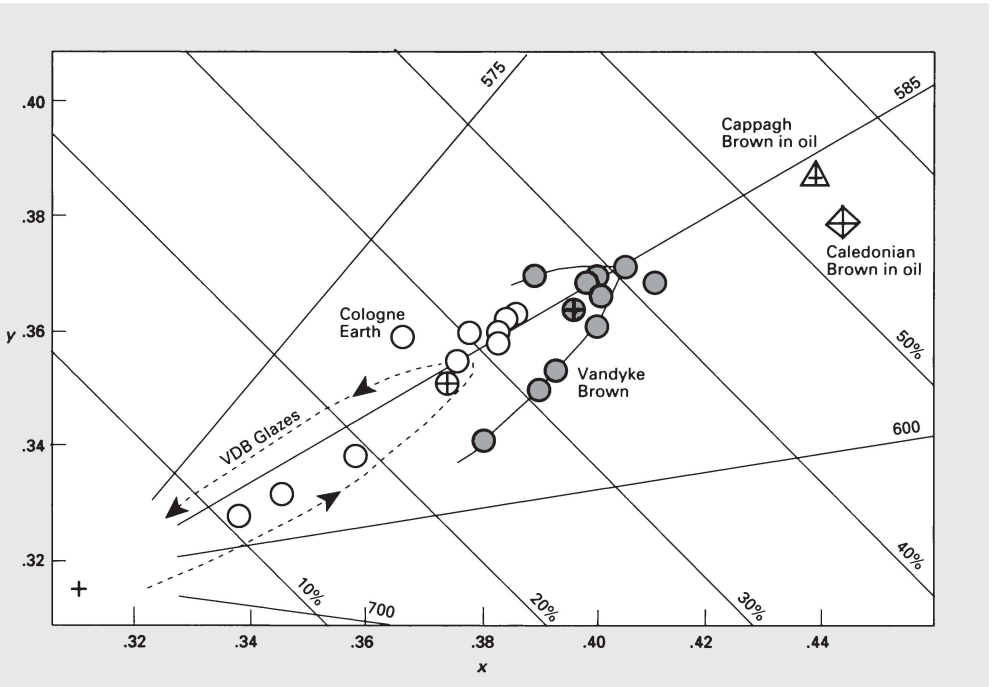


Table 2 **Color of Vandyke Brown Mixed with White Pigments**

White Pigment	*Vandyke Brown Pigment*	*Munsell Notation*		*ISCC–NBS Universal Color Name*[a]
		Hue	*Value/ Chroma*	
White lead	W. Hawley and Son	3.36R	6.53/0.52	Pinkish Gray
	G. and E. Habich's	4.51R	6.44/0.47	Medium Gray
	Wilhelm Urban and Company	0.1YR	6.76/0.41	Light Gray
Zinc oxide	W. Hawley and Son	6.69P	6.64/0.79	Purplish Gray
	G. and E. Habich's	7.07R	6.11/0.89	Reddish Gray
	Wilhelm Urban and Company	6.22P	6.64/0.60	Purplish Gray
Rutile titanium dioxide	W. Hawley and Son	1.16P	6.52/0.81	Light Gray
	G. and E. Habich's	8.52PB	6.11/1.06	Bluish Gray
	Wilhelm Urban and Company	1.08P	6.45/0.47	Medium Gray

a. From Kelly and Judd (1976).

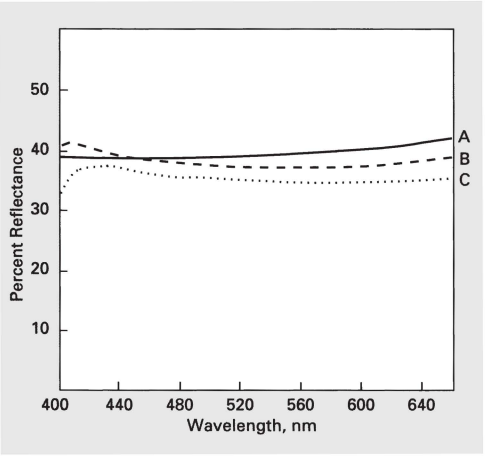


Fig. 7 Spectral reflectance of Vandyke brown (Wilhelm Urban) mixed with (A) lead white (Fezandie and Sperrle), (B) zinc oxide (New Jersey Zinc Horsehead XX505), and (C) rutile titanium dioxide (DuPont Ti-Pure R610) at complete hiding.

except in the sample from Habich's made with titanium dioxide. Compare this with the chroma of a glaze of similar Munsell value (6.4): its chroma is 2.05 (table 1, sample 5). The hue in the glazes is far more yellowish; for sample 5 (table 1) the hue is a definite yellow-red, 7.9YR, approaching a true yellow, 10YR, compared to an average of 6R for the mixtures with lead white, much more bluish than the glazes.

This shift in hue is caused by the higher ratio of light scattering of the white pigments in the violet end of the spectrum to their scattering in the long wavelength red, with rutile titanium dioxide exhibiting the highest ratio. The color data for mixtures with rutile titanium dioxide are given here for the benefit of modern artists who may question the hue obtained with modern white pigments. Mixtures with anatase titanium dioxide, being of lower refractive index than the rutile R610, can be expected to be intermediate in blueness between zinc oxide and rutile. Some "titanium white" paint formulations for artists may also contain zinc oxide (Levison, 1976).

How extensively Vandyke brown may have been used in mixtures with white pigment in the past is not known. That it was so used, however, can be inferred by some of the historical references regarding its permanency (see section 3.3.1).

3.2 Spectral Absorption and Scattering: Tinting Strength and Transparency

The "optical" behavior of a pigment is determined by its ability to absorb and to scatter light as a function of wavelength. Absorption is a function primarily of its electronic structure; scattering is a function primarily of refractive index. Both absorption and scattering are also affected by particle size. The relative amount of absorption exhibited by a chromatic pigment primarily determines its tinting strength, defined as the ability to impart darkness and vividness (chroma) to a white or

other scattering pigment. It is the absorption that imparts chroma when applied thinly as a glaze over a reflecting substrate. The relative level of scattering determines a pigment's translucency or lack of clarity as a glaze. Also, the scattering of a pigment relates to its ability to impart lightness when mixed with an absorbing pigment. (The scattering is often described as the scattering strength or, in the case of white pigments, as their tinting strength.)

Being a complex mixture of natural organic substances, the humic-earth brown has no definite absorption bands in the visible wavelengths (see figs. 2 and 5). However, it does exhibit absorption, lowest in the red region and increasing to the violet. Because the level of absorption is relatively low at all wavelengths, its tinting strength is low. Since it is primarily organic rather than mineral (inorganic), the pigment's refractive index, n_D, is only moderate, about 1.62 to 1.69 (Gettens & Stout, 1966). As a consequence, it scatters little light when mixed with traditional organic vehicles and thus is relatively transparent. Remington (1944) cited its poor hiding power.

The properties of transparency and low chroma were well recognized in many of the historical texts. For example, Dossie (1764) wrote that its principal use was as a watercolor, Condit (1883) described Cassel earth as a good glazing color, and Davidson (1900) cited its use as a stain by grainers. Owing to its characteristics of low absorption, near neutral hue, and low scattering, the color effects achievable with Vandyke brown are unique, unlike any other traditional pigment. As early as the seventeenth century, brown pigments such as Cologne earth and umber were recommended for the coloring of shadows (Williamson & Buckman, 1926).

3.3 **Permanence**

3.3.1 ***History.*** The literature contains many conflicting statements regarding the lightfastness of a pigment designated as Vandyke brown, Cologne earth, or Cassel earth. This is understandable because of the very different materials that over the years have been given these names.

The earliest references to the pigment do not mention its poor lightfastness. Perhaps this was because that property was not of concern to the artists of the time, or the authors had in mind only the rather mild exposure usually experienced by paintings on the walls of homes and churches. Müntz (1760) considered Collens earth "a very good colour of singular use where extraordinary strength is required in foregrounds"; Payne (1798) claimed Vandyke brown to be "the finest rich brown in the world, in itself." Fielding (1852) described Vandyke brown as "a colour in great use and estimation." These remarks, however, do not refer specifically to lightfastness.

In the nineteenth century, serious criticisms began to appear concerning the stability of many artists' pigments when exposed to light. Field (1835) and Moreau-Vauthier (1923) noted that Mérimée (1830) had described a problem with the permanence of Cassel earth. Wiegmann (1836) firmly declared that Cologne earth and Cassel brown were to be "dismissed" because the pigment "almost completely disappears." In *The Handbook of Young Artists* (1879) Vergnaud's manual of 1834 is quoted in which pigments were divided into three classes based on their "solidity" (permanence): the first being "perfectly solid," the second "sufficiently though not perfectly solid," the third "of but little solidity." Vergnaud placed Vandyke brown in the third class (Riffault & Vergnaud, 1851).

Because of the different types of pigment that often went under the various names for Vandyke brown, it is not surprising that conflicting comments on stability are found. Field (1877) classified Vandyke brown, Cassel earth, and Cologne earth in the group of pigments "not at all, or little, liable to change by the action of light, oxygen, and pure air; nor by the opposite influences of shade, sulphuretted hydrogen, damp and impure air; nor by action of lead or iron." Muckley (1880) stated emphatically, "It is permanent. . . . The palette should never be set without it." Carlyle (1991) has also reviewed these and other conflicting statements.

One of the most influential books of the period, Rood's *Modern Chromatics* (1908), emphasized the opposite. The author quoted Field's statements and then proceeded to present results based on his own exposure of watercolor washes "laid on ordinary drawing-paper, exposed during the summer to sunlight for more than three months and a half." Of twenty-five pigments described in order of the relative amounts of damage suffered, the most fugitive colors being placed at its end, Vandyke brown occurs nineteenth in permanence, seventh from the end of the list, a far cry from the claim made by Field. Indeed, in his "Preface," Rood pleaded reluctance to writing prefaces but considered that he must discard Field's theories.

In the period from 1886 to 1888, many ques-

tions were being raised about the stability of pigments used in watercolor paintings, initiated in part by a series of forty-eight letters to the (London) *Times*, dating from 11 March to 27 September 1886; the series had been reprinted in pamphlet form "by Mr. Parnell, 63 Southampton Row, W.C.," (Taylor, c. 1887). John Ruskin also entered the fray in defense of proper care for art objects of all kinds (letter to the *Times*, 14 April 1886). Finally, Winsor and Newton asked J. Scott Taylor to comment on the controversy with facts and descriptions. The result was the remarkable booklet already mentioned, complete with a summary of the controversy and handmade graduated washes of all of Winsor and Newton's watercolor preparations of that time (Taylor, c. 1887). Taylor concluded that the pigment "was probably durable under ordinary conditions," but faded in sunlight. In Russell and Abney's report (1888) on tests of watercolors exposed outdoors in glass tubes open to the air, a sample of Vandyke brown had faded significantly in about four months and had completely faded out in twenty-two months. Their sample of Vandyke brown seemed to be more fugitive than their madder lake. In similar tests made at about the same date by the English color makers, George Rowney and Company, samples of Cologne earth and Vandyke brown watercolors were only slightly changed in six months of outdoor exposure (Seward, 1889). In oil, Vandyke brown was unchanged when it was exposed six months near a window and only slightly changed when it was exposed for the same length of time outdoors. Seward's summary of the watercolor controversy, amounting to fifteen pages and two extensive tables of experimental results, is more detailed than Taylor's. A reading of the history of these events is fascinating.

From this time on, the permanency of the humic-earth pigment was regularly questioned. Hurst (1896) indicated "their value [Cologne earth, Cassel earth, Rubens' brown] as pigments is very variable, and, as their composition cannot be depended upon as being constant, it is advisable to avoid the use of these pigments for all artistic painting." Nonetheless, in 1923 Bearn wrote, "It is a favourite water colour with artists, and is fairly permanent as such, but more so when ground up in oil." Dove (1941), working for a company that he indicated was marketing Vandyke brown from an American source, wrote that it was "permanent to light so far as known, as in every test it outlasts any vehicle tested. Ten years of direct exposure to outside sunlight do not appear to fade it perceptibly." The authors consider this would not be true of the humic-earth pigment.

More recent sources clearly classify the pigment as having poor lightfastness. Heaton (1947) wrote, "It is a very unreliable pigment as regards permanency, fading badly on exposure to light," while Wehlte (1982) indicated unequivocally that it is "unsuitable for all artists' techniques, yet still is found in oil and watercolor." Levison (1976) published test results indicating his sample of Vandyke brown, moderately faded, was nonetheless more lightfast than alizarin lake. Thus, the evidence from the literature points to a tendency to fade, but the question has remained concerning just how sensitive the pigment is. In the following section lightfastness tests of modern Vandyke browns are reported employing more recent photometric techniques and terminology.

Table 3 **Color of Vandyke Brown Glazes Exposed to Daylight Fluorescent Lamps**[a]

		Munsell Notation	
Sample No.	*Days Exposed*	*Hue*	*Value/ Chroma*
1 (Darkest)	0	2.27RP	2.35/0.20
	42	5.21RP	2.39/0.22
	112	8.10RP	2.46/0.34
	162	9.70RP	2.51/0.40
	211	0.54R	2.56/0.41
2	0	9.71R	2.61/0.63
	42	1.22YR	2.75/1.02
	112	2.33YR	2.94/1.32
	162	3.36YR	3.12/1.57
	211	3.87YR	3.27/1.71
3	0	5.40YR	3.60/2.00
	42	5.90YR	4.12/2.58
	112	6.99YR	4.97/2.70
	162	7.60YR	5.38/2.74
	211	7.66YR	5.63/2.63
4	0	7.04YR	4.86/2.37
	42	8.00YR	5.51/2.73
	112	8.34YR	6.81/2.15
	162	8.05YR	7.15/1.99
5 (Lightest)	0	7.93YR	6.40/2.05
	42	8.25YR	7.24/2.05
	112	8.84YR	8.25/1.16
	162	8.32YR	8.51/0.97

a. From Johnston-Feller and Bailie (1982).

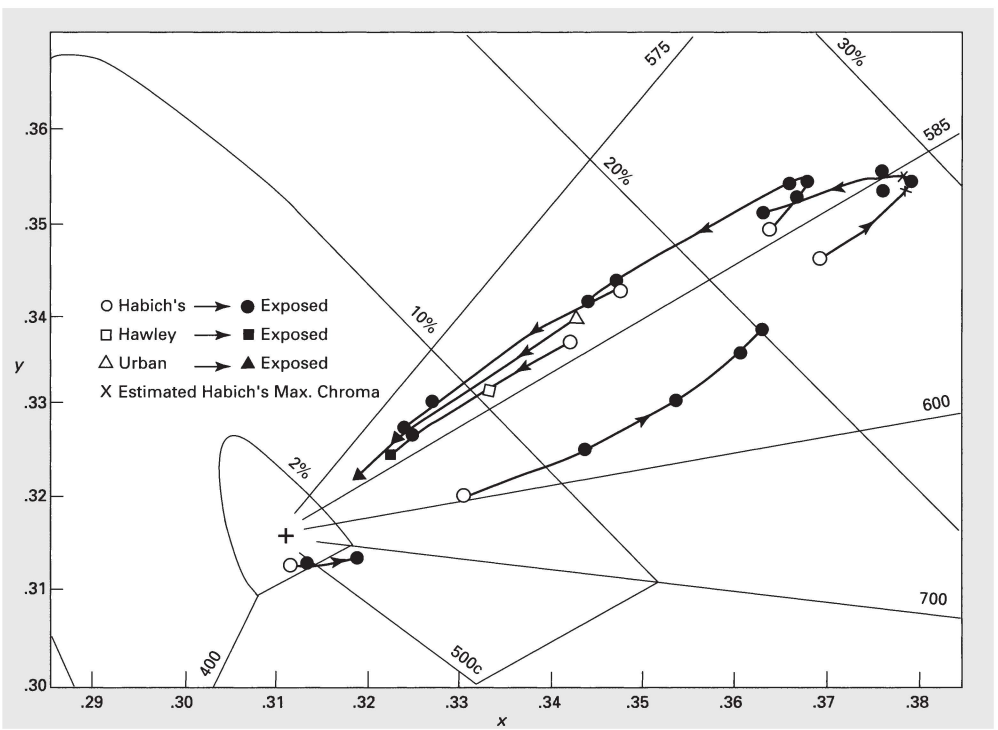
3.3.2 ***Permanence of modern Vandyke browns.*** The authors subjected the glazes and the white mixtures described in section 3.1 to exposure under a bank of daylight fluorescent lamps in a room maintained at 21°C and a relative humidity of 50%. The lamps emitted from 1.5% to 3.8% near-ultraviolet radiation, the rest of the radiation being largely visible. Periodically during exposure the samples were removed for measurement of spectral reflectance.

The five glazes described in table 1 and figure 2 were exposed over a period of seven months for a total of about 60 x 10^6 lux hours, equivalent to about sixty years on the wall of a museum that received about one million lux hours of exposure per year. The Munsell notations determined from the measured reflectance curves and the CIE chromaticity coordinates and luminous reflectance, *Y*, for the intervals of exposure are shown in table 3 (Johnston-Feller & Bailie, 1982). A change in Munsell hue from RP to R to YR can be seen to take place because of the exposure. The chroma reached a maximum of approximately 2.7 on sample 3 exposed for 162 hours and on sample 4 exposed for only forty-two hours, a result close to the estimated maximum chroma achievable with Vandyke brown over the particular white gesso board used.

Figure 8 shows the chromaticity coordinates plotted for the exposed samples on the same diagram as figure 3. For easy reference, the two estimated points of maximum purity, P_e, described in section 3.1 are indicated. It can be seen that there is indeed a critical concentration at which maximum purity is reached. If a color is made using a glaze of this pigment at a concentration higher than this critical concentration, and is then exposed to conditions that cause fading, the fading will result in a continuing increase in purity (chroma) until the critical concentration is reached. Figure 8 also shows that glazes made at concentrations higher than the critical concentration will also become more yellow as they fade until, near the critical concentration, they will make an abrupt change toward a more golden hue, thereafter increasing only slightly in yellowness.

The mixtures with the three white pigments were likewise exposed under the same conditions

Fig. 8 Locus of CIE chromaticity coordinates (*x, y*) of the series of glazes, shown in figure 3, in the course of fading upon exposure to daylight fluorescent lamps.



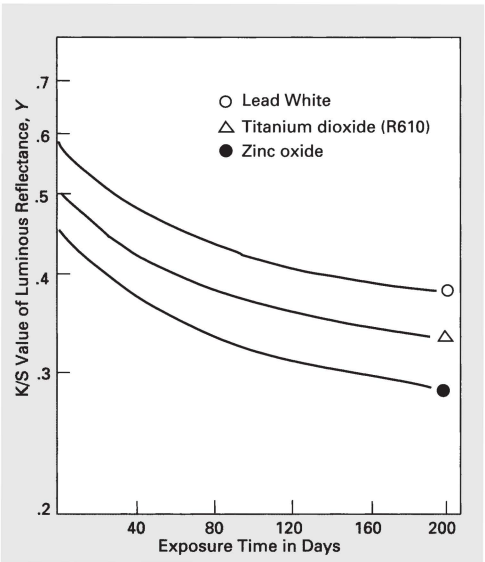


Fig. 9 Fading of Vandyke brown mixtures with three white pigments expressed as the change in the logarithm of the Kubelka-Munk K/S value of the luminous reflectance, Y, versus time. Exposure to daylight fluorescent lamps at approximate level of 13,000 lux.

as the glazes. Figure 9 traces the effective change in concentration during fading as described by the Kubelka-Munk constant, K/S (Kubelka & Munk, 1931). (The constant, $K/S=(1-R)^2/2R$, was determined, in this case, from the CIE luminous reflectance value, Y, simulating the results that would be measured using a broad-band filter. In the case of a relatively nonselective reflectance curve of an unknown complex mixture, this method is more representative of concentration changes than the use of the conventional single wavelength at an absorption maximum.)

The kinetic rate constant is represented by the slope of the logarithm of the concentration changes with time of exposure (Johnston-Feller et al., 1984). The slopes are similar in each case, evidence that the rate of change is about the same, independent of the particular white pigment used. In the course of exposure, the hue and chroma are dominated by the scattering characteristics of the particular white pigment used.

As can be seen by the sloped curves, the rate of fading is not constant. Instead, it decreases as fading proceeds. This is not surprising considering the complex mixture of light-absorbing materials possibly present; some components undoubtedly fade faster than others. Experimental data confirm that the same general behavior of decreasing rates of fading was also observed concerning the exposure of Vandyke brown glazes. A reduction in fading rate achieved using an ultraviolet filter, Plexiglas UF-4, was modest, about 50%.

On the basis of the degree of change of the concentrations of both the glazes and the white mixtures, the samples tested would be classified as being of intermediate light stability, resisting serious discoloration for approximately twenty to one hundred years on a museum wall illuminated by diffuse daylight (see Feller, 1975). On the ISO R105 blue-wool lightfastness scale (British Standard BS1006:1941) both the glazes and the white mixtures were rated as grade five to six, further proof of the classification as intermediate in fastness.

A study by Bailie et al. (1988) suggests that the blue-wool-scale rating might be as low as three to four in certain instances. The first-order rate constant of fading in mixture with titanium white in a poly(vinylacetate) vehicle over a long period of exposure was found to be about 1.4 to 1.5 times faster than alizarin lake when exposed in a xenon-arc fadeometer with Pyrex filters. During the initial period of fading, the rate was about twice this amount (perhaps three times as rapid as alizarin). An increase in relative humidity increased the rate of fading. These results are similar to those of Russell and Abney (1888).

Thus, based on modern studies, Vandyke brown seems to be of intermediate lightfastness. Furthermore, it tends to fade at a declining rate over time. Whether or not the old pigments used by artists would behave similarly has not been determined. Considering that the modern pigments, made with current technology, probably represent the best compromise between the desirable pigment properties, particularly the hue and chroma, and permanency, one can postulate that the humic earths used by the Old Masters may have been no higher in fastness.

3.4 **Chemical Properties**

The principal chemical property of humic earth perhaps is its ability to be dissolved in alkalies. This implies that it is acid in character. Indeed, technical data provided in 1986 by the Bakelite Company in Germany, gave the pH value as 3.8 to 4.8. Other than this, Vandyke brown is relatively inert.

As an organic material it can be expected to oxidize. Undoubtedly oxidation contributes to its

Table 4 **Analyses of Vandyke Brown Samples**

	Holley and Ladd (1908)		*Parry and Coste (1902)*		*Bearn (1923)*	
Composition	*Sample 1*	*Sample 2*	*Sample 1*	*Sample 2*	*Sample 1*	*Sample 2*
Organic Matter and Moisture	**90.95**	**91.10**	**90.50**	**91.41**	**90.34**	**92.20**
Ash						
Iron oxide and alumina	1.43	1.50	3.00	1.81	—	—
Calcium carbonate	4.98	3.28	4.05	5.16	—	—
Other (largely silicate?)	2.64	4.12	2.45	1.62	—	—
Total ash	**9.05**	**8.90**	**9.50**	**8.59**	**9.66**	**8.40**
Total in Percent	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**100.60**

fading on exposure to light and possibly could also take place under the action of chemical bleaches.

3.5 Compatibility

There are no compatibility problems commonly cited other than the pigment's sensitivity to an alkaline medium such as *buon fresco* or modern polymer-emulsion paints formulated with ammonia or other alkaline materials.

3.6 Oil Absorption and Grinding Properties

The pigment is easily pulverized and has long been said to be more easily employed in watercolor than in oil. Wehlte (1982) considered its oil absorption to be abnormally high, about 200% (200 lb. of oil per 100 lb. of pigment). However, in an analysis of an artist's paint, Parry and Coste (1902) reported 40.9% oil and 38.5% organic matter. Koch (1953) listed the oil absorption at 45%. Linke (1924) wrote that it is somewhat soluble in oil.

3.7 Toxicity

There are no toxicity problems mentioned in the literature. The material has at times been used in snuff and in confectionery.

4.0 Composition

4.1 Chemical Composition

Vandyke brown pigment is largely organic in character, consisting primarily of the same kind of brown compounds found in soil humus. Although the character of humic substances is complex, considerable information is known through the science of soil chemistry (Dubach & Mehta, 1963). The references that the authors used to find representative infrared spectra will provide a good introduction for those who wish to pursue further the chemistry of these substances (Mortensen & Himes, 1964).

Published analytical data are not plentiful; Parry and Coste (1902), Holley and Ladd (1908), and Bearn (1923) each provided analyses of two contemporary samples (table 4). The organic elemental composition is reported in table 5. After iron, calcium is the next most abundant metallic ion present (see section 5.3.3). Minor amounts of manganese are also generally detected.

A long-recognized way of distinguishing the humic-earth material from pigments composed of ochers and iron oxides is to heat a bulk sample in the bottom of a test tube. A tarry residue first collects on the walls; this was once a definition of bituminous character. After ignition to red heat, only a small residue will be left. The ash content may vary from 1% to 16% (Dove, 1941; see also table 4). In the case of ochers and iron oxide-based pigments, the residue after ignition would be much greater.

Solubility in alkalies is distinctive. Dove wrote that, when treated with alkali, a good-quality pigment will yield less than 10% insoluble matter. Three samples (table 6) exhaustively extracted with alkali in the authors' laboratory yielded 8.8%, 4.9%, and 11.9% insoluble matter by weight. Of these, 6.5%, 2.2%, and 10.9%, respectively, were plant remains, largely pollen; the rest were minerals.

4.1.1 ***Physical constituents—pollen.*** It is logical to expect that soil humus would contain pollen and other plant remains. However, in the

Table 5 **Organic Elemental Analyses of Contemporary Vandyke Brown Samples[a] (Percent composition)**

Sample	*Carbon*	*Hydrogen*	*Nitrogen*	*Oxygen*[b]
G. and E. Habich's Farbenfabrik, 1968	48.54	4.31	0.62	46.53
Wilhelm Urban and Company, 1968	54.49	5.70	0.54	39.27
W. Hawley and Son, sample from Czechoslovakia	57.20	4.84	1.15	36.81
Bakelite A.G.[c]				
Gesellschaft, 1986	48.10	5.10	0.50	46.70
Scholz,[c] 1986	54.10	5.66	0.59	39.65
For comparison:				
Cellulose	44.4	6.2	—	49.4
Peat humic acids[d]	54.2	4.3	?	42.5

a. Analyses by Galbraith Laboratories, Knoxville, Tenn.
b. By difference. Percentage may include 1% to 3% content of minerals (see table 6).
c. Samples from Josef Riederer.
d. Data from Elofson (1957).

Table 6 **Percent Alkali-Insoluble Fractions of Vandyke Brown**

Product Samples	*Net Insoluble Matter*	*Plant Remains*[a] *Density <2.0*	*Minerals Density >2.0*
Wilhelm Urban and Company U-822	8.8	6.5	2.3
G. and E. Habich's Farbenfabrik	4.9	2.2	2.7
W. Hawley and Son, sample from Czechoslovakia	11.9	10.9	1.0

a. Mostly pollen.

small specimens usually taken in the examination of paintings, it is not likely that sufficient pollen grains can be detected to be of value in characterizing the sample. Nonetheless, to confirm this aspect of Vandyke brown, the three modern specimens examined in detail by the authors were sent to Gerhardt Kremp of the Department of Geosciences, University of Arizona, for pollen analysis. Ralph A. Morgan identified the species of pollen present and reported as follows:

Habich's sample (Germany). Abundant microfossils were observed, light golden-yellow in color and in a good state of preservation. The assemblage was made up mostly of angiosperm pollen, particularly three-pored forms, rounded-to-triangular in outline, with relatively fewer tricolpate-colporate forms. The genera found in the sample are noted in table 7.

Urban sample (Germany). Abundant pollen was present but not so numerous as in the Habich's sample and in a good state of preservation (see table 7). The color of fossils was light pale yellow, indicating somewhat less heat and/or pressure than in the Habich's sample. Assemblage made up of angiosperm pollen with some gymnosperm and algal forms; most abundant types present are two species of oak pollen (tricolpate) with numerous triporate forms of the type found in the Habich's sample but in relatively fewer numbers than in that sample. Algal remains are mostly tiny fragments.

Hawley sample (from Czechoslovakia). Pollen in this sample was in a very poor state of preservation. The few fossils present were dark brown in color, indicating fairly high heat and pressure, perhaps resulting from forced drying of the pigment. Fossil assemblage was mostly spongy-looking algal fragments. Few *Quercus* pollen grains, few monolete fern spores (Polypodiaceae), and few trilete fern spores (Cyatheaceae) were

Table 7 **Species of Pollen Found in Modern Samples of Vandyke Brown**[a]

G. and E. Habich's Farbenfabrik		*Wilhelm Urban and Company U-822*	
	Percent[b]		*Percent*[b]
Corylus	18	*Quercus*	32[c]
Betula	16	*Corylus*	10
Alnus	16	*Nyssa*	9
Myrica	15	*Ilex*	8
Quercus	12	*Pterocarya*	8
Gramineae	7	*Juglans*	6
Pinus	4	*Betula*	5
Castanea	4	*Tilia*	5
Tilia	1	*Alnus*	4
Ilex	1	*Pinus*	4
Artemesia	1	*Carya*	4
Juniperus	*	*Ephedra*(?)	3
Tsuga(?)	*	*Chenopodium*	2
Ericaceae	*	Morus	*
Fungal spores	*	*Ericaceae*	*
Carya	*		
Castanopsis(?)	*		

*=Trace

a. Reported by Ralph A. Morgan, University of Arizona.

b. Based on a 200 grain count.

c. 20% large spores, 12% small spores.

seen. A number of dark brown to black insect wing scales were noted.

In summary, Morgan commented that the two samples from the Kassel region of Germany had basically the same pollen types in their assemblages, making it impossible to use a single guide-fossil type as a fingerprint for a specific source of pigment. The relative abundances of the fossil types, however, were sufficiently different that, if so desired, it appears that it is possible to distinguish between bulk commercial samples by pollen grain counts. There was possibly a slight difference in the color of the unstained fossils in the two German samples, but whether or not this could have been used as a criterion for recognition is doubtful. The Habich's fossils were slightly darker. The Hawley sample was markedly different from the German samples, chiefly owing to the poor state of preservation of the pollen grains but also because of the presence of numerous spongy algal fragments as well as several distinctive fern spores.

4.1.2 ***Physical constituents — trace minerals.*** In the three specimens of pigments examined in detail, exhaustive extraction in alkali revealed that the content of minerals possessing densities greater than 2.0 amounted to only about 1% to 3% (see table 6).

The isolated minerals were further separated by using liquids of varying density. The separated fractions were then analyzed by x-ray powder diffraction by Sidney Pollack of the Carnegie Mellon Research Institute, revealing in all three pigment samples: α-quartz, feldspar, and kaolinite in descending order of abundance. Mica was identified in two samples. Heavy minerals, found to be goethite (hydrated iron oxide) and a monoclinic pyroxene (possibly augite-hedenbergite), might be useful in distinguishing one bulk sample from another; these minerals were not present in all samples.

4.2 Sources

According to Rose (1916), the principal source in Germany was once the region between Bruhl and Bonn near Cologne. Leuchs (1829) mentioned that the deposit there was about fifty feet thick and contained trunks of fallen trees. The place names Kirdorf, Valterberg, Verlerschrist, Rogendorf, Liblar, Hermuhlecin, Pfaffroth, Frechen, and Bensberg are also mentioned. Cremer (1895) suggested that Reincassel and Obercassel-on-Rhein, near Cologne, may have been responsible for the use of the designation Cassel earth. Nonetheless, an important source has long been in the vicinity of Kassel. This major historical source is in the Tertiary formations of brown coal at Habichesberg near Kassel. The mine there was active until 1972. Deposits in the same region, the lower reaches of the Hohen Meissners cited by Walter (1922), were still being mined in 1986 (Dr. Fischer of Bakelite A.G. Gesellschaft, Frielendorf, personal communication to Josef Riederer). Nineteenth-century references also cite deposits near Eisenach (see section 2.1.6) and in the province of Sachsen, Thuringen. Switzerland and England have been mentioned as sources by various authors; locations near Birmingham and on the Mendip Hills were particularly cited (*Practical Treatise*, 1795). Chemapol AS in Prague, Czech Republic, exported the pigment. The authors' initial sample from Czechoslovakia was obtained courtesy of W. Hawley and Son Ltd., England; later, a sample was obtained directly from Chemapol.

Although Dove (1941) stated the material was not exported during World War I, it does not seem likely that it would have ceased to be available in Germany. In the United States sources have been

listed as Hanna, Wyoming; Putnam, New Mexico; and Box Elder, Montana (Wilson, 1929). Dove mentioned that an excellent grade was currently being prepared from American materials.

According to Levison (1973) eight thousand pounds of Vandyke brown was used for artists' pigments in the United States in 1971. This figure may be compared to seven thousand pounds for phthalocyanine blue and twelve thousand pounds for madder lake. Pictures depicting mines for Vandyke brown are rare; two small halftones of poor quality appear in Meere (1950). Figure 10, a pen and ink drawing based on a photograph that appeared in literature from Habich's, shows their mine at Gahrenberg that produced both brown coal and Cassel brown.

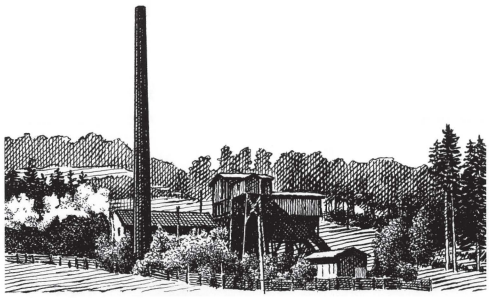


Fig. 10 The former mine of G. and E. Habich's Farbenfabrik in Gahrenberg, Germany, where both brown coal and Cassel brown were produced. Pen and ink drawing (by author [RLF]) is taken from a halftone photograph that appeared in the company literature about 1968.

4.3 Preparation

The finely divided material coming from the earth is easily prepared as a pigment. The wet mass from the digging pits is dried and ground in a ball mill or disintegrator. Older texts sometimes mention the need to separate out a certain amount of sand. Zerr and Rübencamp (1908) wrote that levigation was superfluous.

The soluble stain is prepared by evaporating to dryness the brown fluid resulting from alkaline extraction; the dark, shiny mass that remains is used as a stain for wood. Such material can be expected to test alkaline; indeed this was the case with a modern sample from Germany acquired by the authors. Harrison (1930) indicated that dextrin is usually added in the preparation of a solid substance sometimes known as Vandyke crystals.

4.4 Adulteration and Sophistication

As mentioned, Church (1915) stated that three types of pigments in the commerce of his day were called Vandyke brown—the first type was based on ochers, the second, a brown mineral earth, and the third, a "brown earth containing some iron oxide and a good deal of organic substance." The latter, of course, is the pigment under discussion. However, the humic-earth pigment does not come about through a costly manufacturing process; hence there was little need to adulterate it. Nonetheless, perhaps its hue may at times have been altered somewhat by addition of carbon black, iron oxide, or ocherous pigments. There are references to carbon black being occasionally added to darken the tone.

Occasionally beechwood bark and cork were heated to approximately 300°C with exclusion of air to give an organic-based brown (Heaton, 1947). Harrison (1930) wrote of ingredients such as partially baked sawdust, leather cuttings, and dust. Substitutions for the pigment were also based on mixtures of blacks with red and brown earths. Ignition and examination of the ash is a practical way to test for adulteration involving the addition, if not substitution, of iron oxide pigments. As mentioned, little ash (less than 10%) is expected from the humic-earth pigment.

Toch (1911) indicated that Caledonian brown was often a mixture of umber and raw sienna or of Vandyke brown and sienna. He also described Vandyke madder as being a mixture of madder lake with either Vandyke brown, umber, or black. Gardner (1905) wrote that the product made from calcining ochers found in the south of France frequently contained brown grit (glass sand) added to increase the weight.

5.0 Identification and Characterization

5.1 Optical and Chemical Microscopy

As they are primarily noncrystalline, the particles of Vandyke brown have an irregular outline when viewed in a microscope slide (fig. 11A and B) often with contours that resemble the convolutions of the brain (fig. 11C). The color by transmitted light is usually a rich translucent brown. Under crossed polars, the granules are essentially isotropic, but occasional specimens exhibit a faint hematite-red birefringence, undoubtedly because of the presence of iron-containing constituents. Because the refractive index is only about 1.62 to

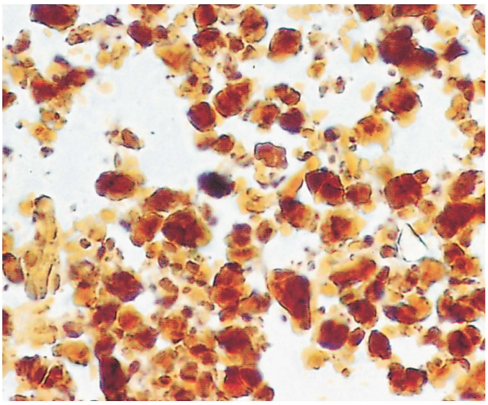
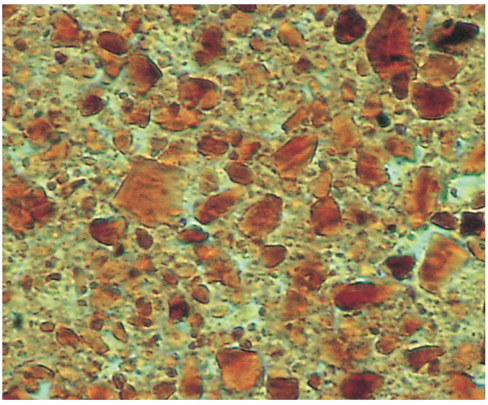
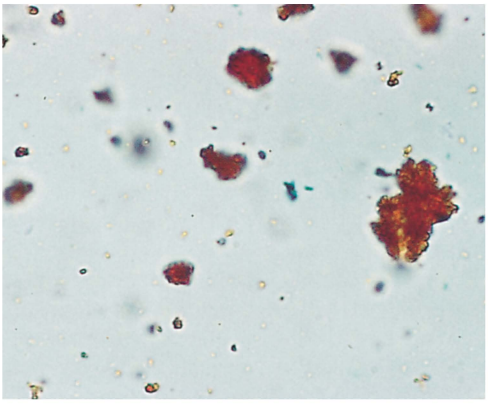


Fig. 11 Photomicrographs of Vandyke brown by transmitted light. Mounted in Canada balsam, n=1.53. 970x.

A. *Kasslerbraun*. G. and E. Habich's Farbenfabrik.



B. Vandyke brown. Winsor and Newton, Forbes Collection 4.05.1, Research Center on the Materials of the Artist and Conservator, Carnegie Mellon Research Institute, Pittsburgh.



C. Ground of eighteenth-century American portrait of John Sanders.

1.69 (Gettens & Stout, 1966), the particles exhibit a low profile in customary mounting media.

5.2 Chemical Identification

There are few chemical tests that can be made on this pigment. A 2% to 5% solution of sodium hydroxide will gradually dissolve the particles, forming an amber-colored solution as one observes dissolution under the microscope. Similarly, bistre also dissolves in alkali (Schwahn, 1987). The trace elements and minerals are normally at such a low concentration that most spot tests are of little use. The detection of iron in a spot test on a brown paint, even if successful, would not be particularly significant because traces of iron-bearing substances are ubiquitous.

A. Burmester (personal communication, 1993) described the following test developed by J. Koller that depends on the characteristics of humic acids, which are the major components of *Kasslerbraun*. The steps of this test are:

(a) The brown paint sample is extracted with chloroform. Part of the *Kasslerbraun* ("dehydro-humic acids") is soluble in this solvent.

(b) The dried chloroform extract is hydrolyzed by methanolic KOH (10%). The dried oil components of the paint sample are thereby dissolved but the humic acids remain undissolved.

(c) Upon dilution with water, the humic acids will dissolve giving a dark brown solution. This solution is centrifuged, decanted into another centrifuge tube, and acidified (c. pH 1) by 3N HCl. A brown and cloudy precipitate results.

(d) A little diethylether is added, the tube shaken well, and centrifuged for about five minutes. All humic acids are now arranged as a fluffy brownish layer between the separated phases with parts of the humic acid hanging like roots into the acidified waterphase.

5.3 Instrumental Methods of Analysis

5.3.1 ***X-ray diffraction.*** Because there is little mineral content in Vandyke brown, x-ray powder diffraction usually yields a diffuse pattern similar to that obtained from poorly crystalline organic compounds. A weak, ill-defined, pattern obtained from one sample seemed to resemble that of xanthine, a compound found in soil.

As discussed in section 4.1.2, x-ray powder diffraction can be used to detect trace minerals, particularly if the mineral fraction is isolated. Lines due to trace amounts of goethite, α-quartz, and kaolinite are frequently observed. Quartz was detected in a majority of the bulk samples examined as well as in samples from paintings.

Table 8 **Assignment of Absorption Bands in Organic Matter Extracted from Soil**[a]

Band (cm^{-1})	*Assignment*
3400	OH groups polymerically bonded through intermolecular hydrogen bonds
2900	C–H bonds
1725	Carboxylic acid and ester groups
1600	Carboxylate ion (associated with iron?)
1400–1200	Carboxylate ion
1100	Pyrophosphate(?)
1025	Silicate structure in the clay
1100–1140	Silicon-oxygen bonds[b]
1075	Si–O–Al stretch (symmetric)[b]
1000	Si–O–Si and Si–O–Al stretch (asymmetric)[b]

a. Data from Schnitzer et al. (1959).
b. Assignments by Wright et al. (1968) in faujasites (zeolites). These bands are also present in yellow ocher.

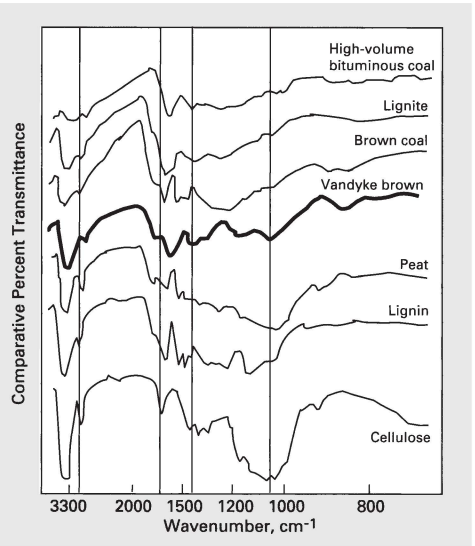


Fig. 12 Comparison of the infrared transmission spectra of a series of materials progressing from bituminous coal through Vandyke brown to lignin and cellulose. Adapted from Kinney and Doucette (1958).

5.3.2 ***Infrared spectroscopy.*** The infrared spectrum of the pigment is almost exactly like that attributed to the polysaccharides found in soil fractions. Band assignments are given in table 8. Elofson (1957), Zeichmann (1964), and Van der Marel and Beutelspacher (1976) published the infrared spectra of many humic materials. Kinney and Doucette (1958) published a series of fourteen spectra in the coalification series from cellulose and lignin to anthracite. Some of these spectra are shown in figure 12 along with that of Vandyke brown. It can be seen that the spectrum is similar to that of brown coal and lignite.

Rarely if at all have any of the infrared bands been attributed to nitrogen even though amino sugars are constituents of soil organic matter. Compounds such as cytosine, xanthine, and hypoxanthine, all containing nitrogen, have been identified in soil (Mortensen & Himes, 1964). Between 0.5% to 1.15% nitrogen is reported in the elemental analyses (see table 5).

Infrared absorption spectra of several samples of Vandyke brown prepared in KBr pellets are shown in figure 13; two are from the grounds of eighteenth-century American portraits, *Mr. Willson* (fig. 14) and *John Sanders*. The bands at about 3450, 2960, and at 1625 to 1710 cm^{-1} have been found to be characteristic of a number of the pigments examined. Details of the absorption around 1040 and 1120 cm^{-1} tend to vary, however. This region is dependent largely upon siliceous and polysaccharidic materials that may be present. Samples primarily differ in the relative absorptions in this region of the spectra. Figure 15 compares the infrared spectra of bitumen, bistre, and a representative Vandyke brown.

When conventional methods for identifying pigments used in a painting—such as x-ray diffraction, microscopic, and spectrographic techniques—fail to identify the brown color as an inorganic pigment, the assumption is made that it is probably organic. This, of course, is not proof that it is Vandyke brown. The presence of bistre, and perhaps sepia, may cause initial problems in identification (Schwahn, 1987). It also is prudent to remember that brown colors could have been made in many ways using organic pigments, even in very old paintings (White, 1986). Using an appropriate selection among alizarin, indigo, gamboge, sepia, bistre, and bitumen, for example, a brown with similar optical characteristics to Vandyke brown could be made. Using modern colorants, the list can be extended significantly. Because of the many possibilities for making non-

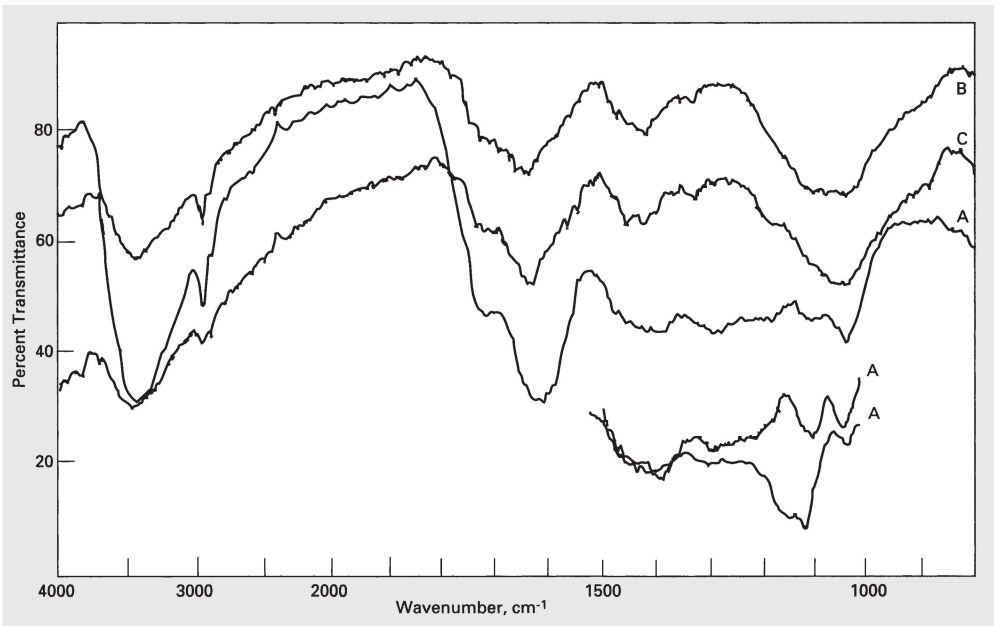


Fig. 13 Infrared transmission spectra showing particularly the differences observed in the region of 1000 to 1500 cm^{-1}. (A) three modern Vandyke browns. Two samples from the grounds of eighteenth-century American paintings are (B) *Mr. Willson* (see fig. 14), and (C) *John Sanders*, Abbey Aldrich Rockefeller Folk Art Center, Colonial Williamsburg, Va. From Feller (1972), with permission.

inorganic brown colors, an infrared curve remains the major reliable means for identification.

5.3.3 ***Spectrochemical analysis.*** The results of emission spectrographic analyses on six modern Vandyke brown pigments and three samples of grounds from portrait paintings (table 9), clearly show that iron is a major element in the inorganic component of the samples with calcium the next most abundant. The presence of relatively high concentrations of calcium is a significant feature. Silicon and aluminum are also present in notable amounts, as might be expected in an earth. These are followed by traces of magnesium, manganese, titanium, barium, and copper. All nine samples gave similar analyses.

Many early references state that the pigment contains manganese. Indeed, all samples examined seemed to have 10 to 1,000 ppm manganese present. Nevertheless, this does not appear to be a characteristic feature. Many sources have long stressed that the pigment is a poor drier in oil. If manganese, which facilitates drying, were present in significant concentration, the slow drying in oils would not be a characteristic.

5.3.4 ***Neutron activation.*** During his association with the National Gallery of Art Research Project at the Mellon Institute in the 1970s, Bernard Keisch analyzed a number of samples of the pigment by using neutron activation analysis. His findings, hitherto unpublished, are given in table 10. Not reported in the table is sodium in the range of 100 to 2,000 ppm, tungsten in the range of 1 to 2 ppm (100 ppm in the lignite sample), potassium in the range of 0.05 to 0.20 ppm, and scandium in the range of 1 to 6 ppm.

5.3.5 ***Mössbauer spectroscopy.*** This measurement reflects the electronic state of iron atoms in iron-containing compounds. Keisch (1973) reviewed the type of spectra that may be obtained from various iron-bearing pigments. The spectrum of Vandyke brown in figure 16 is representative of a type that he called "ME I," typical of very fine particle-sized α-FeOOH. Neutron activation analyses showed that there was only 0.8% to 2% iron in Vandyke brown (see table 10). The type of ME I spectrum was also observed in raw Turkey umber, in a modern Cappagh brown from Winsor and Newton, and in a low-fired terra cotta.

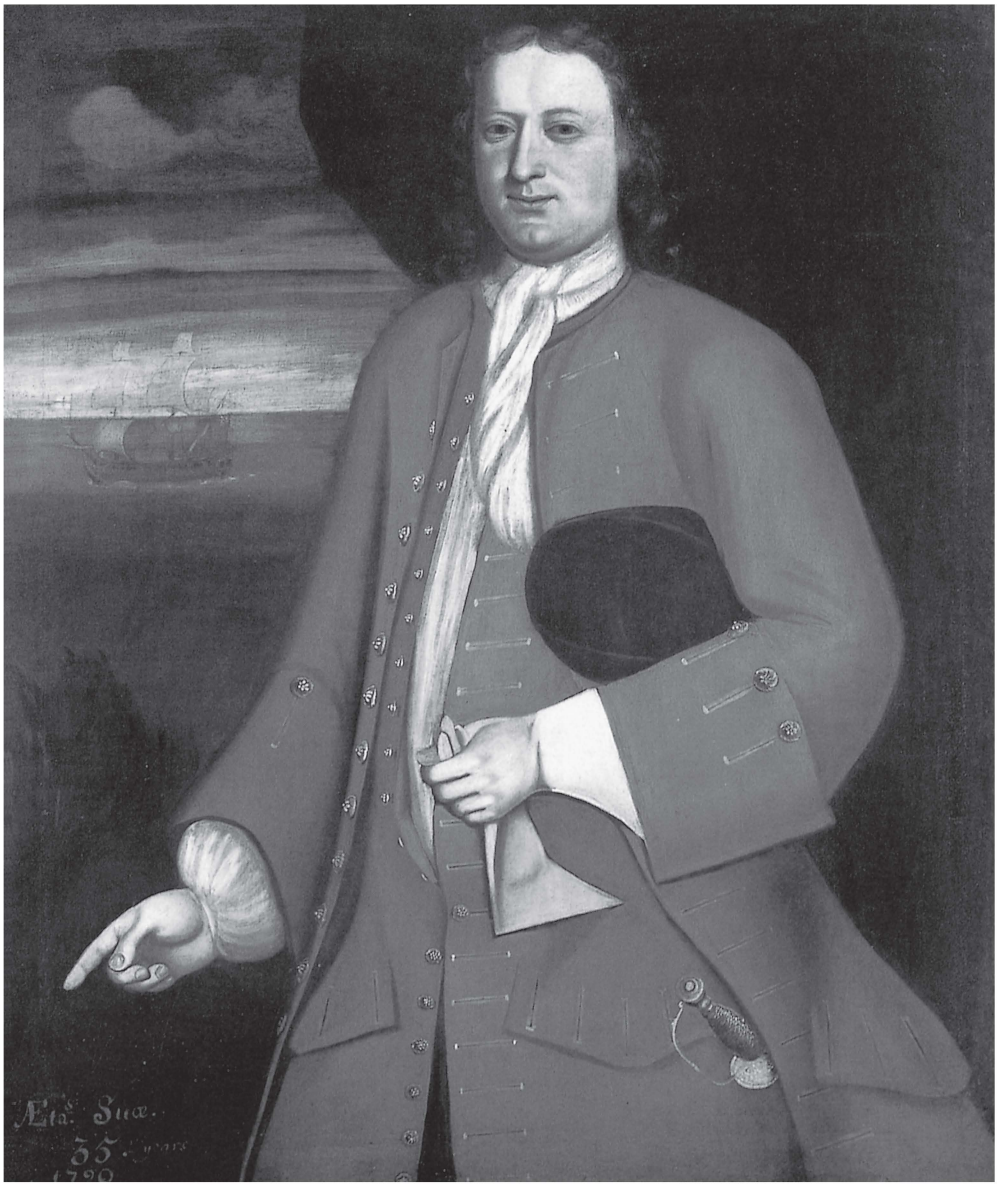


Fig. 14 The ground and shadow in the proper right hand are pigmented with Vandyke brown in *Mr. Willson*, attributed to The Schuyler Limner (possibly Nehemiah Partridge), c. 1720, oil on canvas, National Gallery of Art, Gift of Edgar William and Bernice Chrysler Garbish 1957.11.9.

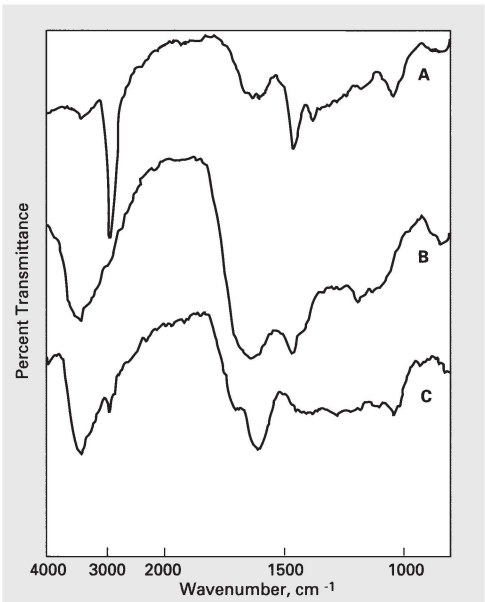


Fig. 15 Comparison of the infrared transmission spectra of three traditional organic brown pigments: (A) bitumen, (B) bistre, and (C) Vandyke brown. From Feller (1972), with permission.

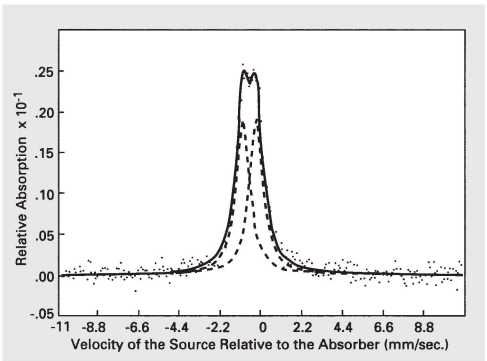


Fig. 16 Mössbauer spectrum of Vandyke brown U-822. From Keisch (1973), with permission.

Fig. 17 Detail of *Mr. Van Vechten* (see also fig. 1). Vandyke brown ground is seen in the dark shadows in the hand.

By Mössbauer spectroscopy, the iron in these pigments is distinguishable from that found in red iron oxides and ochers. The latter, in turn, differ from the spectra of iron in Fe_3O_4. This infrequently employed method of analysis is noted here in the hope that it might prove useful in future studies of this pigment and related iron-bearing materials.

5.4 Criteria for Identification

Because it is largely amorphous and understandably variable in the minor constituents, the positive identification of this pigment is not a straightforward matter. The infrared spectrum is characteristic as described in section 5.3.2. Although the absorptions in the region around 1040 to 1120 cm^{-1} will vary depending on the nature of accessory substances, the most highly probable identification of the presence of a humic earth can be achieved by infrared spectroscopy. This would be especially true if the sample had been dissolved in alkali and either the dried extract or the material that had been reprecipitated by the addition of dilute acid yielded the characteristic absorption spectrum. Bistre tends to dissolve in alkali and has an infrared spectrum that may on occasion appear somewhat similar (see fig. 15).

The infrared spectral evidence should be supplemented by the determination of the following properties by microscopic examination: (1) solubility in alkali yielding a brownish colored solution, (2) irregular particle shape, (3) rich brown color by transmitted light, and (4) little or no birefringence. Sometimes a mottled, very faint red birefringence reminiscent of hematite is seen. Further confirmation using more elaborate tests would involve (5) determination of the ash content, expected to be less than 10%, (6) evidence of α-quartz found by x-ray diffraction, (7) emission

Table 9 **Emission Spectrographic Analyses of Principal Elements Derived from Minerals in Vandyke Brown**[a]

	Commercial Samples					
Element	*G. and E. Habich's*	*W. Hawley and Son*[b]	*Winsor and Newton 234*	*Wilhelm Urban and Co. U-822*	*E. W. Forbes Collection Oberlin 4.05.01*	*John Lucas Company*
Iron	Major	Minor	Major	Major	Major	Minor
Calcium	1,000+	0.1?	10,000+	10,000+	10,000+	10,000+
Silicon	100–1,000	100	1,000+	1,000+	1,000	100
Aluminum	1,000	1,000	1,000++	1,000	100	1,000
Magnesium	10–1,000	10	100	10–100	100	10
Manganese	100	N.S.	1,000	10	10–100	10
Titanium	100	10–100	1,000	100	100	100
Barium	10	10	10	10	10	10
Copper	10	N.S.	1–10	100	100	1–10

N.S.=Not significant
+=Readings in excess of this amount
++=Readings substantially in excess of this amount
a. Values in parts per million. Data from E. Hodge, Mellon Institute, Pittsburgh, Pa.
b. Sample from Czechoslovakia.
c. National Gallery of Art, Washington, Andrew W. Mellon Collection.
d. Abbey Aldrich Rockefeller Folk Art Center, Colonial Williamsburg, Va. (See also fig. 13, showing infrared spectra of samples from portrait of Robert Sanders' brother, *John Sanders*, also in the Abbey Aldrich Rockefeller Folk Center.)
e. Private collection

Table 10 **Neutron Activation Analyses of Vandyke Brown**[a]

	Major Components (%)		*Minor Components (Parts Per Million)*							
Sample	*Iron*	*Calcium*	*Lanthanum*	*Manganese*	*Bromine*	*Arsenic*	*Cobalt*	*Thorium*	*Cesium*	*Titanium*
W. Hawley and Son sample from Czechoslovakia	0.78	11	11.4	4	4	44	12	16	6	40
W. Hawley and Son "Lignite," sample for comparison	1.17	14	28.3	64	16	60	7	93	110	70
Wilhelm Urban *Kasslerbraun* U-822	2.0	14	23	7	5	7	8	27	4	120
G. and E. Habich's *Kasslerbraun* HS	0.77	5	20.4	8	5	4	3	8	2	20
Reichert-Coulston (Imported)	1.21	17	20	17	6	7	7	14	4	60

a. Data provided by Bernard Keisch

Table 9 Continued

Samples from Colonial American Portraits		
Mr. Van Vechten[c]	*Robert Sanders*[d]	*Mr. Van Dyck*[e]
Major	Minor?	Major
10,000+	10,000+	10,000+
100	100	1,000
10	10	1,000++
100	10	100–1,000
100	100	1000
100	10	100–1,000
10	10	10
1–10	10	1–10

spectroscopy or x-ray fluorescence showing iron, calcium, and lower amounts of silicon and aluminum, and (8) carbon and hydrogen analysis yielding 48% to 55% carbon, 4.3% to 5.7% hydrogen. None of the above eight analytical methods alone would yield adequate positive identification. Measurement of the infrared spectra is the preferred method; the others are supplementary.

6.0 **Occurrences**

Because the pigment has been difficult to identify with assurance, few thoroughly documented cases of its presence in works of art can be cited. One of the most extensive series of positive identifications by infrared spectroscopy was carried out by one of the authors on the brown grounds of a series of American paintings of the period from 1800 to 1850 from the Upper Hudson Valley. The brown ground in many of these paintings was found to be part of the dark shadows of the design, as can be seen in the detail (fig. 17) from the Van Vechten portrait (see also fig. 1) (Quandt, 1971). Identification in another painting, *Mr. Willson* (see fig. 13), also by the Schuyler Limner, was by infrared spectroscopy and optical microscopy.

A. Burmester in a personal communication (1993) informed the authors that *Kasslerbraun* has been identified in sixty-one paintings examined at the Doerner Institut, Munich, most of them from the nineteenth century. The formation of a brown solution as the result of treatment of brown amorphous material with dilute sodium hydroxide solution and the detection of iron and manganese by optical emission spectroscopy were the methods customarily used for identification. Thus, Von Sonnenberg (1979) reported the pigment in the palette of Peter Paul Rubens (1577–1640), and Kühn (1977) listed it in the palette of Rembrandt van Rijn (1606–1669). Kühn (1969) also reported finding *Kasslerbraun* in two paintings by A. Wolf from the 1870s in the Schack Galerie, Munich.

There have been a number of occurrences cited in the conservation literature that have undoubtedly relied heavily on the appearance of the pigment by optical microscopy, and on some emission spectrographic or x-ray fluorescence analyses for principal elements. Butler (1976) reported that an organic brown pigment was found in two paintings of 1500 to 1511 attributed to Gerard David (c. 1460–1523). If this instance could be proved unequivocally to be Vandyke brown, it would extend the earliest date of usage considerably.

Butler (1970) also reported the pigment in a painting by Francesco Guardi (1712–1793). Zucker (1980) noted its presence in two eighteenth-century scripture-history paintings from New York State. Newman and McKim-Smith (1982) found an organic brown in paintings by Diego Velázquez (1465–1524). Notable bulk samples were found in a collection of nineteenth-century pigments examined by Richter and Härlin (1974) and in another by Pey (1987). An organic brown was found in a box of watercolor pigments owned by Winslow Homer (1836–1910) (Newman et al., 1980). Carlson and Krill (1978) also reported the presence of Vandyke brown and Cologne earth in two nineteenth-century watercolor boxes in the Henry Francis du Pont Winterthur Museum.

From literary sources, one finds that Moreau-Vauthier (1923) placed the Vandyke brown in the palettes of Jacques-Louis David (1748–1825), J.A.D. Ingres (1780–1867), and Adolphe-William Bouguereau (1825–1905). In *History of Color in Painting*, Birren (1965) cited others who employed it in their palettes: Théodore Gericault (1791–1824), Eugène Delacroix, Jean-Baptiste-Camille Corot (1796–1875), André Derain (1880–

1954), and Giorgio De Chirico (1888–1978). Many of these citations may refer to an iron oxide or ocherish pigment according to the French usage. The pigment was apparently popular among watercolorists; of the forty-six artists in this medium who listed their pigments for Russell and Abney (1888), thirty-three claimed the use of Vandyke brown (Seward, 1889). It has recently been noted that Cologne earth was said to have been used by Thomas Gainsborough (1727–1788) (Bomford et al., 1988). The authors must emphasize, however, that the literary references may be unreliable because of the confusion as to the chemical identification of the pigment called Vandyke brown.

Acknowledgments

The authors wish to thank Josef Riederer, director of the Rathgen-Forschungslabor, Berlin, for supplying a dozen references from the German literature and especially for obtaining samples and information regarding recent sources of the pigment; a letter from Dr. Fischer of Bakelite A.G., Frielendorf, was particularly informative. Also appreciated are the comments of Andreas Burmester, Doerner Institut, Munich, regarding his experience in detecting numerous occurrences of the pigment, in particular by traditional and more recently developed microchemical tests. The authors also are grateful to Gerhardt Kremp, Ralph A. Morgan, and Owen K. Davis of the Department of Geosciences, University of Arizona, for their analyses and discussion of the pollen found in various samples. We appreciate the opportunity given us by Russell and Eleanor Quandt over two decades ago to examine pigments from the grounds of a number of early American paintings, which were in the conservation process. Sidney Pollack reported the trace minerals found by x-ray diffraction. Measurements of color and fading throughout the manuscript were carried out by Catherine Bailie. Numerous references were gathered and checked by Mary Curran. Else Pomerantz provided the translation of the remarks by Simis (1801). Special thanks go to Sandra Melzer for typing and carefully shepherding the manuscript through numerous drafts.

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7
Prussian Blue

BARBARA H. BERRIE

1.0 **Introduction**

Prussian blue, introduced in the early 1700s, has been called the first of the modern pigments. It has been described as "a rich and fascinating pigment to the colorist, but not to be depended upon; and yet difficult to avoid" (Linton, 1852).

Until recently, Prussian blue was a widely used pigment and many varieties are available. Some examples are potash or non-bronze blues, bronze blues (used in printing inks), and dispersible blues. After c. 1730 its manufacture was widespread. The addition of extenders such as barium sulfate ($BaSO_4$) or calcium sulfate dihydrate ($CaSO_4.2H_2O$) provide variations, leading to a series of pigments sometimes called Brunswick blues (Hasluck, 1916).

Prussian blue was widely used in the past; after 1970, however, it has often been replaced as an artists' pigment by phthalocyanine blue.

1.1 **Pigment Definition**

Prussian blue is a hydrated iron hexacyanoferrate complex. Sometimes the chemical formula contains no other elements; at other times sodium, ammonium, and/or potassium ions are included. Prussian blue is listed as CI Pigment Blue 27 in the *Colour Index* (1971); CI no. 77510 is $Fe_4[Fe(CN)_6]_3.xH_2O$ and CI no. 77520 is $KFe[Fe(CN)_6].xH_2O$. The generic term iron blue is now used for all types of Prussian blue. Iron blues have a wide diversity of hue and handling properties because of the variety of manufacturing processes, although all modifications are chemically similar.

1.2 **Current Terminology**

English: Prussian blue, iron blue
German: Preussisch Blau, Berlinerblau, Pariserblau, Turnbullsblau
Russian: берлинская лазурь
French: bleu prussien, bleu de Prusse
Italian: azzurro di Prussia, azzurro di Berlino
Spanish: azul de Prusia, azul de Berlin
Japanese: konjō, berensu
Chinese: yang lan (pinyin and Wade-Giles)

Particularly in the United States Prussian blue is now known as iron blue, which covers all formulations of ferric ferrocyanide and alkali ferric ferrocyanide (see section 4.0). Milori blue is another commonly used name. Names in *Chemical Abstracts*, registry no. 12240-15-2, for Prussian blue are ammonium Prussian blue, Ariabel dark blue 300308, Berlin blue, Chinese blue, iron blue, Milori blue HCB, Milori blue 690, Paris blue (6CI), and radiogardase. Gleason et al. (1969) also gave lacquer blue as a synonym. Other names for Prussian blue in Gardner et al. (1978) are American blue, Antwerp blue, Berlin blue, Chinese blue, Erlangen blue, gas blue, Hamburg blue, Milori blue, mineral blue, new blue, oil blue, Paris blue, paste blue, and steel blue. Companies producing Prussian blue often name their own formulations; for example, the term Vossen blue is used by Degussa, and Manox iron blue no. 298 is used by Manox, Ltd. (now known as Manchem). Milori blue, described as a pale non-bronze blue, is a potash blue and Chinese blue is termed a bronze blue.

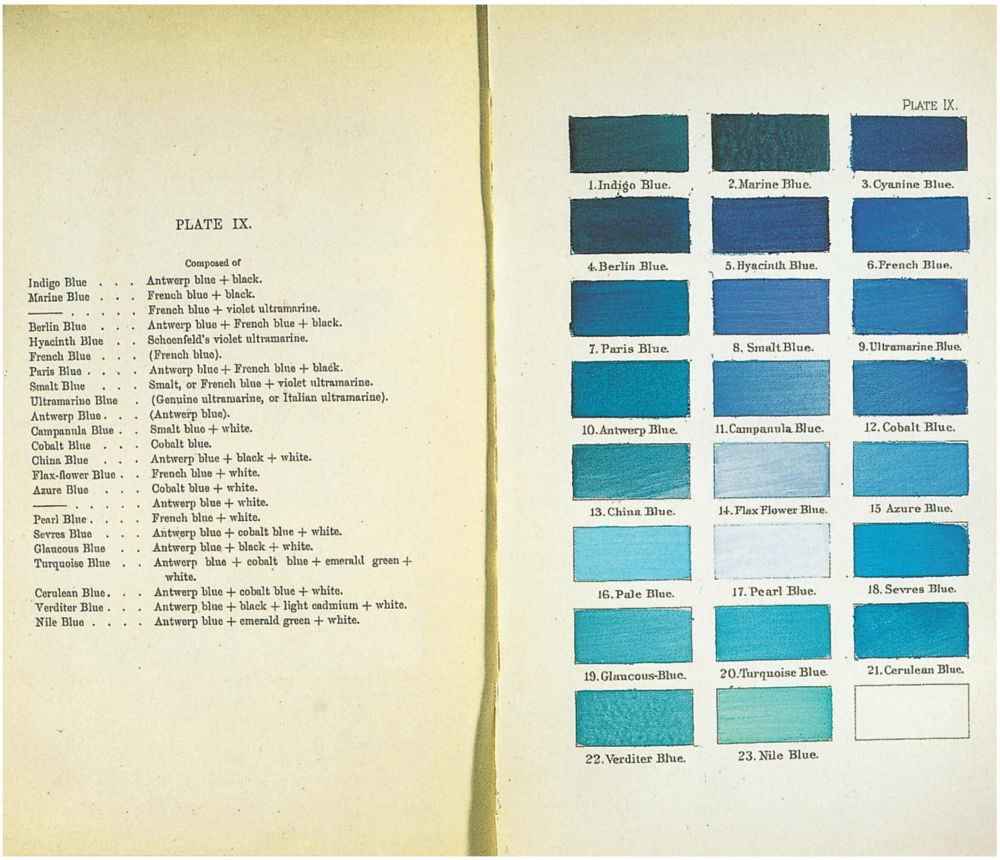


PLATE IX.

	Composed of
Indigo Blue	Antwerp blue + black.
Marine Blue	French blue + black.
——	French blue + violet ultramarine.
Berlin Blue	Antwerp blue + French blue + black.
Hyacinth Blue	Schoenfeld's violet ultramarine.
French Blue	(French blue).
Paris Blue	Antwerp blue + French blue + black.
Smalt Blue	Smalt, or French blue + violet ultramarine.
Ultramarine Blue	(Genuine ultramarine, or Italian ultramarine).
Antwerp Blue	(Antwerp blue).
Campanula Blue	Smalt blue + white.
Cobalt Blue	Cobalt blue.
China Blue	Antwerp blue + black + white.
Flax-flower Blue	French blue + white.
Azure Blue	Cobalt blue + white.
——	Antwerp blue + white.
Pearl Blue	French blue + white.
Sevres Blue	Antwerp blue + cobalt blue + white.
Glaucous Blue	Antwerp blue + black + white.
Turquoise Blue	Antwerp blue + cobalt blue + emerald green + white.
Cerulean Blue	Antwerp blue + cobalt blue + white.
Verditer Blue	Antwerp blue + black + light cadmium + white.
Nile Blue	Antwerp blue + emerald green + white.

PLATE IX.

1. Indigo Blue. 2. Marine Blue. 3. Cyanine Blue.
4. Berlin Blue. 5. Hyacinth Blue. 6. French Blue.
7. Paris Blue. 8. Smalt Blue. 9. Ultramarine Blue.
10. Antwerp Blue. 11. Campanula Blue. 12. Cobalt Blue.
13. China Blue. 14. Flax Flower Blue. 15 Azure Blue.
16. Pale Blue. 17. Pearl Blue. 18. Sevres Blue.
19. Glaucous-Blue. 20. Turquoise Blue. 21. Cerulean Blue.
22. Verditer Blue. 23. Nile Blue.

Fig. 1 Colors painted out, showing the wide variety of colors that can be achieved using Prussian blue in mixtures and also the historically lax use of descriptive names. From Robert Ridgway, *A Nomenclature of Colors for Naturalists and Compendium of Useful Knowledge for Ornithologists*, Little, Brown, and Co. (Boston, 1886).

2.0 **History**

2.1 **Archaic and Historical Names**

Prussian blue has had many names (fig. 1). Some of these names indicate the variety of physical properties Prussian blue may have depending on the conditions of its manufacture; others represent colors that are pigment mixtures containing Prussian blue. During the early use of Prussian blue, attempts were made to distinguish ferric ferrocyanide from ferrous ferricyanide and different names were suggested for the different compounds. It is now known that there is no chemical difference between them (Robin & Day, 1967).

Early names for Prussian blue, especially in Germany, suggest places of manufacture; thus, Erlangen blue, Hamburg blue, Paris blue, and others were all Prussian blue. Names applied to Prussian blue and its mixtures that give blue pigments have included bronze blue, celestial blue, cyanine, French blue (a term more frequently used to describe synthetic ultramarine), Haarlem blue, Leitch's blue, oriental blue, Persian blue, potash blue, soluble blue, soluble Turnbull's blue, toning blue, Turnbull's blue, and Williamson's blue. The name gas blue may be from the large-scale production of Prussian blue as a byproduct of gas manufacture (Hasluck, 1916). "Artificial

Saxon blue" was prepared by "mixing a divided earth with Prussian blue at the moment of its formation and precipitation" (Tingry, 1830). The term Saxon blue was also used for smalt and for an indigo solution in sulfuric acid.

Various forms of the pigment contain starch and/or alumina (Al_2O_3). Prussian blue mixed with extenders such as barytes ($BaSO_4$) or pipe clay has been called mineral blue and Brunswick blue (Bersch, 1901). Bersch described Antwerp blue as a mixture of Prussian blue and alumina. Field (1845) described Antwerp blue and "Haerlem" blue as being brighter than Prussian blue as "they are a ferroprussiate of alumine." Harley (1982) quoted John Payne, who wrote in 1788 that Antwerp blue was a term applied to iron- and copper-containing compounds mixed with a white pigment.

Riffault et al. (1874) described Antwerp blue and mineral blue as mixtures of Prussian blue, alumina, magnesia, and zinc oxide. However, the name mineral blue has also been used to describe white earths (such as kaolins) colored with indigo and hydrated copper oxide. These authors also described how mixing "yellow prussiate of potassa, perchloride of iron, chloride of barium, and sulphate of ammonia" leads to the production of "celestial or Marie-Louise blue." Heaton (1947) described celestial blue and daylight blue as pale tints prepared by precipitating 5% to 10% of Prussian blue on barytes. Cyanine and Leitch's blue were said to be mixtures of Prussian blue and cobalt blue (Fischer, 1930; Gleason et al., 1969). Oriental blue is a mixture of ultramarine and Prussian blue (Crown, 1968). Native Prussian blue was a term applied to "a blue phosphate of iron found in Cornwall [England] and North America" (*Handbook of Young Artists*, 1854); it has also been identified as what is probably the same material, the mineral vivianite, a hydrated iron phosphate (Booth & Morfit, 1872). In a 1754 newspaper advertisement placed in *The New York Gazette*, G. Duychkinck described for sale, "Just imported in the last ships from London . . . Smalt's Prusian blue" (Gottesman, 1938).

Other names given by Bersch (1901) include: "*bleu de Paris, bleu de Berlin, bleu d'Anvers, Sächsischblau* [Saxon blue], *Neublau, Oelblau, Wasserblau, Mineralblau, Erlangerblau, Zwickauerblau, Waschblau, Louisenblau*, [and] *Raymondblau*. The term *Antwerpener blau* is used in German for the pigment reduced with a white extender."

Nineteenth-century French names for Prussian blue are *bleu de flore*, *bleu de gaze*, and *bleu d'acier* (Colinart, 1988). Names given to the pigment mixed with other compounds include: *bleu de Charron* (with barium sulfate), *bleu mineral* (with barium sulfate and kaolin), *bleu de France* (with alumina), and *bleu de fécule* (with starch). *Bleu de Charron* was one of the pigments Gauguin ordered from Paris while he was in Tahiti (Rewald, 1943). *Bleu de Bâle*, which was used for painting and laundry whitening, was a name for a mixture of Prussian blue, barium sulfate, and starch.

An early nineteenth-century collection of pigments in the Netherlands contains several examples of pure and mixed Prussian blue, all with different names (Pey, 1987). Richter and Härlin (1974a, b) analyzed the contents of nineteenth-century German and Swiss paint boxes and found the following German names for pigments that contained Prussian blue in mixtures with white pigments and extenders: "*Ferrum hydrocyan . . ., Berliner Blau, echtes helles Pariser Blau, Pariser Blau, Mineralblau, 'Mineral Blau, Bergblau, Kupferlasur*, and Indigo 21.'"

2.2 History of Use

Until recently, Prussian blue was an extremely popular pigment. Its first synthesis is shrouded in mystery; however, it is clear that there was a very short time between the discovery of Prussian blue in 1704 or shortly thereafter, and its use as an artist's pigment. Diesbach, a color maker working in Berlin, is credited with the first preparation. Serendipity played its part when Diesbach used alkali prepared from "animal oil" by an alchemist named J. C. Dippel. Stahl (1731) wrote:

> The pigment maker Diesbach used to make Florentine lake by boiling cochineal, adding alum and some ferrous sulfate, and precipitating this with fixed alkali (potash). One day when he ran out of alkali he borrowed some from J. C. Dippel, in whose laboratory in Berlin he was working. Dippel gave him some alkali he had repeatedly distilled from his animal oil and no longer was usable for this purpose. To Diesbach's surprise, when he used this a very beautiful blue pigment appeared, instead of the red color that he expected.

The first written reference to Prussian blue was in an anonymous paper in Latin, "Notita Coerulei Berolinensis nuper inventi" in 1710, which has been translated by Jo Kirby and Raymond White (Kirby, 1993).

Apparently, Diesbach communicated the method of manufacture of Prussian blue to his

pupil, de Pierre, who began to manufacture it in Paris (Bearn, 1925). Simon Eikenlenberg, a Dutch painter, wrote in *Notes on Paint and Painting* that in 1722 Joan George Collazius announced that he had for sale "the genuine Prussian blue of Mr. Mak from Leipzig" (Buck, 1965). By 1724 the preparation of Prussian blue was known in England and was published by Woodward (1724). Preparation of the pigment involved heating equal amounts of saltpeter (KNO_3) and potassium tartrate in a red-hot crucible and then adding dry, powdered cattle blood and heating the mixture to incandescence. The resulting mass was washed with water; the wash water was then treated with a solution of alum ($K_2SO_4.Al_2(SO_4)_3.24H_2O$) and ferrous sulfate. A greenish precipitate turned blue on addition of hydrochloric acid. In his second edition of *The Handmaid to the Arts*, Dossie (1764) quoted entirely Woodward's preparation of Prussian blue. The recipe had been omitted from the first edition; however, in 1764 its importance warranted its inclusion along with other recipes.

There was significant interest in the chemistry of Prussian blue following its discovery, with substantial research immediately undertaken. Brown (1724/1725) showed that iron was necessary for the blue color. Von Delius (1778) reported in a footnote, "D. Krüniz has provided a list of the most important authors on Berlin or Prussian blue accompanying a translation of an article by Scopoli in the latest *Hamburgischer Magazin* VII, vol 41, p 432, new series."

The pigment enjoyed immediate popularity worldwide and was soon sold not only in Europe but also in America, where it was used as early as 1723 for interior painting (Batcheler, 1981). In 1748, John Humble of New York was selling Prussian blue newly imported from London (Gottesman, 1938). By 1761 "various sorts" of Prussian blue were available for sale (Dow, 1927).

Prussian blue was being produced in Gorodets, Siberia, before 1778, where the manufacturer sold it and also used it for printing calico (Von Delius, 1778). Although Dossie (1764) noted that Prussian blue was available from many sources, he indicated it was best prepared by the artist to ensure purity and quality of the product. In 1770 a pound of Prussian blue manufactured in England sold for two guineas. Prussian blue made in America was less expensive, apparently because its indigenous raw materials were less expensive (Coleby, 1939).

As early as 1720, the Japanese traded with the Dutch through the port of Nagasaki (Akiyama, 1961). Sasaki (1985) stated that Prussian blue has been extensively used in Japan since 1829. Prussian blue has been found in early nineteenth-century Japanese prints and paintings, when it began to supplant the use of indigo (E. W. Fitz-Hugh, personal communication, 1988). The use of Prussian blue in Japanese paintings and printmaking is not well documented. It has been said that use of the imported pigment began in 1825 in Osaka and in 1828 in Edo (Tokyo) (Keyes, 1989). Two Japanese names for Prussian blue indicate its origin: *berensu* probably comes from *Berlinerblau* (K. Yamasaki, Nagoya University, personal communication, 1978); *herorin* means from Berlin (Sasaki, 1985).

Dossie (1764) wrote that Prussian blue could be used as a watercolor, but it first had to be ground to an "impalpable powder." Bowles (1800) described its use in oils, watercolors, reverse glass painting, and pastels; he gave instructions on how to prepare it, including the use of "white beer" for making Prussian blue pastels and inks.

European easel paintings examined by Kühn (1970) showed a steady increase in the use of Prussian blue following its introduction in the early 1700s to 1800. Prussian blue was listed in 1886 by the German Society for the Advancement of Rational Painting, Munich, as a pigment to use. In the nineteenth century, Lloyds (n.d.) described Prussian blue as "a powerful blue, hitherto scarcely used in distemper, but likely to be of much use," adding that Prussian blue required "good grinding."

A list of watercolors sold by Winsor and Newton in 1878 included both dry and moist Antwerp blue, Prussian blue, Hooker's green no. 1 and no. 2, and Prussian green. The greens are Prussian blue and gamboge mixtures.

Prussian blue has also been found mixed with Naples yellow, yellow ocher, chrome yellow, and cadmium yellow to give green paint (see section 4.4). Prussian blue mixed with bone black was used to produce intensely black shades (Toch, 1925).

An important early use of Prussian blue was in house paints and wallpapers. J. P. Maquer, a chemist who experimented with Prussian blue, reported it was also used as early as 1749 for dyeing fabrics (Vitalis, 1842). It was extensively used as a direct dye for silk. The process involves

"impregnating the fibres with potassic iron cyanide and then dipping them in $FeCl_3$, so the blue colour is precipitated inside the fibres" (Brunello, 1973). For calico printing, Porter (1830) described the process:

> Print the cloth in the mordant for a black; age one week, and dung the pieces as for madder colours; then winch them in a solution of prussiate of potash slightly acidulated with sulphuric acid . . . the prussiate is decomposed by the sulphuric acid, which unites with the potash, forming sulphate of potash, and the disengaged ferrocyanic acid combines directly with the peroxide of iron, forming the beautiful compound, so well known as a pigment, prussian blue, or the ferrocyanate.

Prussian blue was used for cyanotypes, which were an early form of photograph and the precursor of blueprints. The cyanotype process had been discovered in 1842 by John Herschel (Crawford, 1979). The paper was treated in the dark with a solution of ammonium ferricyanide and ferric citrate. On exposure to light, iron(III) is reduced by the citrate ion to iron(II) with the formation of Prussian blue. The print is fixed by washing out unreacted material with water (Latimer & Hildebrand, 1951). Prussian blue has also been used to color linoleum, leathercloth, plastics, laundry bluing, fungicides, cosmetics, automotive paints, and coatings, and has histological uses.

Prussian blue, when dissolved in oxalic acid, has been used as an ink. It was also added to iron gall inks to give them their initial dark color. Prussian blue has been extensively used in printers' inks although its use has declined since the introduction of aniline dyes. *The Printing Ink Manual* by Bisset et al. (1979) discusses use of Prussian blue in printing inks. Prussian blue is also used to color paper; for this purpose it can be ground with a water-soluble material such as dextrin or casein and applied to the paper, which is then smoothed. A bulk aqueous process for coloring paper may also be used (Degussa, 1974).

In 1939 in the United States, more than seven million pounds (over 3,000 metric tons) of Prussian blue were produced as a blue colorant, and a further two million pounds (900 metric tons) were used in mixtures to make green (Holtzman, 1945). Fifty thousand metric tons were used annually in Western nations (Ludi, 1988).

2.3 Dates of Use

Prussian blue has been widely distributed since the early 1700s and was one of the most commonly used blue pigments until about 1970; phthalocyanine blue is now often used in its place.

3.0 General Pigment Properties

3.1 Color and Spectral Reflectance

The origin of the color of Prussian blue is an electronic transition from a low-spin Fe^{2+} ion in a carbon-coordination center to a high-spin Fe^{3+} ion in a nitrogen-coordination center that occurs when visible light is absorbed at 680 nm (ε=9800 mol^{-1} cm^{-1}) (Robin & Day, 1967). This absorption, called the intervalence transfer band, produces the intense color of Prussian blue. Although Prussian blue is intensely deep blue, it can have reddish or green undertones, depending on preparation conditions such as the oxidizing agent, reactant concentrations, pH, temperature, and batch size. The name Chinese blue is used for preparations that are deep jet blue and have a greenish undertone. The name Milori blue is used for those pigments that are less jet blue and more plum colored, with a redder tint. Today, manufacturers often give numbers rather than names to their formulations that have different optical, as well as physical, properties.

Iron blues tend to bronze, especially on environmental exposure. Bronzing occurs because the refractive index of the pigment blue rises rapidly at the red end of the spectrum and is most readily perceived when the paint is observed at near-glancing angles (McLaren, 1983). Bronzing is most noticeable in the pure and nearly pure pigment and is more pronounced in the Chinese blues (Legnetti, 1984; see also section 3.3). The bronze tone is prized in some applications such as printers' ink.

Figure 2 shows paint outs of Prussian blue in pure form, and in mixtures with lead white (Cremnitz white) and with yellow pigments to make green. Field (1850) described Prussian blue as:

> a rather modern pigment . . . of a deep and powerful blue colour, of vast body and considerable transparency, and forms tints of much beauty with white lead, though by no means equal in purity and brilliancy to those of cobalt and ultramarine, nor have they the perfect durability of the latter.

Ruhemann (1982) suggested Prussian blue as a pigment for retouching as "it replaces the more fugitive indigo and, to some extent in mixtures, blue copper pigments such as azurite and blue bice." McLaren (1983) reported that a tube of paint containing only Prussian blue would have to be labeled "black" to avoid infringing on trade description acts because of the intensity of its color.

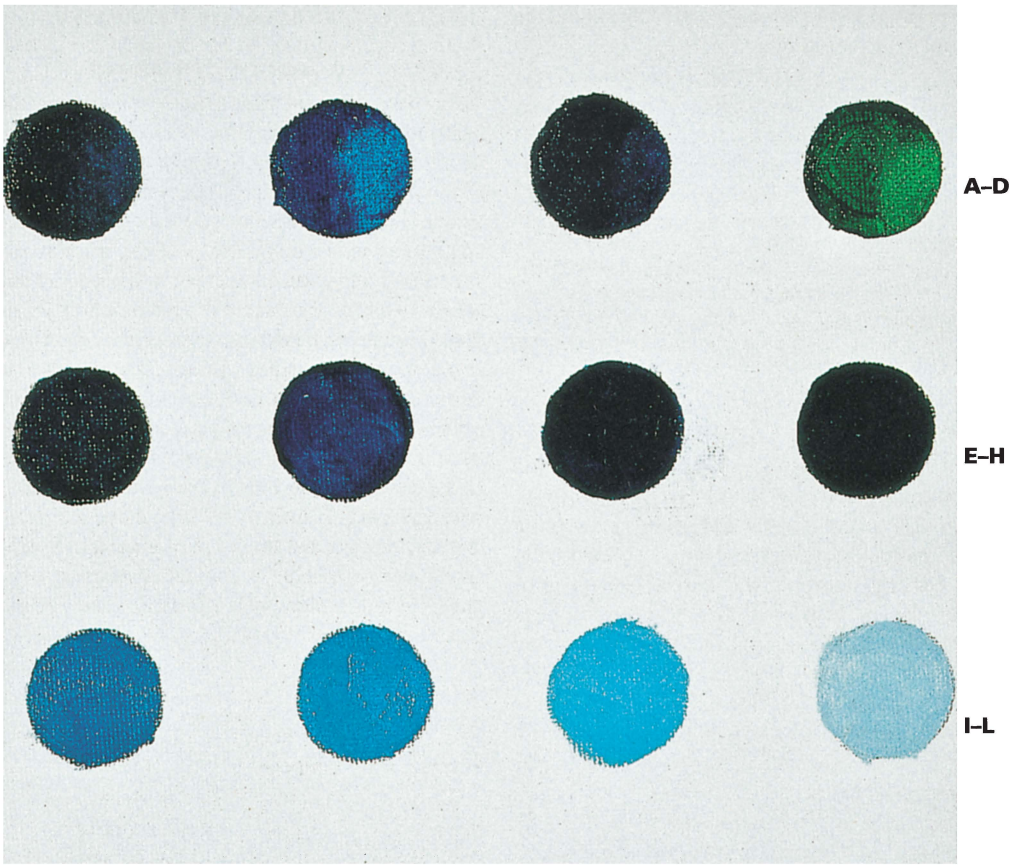


Fig. 2 Paint outs showing Prussian blue, pure and in mixtures.
Top row, left to right:
A. Winsor and Newton, Artists' Oil Colour Prussian Blue.
B. Winsor and Newton, Oil Colour Antwerp Blue.
C. Rembrandt, Oil Colour Prussian Blue.
D. Grumbacher, Artists' Oil Colors Pre-tested Prussian Green.
Middle row, left to right:
E. Winsor and Newton, Griffen Alkyd Colour Prussian Blue.
F. Winsor and Newton, Artists' Water Colour Antwerp Blue.
G. Winsor and Newton, Water Colour Prussian Blue.
H. Winsor and Newton, Artists' Water Colour Prussian Green.
Bottom row, left to right:
Winsor and Newton, Artists' Oil Colour Prussian Blue mixed with Winsor and Newton, Artists' Oil Colour Cremnitz White (lead white) in various ratios.
I. 1:2.
J. 1:6.
K. 1:150.
L. 1:600.

In figure 3 the spectral reflectance of three samples of Prussian blue are shown, and the variation of the spectrum of the blue pigment diluted with white is shown in figure 4. The relatively low transmittance in the long wavelength region of the visible spectrum is characteristic of all types of iron blue.

3.2 Tinting Strength and Infrared Absorbance

The tinting strength of Prussian blue is high, especially compared to other low refractive index pigments; Hurst (1902) indicated that "one half an ounce will tint 20 pounds of lead white a perceptible blue."

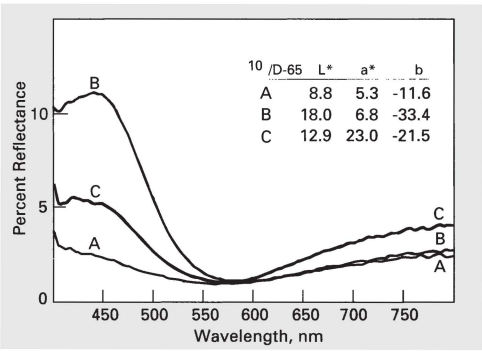


Fig. 3 Reflected-light dark-field spectra of three Prussian blue samples. The spectra were obtained of dry samples that were mounted on flat black paper. A Leitz Orthoplan microscope, with MMPV–SP microspectrophotometer and a quartz halogen lamp at 2,800 K, was used. Calculated L*a*b values are given for the powders for a 10° observer and a D-65 illuminant. (A) Conservation Materials, Ltd. (B) Winsor and Newton (C) Aldrich Chemical Company. From John Ossi, Bunton Instruments, Rockville, Md.

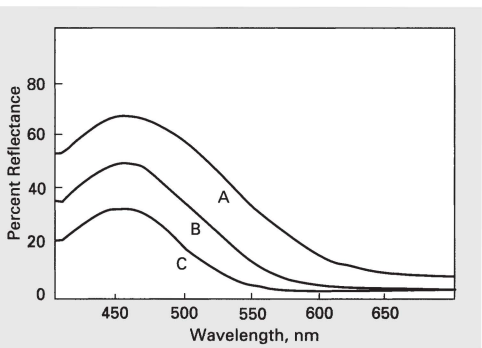


Fig. 4 Spectral reflectance of paint made from Prussian blue mixed with white. Based on information from Manox Ltd. (A) 35% Prussian blue (B) 15% Prussian blue (C) 5% Prussian blue.

The refractive index of Prussian blue is 1.56 in blue light (McCrone et al., 1973). This relatively low value makes it a transparent pigment useful for glazing. Prussian blue has extremely high absorbance in the photographic infrared region of the spectrum of 700 to 900 nm. Less than 1% Prussian blue added to a strongly reflecting white surface reduces its reflectance by 50% (Taylor, 1958). Therefore, even pale blue tints such as Brunswick blues are strongly absorbing in the infrared region. Figure 5 shows this effect in *La Mousmé* by Vincent van Gogh. Neither the color picture (fig. 5A) nor the black and white photograph (fig. 5B) provide strong evidence for the use of two different blue pigments; however, the infrared photograph (fig. 5C) clearly shows this to be the case. Pigments that strongly absorb infrared radiation appear dark in the infrared photograph. The short blue line below the upper lip, the light blue shadow on the white collar, the first and third blue stripe on the proper right side of the jacket are all very dark in infrared illumination. This implies that Prussian blue is present. However, other blue stripes in the jacket are pale in infrared and the skirt has two tones on the background. From this it is evident that Van Gogh had at least two different blues on his palette. The green leaves of the bunch of flowers being held are very dark in infrared illumination; from this we may deduce that the leaves are perhaps a mixture of Prussian blue and a yellow pigment. For the pigment's electronic spectrum see section 5.3.3.

3.3 **Permanence**

Prussian blue has been described as being both permanent and impermanent.

Delaval (1785) wrote that "Prussian blue . . . was discovered by an accidental mixture of the ingredients, which enter into the composition of it. Nor is it so durable as the blue paints, which were in use before its introduction." Field (1845) indicated that Prussian blue was not noted for its permanence. Toch (1925) reported that Prussian blue is not part of the permanent palette and should be avoided, especially in mixtures. However, he considered it useful, mixed with zinc white for sky tones and indicated it is permanent when used unmixed, unglazed, or varnished. He also reported that when mixed with media such as copal or megilp, Prussian blue turns green. Megilp is a mixture of resin, often mastic, and oil and was used as a paint medium, especially in the nineteenth century. Toch mentioned that when Prussian blue is mixed with lead white discoloration occurs and often a greenish tone develops. However, the greenish tone may be a consequence of the yellowing of the medium rather than the pigment.

Iron blues are chemically reduced in the presence of oxidizable media and when stored tend to lose their color. Color loss is corrected when the paint is brushed out and exposed to air, which causes reoxidation of Prussian blue. Decoloriza-

Fig. 5 A. Vincent van Gogh, *La Mousmé*, 1888, oil on canvas, Chester Dale Collection, National Gallery of Art, Washington 1963.10.151.

B. Viewed under normal light.

C. Infrared photograph. A Wratten 70 (660–900 nm) filter was used on the camera lens.

tion of Prussian blue on exposure to light and the return of blue color on storage in the dark was first noted by Franz Fernback in 1834 (Kirby, 1993) and later by Field (1845). Kirby (1993) investigated the fading and color changes of early examples of Prussian blue.

Prussian blue is considered permanent based on experiments using full-strength color paint outs. However, Levison (1976) pointed out that this pigment is inappropriate for artists since it is well known that while Prussian blue is permanent when pure, it is not when mixed with white pigments. The permanence rating drops from eight (permanent) when pure, to only four when mixed 1:10 with titanium white (TiO_2) (Degussa, 1974). In their literature on permanence, Winsor and Newton listed both Antwerp blue (iron blue mixed with alumina) and Prussian blue as class A durable watercolors. As an oil color, Prussian blue is rated class A, durable; Antwerp blue is rated class B, moderately durable; both colors have a lightfastness rating, per ASTM D4302, of 1 (1990b). Levison (1976) listed tristimulus values for Prussian blue in an oil vehicle as X=32.12, Y=34.79, Z=67.77; the values changed after exposure to the Florida sun (25,000 Langleys) to X=32.42, Y=35.16, Z=67.38. Whitmore and Cass (1988) showed Prussian blue to be moderately stable in the presence of ozone and further indicated (1989) it is stable in the presence of nitrogen dioxide.

Standardization of its preparation and differences in care taken by various manufacturers have caused variations in Prussian blue's permanence. Harley (1982) quoted a description of the appearance of yellow when water was applied to Prussian blue watercolor cakes. The yellow must have been a water-soluble impurity, possibly yellow prussiate of potash, which is potassium ferrocyanide. Earlier preparations of Prussian blue may have been less permanent than modern preparations due to a higher proportion of adsorbed impurities caused by less efficient washing of the final product or using less pure starting materials.

3.4 **Chemical Properties**

From the time of its invention, Prussian blue was widely studied by chemists. Coleby (1939) summarized early work on its chemistry. Prussian blue can be either an insoluble polymeric ferric ferrocyanide or an alkali ferric ferrocyanide (see section 4.1). It is a stable inert transition metal complex, of the class termed type II mixed-valence and has semiconductor properties. Its room temperature resistivity is 10^7 ohm cm

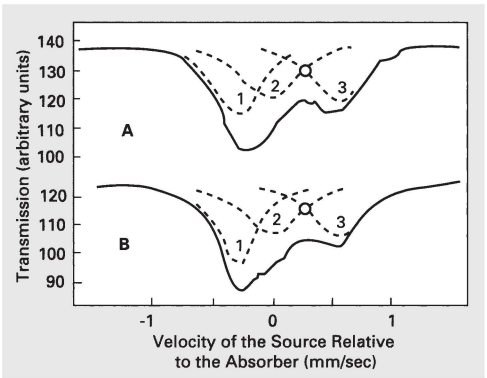


Fig. 6 Mössbauer spectra at –130°C of (A) insoluble Prussian blue and (B) Turnbull's blue. The ratio of Fe^{2+} to Fe^{3+} for both types of Prussian blue is 3:4. The solid lines are the experimental data. Curves 1, 2, and 3 are calculated for the $[Fe(CN)_6]^{4-}$ moiety (1), and the Fe^{3+} ion with quadruple splitting (2 and 3). The ratio of the intensity of the lines 1:(3+4) is close to the theoretical value 0.75 expected from the empirical formula of Prussian blue. Adapted, with permission, from Fluck et al. (1963).

(Robin & Day, 1967). The compound exhibits ferromagnetic behavior at extremely low temperatures, below –267°C.

Prussian blue dissolves in concentrated mineral acids, in 10% oxalic acid, and with decomposition in dilute alkali. It is resistant to dilute (10%) mineral acids, polar and nonpolar solvents, fatty acids, drying oils, and plasticizers, and it has excellent bleed resistance. It is stable to at least 140°C; it may ignite at higher temperatures. The ASTM D93-52 (1990a) standard for Prussian blue is a flash point of 600°C to 615°C. Hydrogen cyanide is evolved when hot sulfuric acid is added to Prussian blue. Prussian blue is zeolitic, that is, it acts like an ion-exchange resin, and readily exchanges group I cations, that is, lithium, sodium, potassium, rubidium, and cesium.

Mössbauer spectroscopy (Fluck et al., 1963) (fig. 6) and photoelectron spectroscopy (Wertheim & Rosencwaig, 1971) show that low-spin iron(II) is coordinated octahedrally to six carbon atoms and high-spin iron(III) to the six nitrogen atoms of cyano groups. The electrochemistry of Prussian blue has been reviewed by Itaya et al. (1986). Other information on the chemistry of this compound is found in Gmelin (1932).

Prussian blue may be oxidized to give a dark brown ferric complex, $FeFe(CN)_6$, which is subject to autoreduction. This formula has also been given to a salt referred to as Everitt's green. Chadwick and Sharpe (1965) suggested that Everitt's green (also called Berlin green) is, in fact, a product of partial reduction of the completely oxidized brown material, the intensity of the green color implying the presence of at least low concentrations of Fe(II).

3.5 Compatibility

Prussian blue is very sensitive to alkali and cannot be used in fresco or alkaline media such as lime paints, sodium or potassium silicates, alkaline polymer emulsions, or casein paints. The use of any alkaline material such as a soap or ammonia in cleaning areas that were painted with Prussian blue is likely to be detrimental.

Hasluck (1916) warned against using Prussian blue in distemper for the walls of new buildings containing lime or whiting as the alkali will turn the blue into a "dirty-brown colour." No studies on the effect of paper deacidification on the color of Prussian blue appear to have been published. Since Prussian blue was used to tone paper, a test should be made before using alkaline materials in treating blue paper or watercolors. The literature frequently reports that Prussian blue can be mixed with all pigments except those that are alkaline—specifically calcium carbonate and lead white—although there is little evidence of any detrimental interaction in modern formulations. The decolorization of Prussian blue in mixture with zinc white was described by Kühn (1986). Prussian blue mixed with zinc yellow to give "zinc green" is converted to zinc ferrocyanide, thereby destroying the paint's color (Gob, 1955). Porter (1830), when he described Prussian blue's use as a dye for calico (see section 2.2), indicated that Prussian blue lacked the essential fast dye requirement of "resisting the action of alkalies and soaps." The sensitivity of Prussian blue to alkali is exploited for microchemical testing to identify the pigment (see section 5.2). In modern formulations of Prussian blue the addition of nickel improves its resistance to alkali.

3.6 Oil Absorption and Grinding Properties

The oil absorption of Prussian blue during grinding varies depending on the quality and type of Prussian blue used. Treatment with surfactants can effect drastic changes in the physical properties of Prussian blue, including oil absorption. Technical data supplied by Degussa (1974) showed a variation in oil absorption depending

on the type of Prussian blue used, with a range of oil absorption for each formulation. The total variation for oil absorption of all types of Prussian blue was from 40 to 72 ml of oil per 100 g Prussian blue. The *Kirk-Othmer Encyclopedia* (1978) listed 35 to 56 g oil absorbed per 100 g of Prussian blue. The National Institute for Standards and Technology (formerly, National Bureau of Standards) requirement for Prussian blue is a minimum of 48% by weight of Prussian blue in linseed oil. A large proportion of poppy-seed oil, 65% to 110% (that is, 65 to 110 lbs. per l00 lbs. Prussian blue), is required (Wehlte, 1975). The high proportion of oil required to produce a workable paint, combined with the low refractive index of Prussian blue, means that visible changes in the color of the medium are easily perceived and changes in the color of the paint are often due to changes in the medium and not the pigment itself.

It is difficult to mix Prussian blue in water-based paints and therefore artists frequently add alcohol to help form a good paint. If alcohol has not been added, the particles of Prussian blue tend to "float" on the surface. Manufacturers use polyalcohols and surfactants to produce workable paints.

Prussian blue is a hard material and very difficult to grind. During grinding, care must be taken to avoid overheating as it may possibly ignite. The formulation produced by the A. Milori Company, Paris, was the first to provide an easily worked material. The differences in working properties and texture of different preparations usually depend on the handling of the immediately precipitated material since it tends to agglomerate rapidly. High moisture content makes it easier to produce smaller aggregates of the pigment. It is thought that some of the problems in grinding result from unremoved impurities that include excess starting material. Treatment with surfactants helps to remove impurities but markedly affects the physical properties of the pigment. Adding aluminum stearate to Prussian blue oil paint provides a smooth and workable texture (*Kirk-Othmer*, 1978).

3.7 **Toxicity**

In 1710, Prussian blue was said to be nonpoisonous, as it contained no arsenic and was therefore recommended not only for painting but also as a medicine. Prussian blue is used as a medicinal antidote to radioisotope and heavy-metal poisoning (see, for example, Simonovic et al., 1986).

Prussian blue is not listed in the 1982 *Registry of Toxic Effects of Chemical Substances*; no acute toxicity data exist. The pigment is listed in the *GRAS* File, the U.S. Food and Drug Administration list of chemicals generally believed to be safe (CFR, 1991). Prussian blue is nonmutagenic in the Ames Salmonella test (Milvay & Kay, 1978). Because of its low toxicity, it is used in cosmetics. The dry pigment, however, is a colloidal powder and inhalation of any powder is irritating to the lungs and should be avoided. Prussian blue burns and evolves cyanogen, which is highly toxic.

4.0 **Composition**

4.1 **Chemical Composition**

Two formulas for Prussian blue are usually given: $KFe[Fe(CN)_6]$ and $Fe_4[Fe(CN)_6]_3$. Modern formulations of Prussian blue are $M^{I}Fe^{III}Fe^{II}(CN)_6 \cdot nH_2O$, where M^{I} is a potassium (K^+), ammonium (NH_4^+), or sodium (Na^+) ion and n=14–16. Currently, use of both sodium and ammonium ions predominates. The use of ammonium ion in the formulation was first introduced in the United States following World War I, when potassium was an expensive commodity (Sistino, 1973).

Because of the colloidal nature of Prussian blue, there are many surface-adsorbed ions, which confound analytical results. The correct formulation has been determined using x-ray diffraction methods (Buser & Ludi, 1976) and neutron scattering (Herren et al., 1980). These sources showed that interstitial water, water of crystallization, and adsorbed water molecules are present (fig. 7).

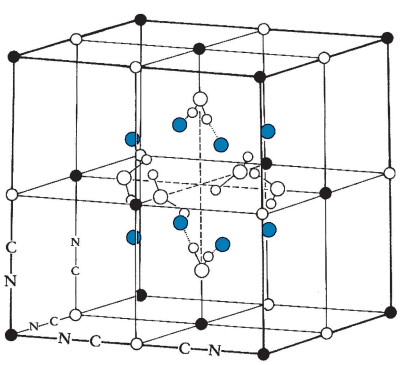


Fig. 7 Crystal structure of Prussian blue, a variant with one vacant iron-coordination in the cubic crystal structure. *Key:* filled black circles=Fe(III); empty black circles=Fe(II); large, filled blue circles=oxygen atoms of coordinated water; empty blue circles=the oxygen atoms of zeolitic water; small, filled black circles=hydrogen atoms. Reprinted, with permission, from Ludi (1988).

Wilde et al. (1970) showed that various preparations of Prussian blue contained from 5% to 15% αFe_2O_3 as an impurity.

The formulation of Prussian blue where M^I is a potassium ion has been described as soluble Prussian blue or soluble Turnbull's blue, although the complex is insoluble; it is, rather, easily peptized—that is, dispersed—in aqueous solutions. At one time, it was thought that using ferrous salts and potassium ferricyanide in manufacture resulted in Turnbull's blue, and using ferric salts and potassium ferrocyanide as starting materials resulted in Prussian blue. It is now known that both methods produce the same compound identified as $Fe^{III}_4[Fe^{II}(CN)_6]_3$ (Chadwick & Sharpe, 1965). Adjusting the molar ratio of reactants to 1:1 yields $KFe[Fe(CN)_6]$. The ASTM (1990c) standard for the dry pigment, D261-25, reapproved 1987, allows for no extenders, organic colors, or lakes. The maximum moisture content is 8%. Up to 5% of other materials may be added to improve the handling characteristics of the pigment.

4.2 Sources

Although the *Pigment Handbook* (Sistino, 1973) and *Colour Index* (1982) list several sources for Prussian blue, many of these companies no longer distribute or manufacture the pigment. Manchem is currently the sole producer in the United Kingdom and is also the distributor in the United States. Degussa (Germany) and Dainchiseika (Japan) continue to produce Prussian blue. Artists may obtain the dry pigment from a number of paint and pigment suppliers.

4.3 Preparation

A general recipe for the preparation of Prussian blue was described in *The Encyclopedia of Chemistry* (Booth & Morfit, 1872):

> When a protosalt of iron is added to ferrocyanide of potassium in solution, so that a portion of the latter remains undissolved, the white precipitate of ferrocyanide of potassium is exposed to the air, from which it absorbs oxygen and becomes blue; having the form $3FeCy, 2Fe_2Cy_3 + Fe_2O_3$ [Cy is equivalent to cyanide]. It is *basic Prussian blue*, [Booth & Morfit's italics] or oxy-ferricyanide of iron and Prussian blue.

The authors further indicated that the Prussian blues of commerce varied in constitution according to the mode of manufacture and that most of them are mixtures of the compounds described. Potassium cyanide (KCN) was frequently used as a starting material for the manufacture of Prussian blue. It was prepared from nitrogenous organic material such as, blood, hooves, horns, hide, hair, leather, and other material that was calcined with potassium hydroxide. Horn provided the highest yields of KCN; rendered tallow, suet, and lard were the most economical sources.

Riffault et al. (1874) listed seven different processes for the manufacture of Prussian blue and many more for Paris blue. Bersch (1901) reported a special process for the manufacture of Chinese blue, which is the highest quality of Prussian blue, using manganic chloride as the oxidizing agent. He indicated that in 1896 chromic acid was too expensive for commercial use as an oxidizing agent.

The two commercial preparation methods of Prussian blue have been called direct and indirect (see, for example, Heaton, 1947). Of these, the indirect method is more commonly used and remains similar in outline to procedures used since early in the history of Prussian blue. The chemical equations for the two methods are:

Direct method

$$Fe^{3+}_{aq} + K_4Fe(CN)_6 \rightarrow \text{Prussian blue}$$

Indirect method

$$2FeSO_4 + K_4Fe(CN)_6 \rightarrow Fe_2Fe(CN)_6 + 2K_2SO_4$$

$$Fe_2Fe(CN)_6 \xrightarrow[H_3CrO_3]{Cl_2\ or} \text{Prussian blue}$$

For the direct method, the aqueous iron salt most commonly used was ferric chloride (Smith, 1984) although ferric nitrate has also been reported. The solution of Fe^{3+} salt is added to a boiling solution of acidified hexacyano ferrate ($K_4[Fe(CN)_6]$).

The insoluble intermediate in the indirect method is called Berlin white. The formulation of Berlin white is sometimes given as $Fe_2Fe(CN)_6$ and at other times as $FeK_2Fe(CN)_6$. Berlin white can be air oxidized, as was the case during the early development of Prussian blue, accounting for the observations that the color became more intense and beautiful with painting out. However, more powerful oxidants than air are generally used to convert Berlin white to Prussian blue, most often either chlorine (Cl_2) or chromic acid (H_3CrO_3).

The physical properties of Prussian blue make its preparation difficult. The low specific gravity and the extreme fineness of the particles make the product difficult to separate from the starting materials. The colloidal nature of Prussian blue causes frequent adsorbance of excess starting material as impurities. Alumina (Al_2O_3) is some-

times added not only as an extender but also to help in the settling of the powdery product. Recent changes in manufacturing processes, including the addition of surfactants and better removal of starting materials and impurities, have improved Prussian blue. A novel method designed to overcome some of the preparation problems was patented by BASF (Kranz et al., 1982). This method involves anodic oxidation of iron in hydrogen cyanide acid. The process yields strongly colored, easily dispersible pigments that have a brilliant, lustrous coloration that is redder than the Prussian blue formed by the reaction of iron(II) salts with sodium or potassium ferrocyanide. Small percentages (0.01%–0.2% by weight) of polyalcohols are added to improve dispersibility in water.

4.4 Adulteration and Sophistication

Prussian blue is supplied as the pure pigment and also mixed with extenders and bulking agents. Often when extenders are used the prepared pigment is given another name (see section 2.1). These extenders include alum, iron oxide, calcium carbonate, calcium sulfate (gypsum), barium sulfate, also described as "heavy spar," starch, alumina, magnesia (Riffault et al., 1874), and clay or pipe clay. Prussian blue was also sold in mixtures reduced with white pigments, usually zinc white, although not usually under the name Prussian blue (see section 2.1). Antwerp blue was described by Riffault and colleagues as a mixture in variable proportions of Prussian blue, alumina, magnesia, and zinc oxide. The date of the earliest commercial mixture with zinc oxide is unknown but Bowles (1800) described the use of zinc white mixed with Prussian blue. Jameson (1897) gave a recipe for Prussian blue paint that contains "1 qtr Prussian blue, 14 lbs terra alba or barytes to 1/2 gallon of refined linseed oil or alternatively 1 cw Prussian blue, 1 qtr barytes, and 1 qtr whiting in linseed oil to consistency."

Development of formulations that include nickel or cobalt (Holtzman, 1945) have reduced the sensitivity of Prussian blue to alkali. Much earlier Bersch (1901) defined Antwerp blue as a pigment that was prepared by precipitating "a solution of two parts of zinc sulphate and one to two parts of green vitriol (according as pale or deep blue is required) by a dilute solution of yellow prussiate." This was said to be a mixture of Prussian blue with zinc cyanogen compounds. Hurst (1902) gave a similar recipe for Antwerp blue and also indicated that Brunswick blues (Prussian blue mixed with barium sulfate) had all but replaced Antwerp blue.

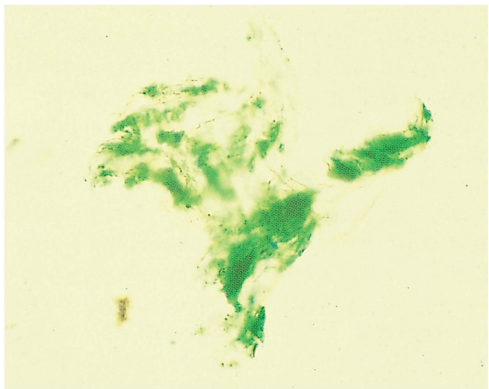
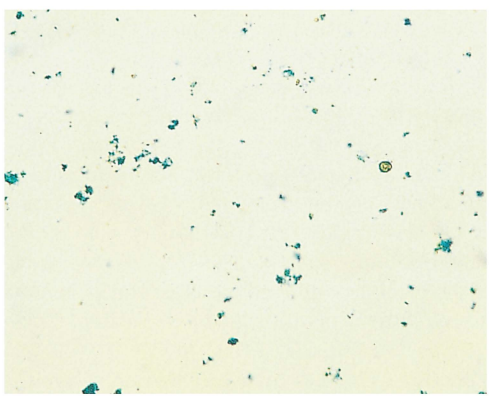


Fig. 8 Photomicrographs by transmitted light of chrome green, a mixture of Prussian blue and chrome yellow. Mounted in Aroclor 5442, n=1.66. 440x.

A. Rowney and Company (188?) sample on paper.



B. Chrome green from Albert Bierstadt, *Last of the Buffalo*, 1888, oil on canvas, Corcoran Gallery of Art, Washington. Gift of Mary (Mrs. Albert) Bierstadt, 1909.

Nickel-containing preparations have been used in architectural applications since about 1938 (Crown, 1968). These preparations have the formula $Ni_2Fe_2[Fe(CN)_6]_3$. A modification that substitutes zinc for nickel also found minor use in architectural applications.

Prussian blue has been, and still is, often used in mixtures with yellow pigments to form green. One such commercial mixture is chrome green (or cinnabar green), which is comprised of Prussian blue, chrome yellow ($PbCrO_4$), and greater or lesser amounts of white pigments or extenders. Small rods or spheres (1–2 μ) of chrome yellow are coated with Prussian blue to give a green color (fig. 8). Chrome yellow became commercially

available in the early 1800s and its mixture with Prussian blue was used shortly thereafter (Kühn & Curran, 1986). Originally, and more commonly, the term Brunswick green was given to copper compounds but later was also used for a mixture of chrome yellow and Prussian blue. Prussian blue has been also used to make zinc green pigments. The name Victoria green was applied to a mixture of zinc yellow and Prussian blue (Crown, 1968), although Victoria green was also used for a mixture of zinc chrome green and hydrated chrome oxide (Kühn & Curran, 1986). Prussian blue has been also mixed with organic yellows, white pigments, and extenders. A mixture of Prussian blue and gamboge has been called Prussian green, malachite green (Gleason et al., 1969), or Hooker's green, which was used in oil and watercolor painting. These pigments are now being replaced by more stable mixtures. Olive lake was a mixture of a yellow lake and Prussian blue (Crown, 1968).

Monthiers blue, named after its discoverer (Monthiers, 1846), is a modification of the formula, resulting from the reaction of ordinary Prussian blue with ammonia; it was described as having a finer color and being more durable. Gardner et al. (1978) described Monthiers blue as "a coloured compound obtained from the oxidation of the precipitate formed by the action of ammoniacal ferrous chloride upon potassium ferrocyanide, $(Fe_2)_2Fe(CN)_6.6NH_3.9H_2O$."

Prussian blue has been prepared on substrates such as mica to give pearlescent greenish pigments (Armanini & Johnson, 1977).

Modifications of Prussian blue to produce brown compounds have been described. These compounds were useful as transparent glazes. One such modification to produce a pigment called Prussian brown was described by Linton (1852). He described adding yellow prussiate of potash ($K_4[Fe(CN)_6]$) to a solution of copper sulfate to produce a rich chocolate-brown pigment. Its disadvantage was that it was "totally destroyed by alkaline solutions which are frequently used as abstergents in picture-cleaning."

Prussian brown is, however, most frequently described as resulting from calcining (heating) iron blue. The discovery of this method has been credited to a Mr. Toepffer (*Handbook of Young Artists*, 1854). Calcining to give a black pigment was described by J.F.L. Mérimée (Taylor, 1839).

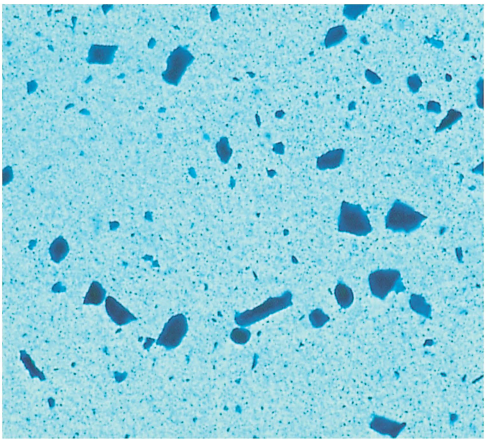
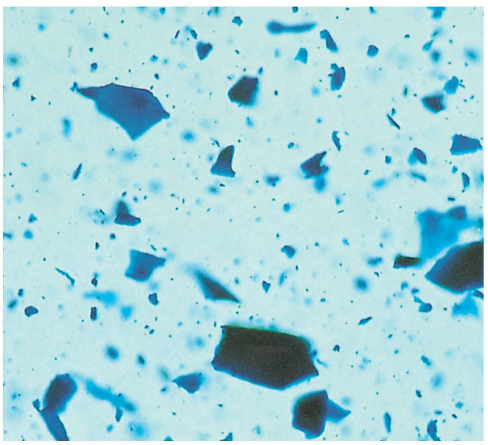


Fig. 9 Photomicrographs of Prussian blue dry pigment mounted in Cargille Meltmount, n=1.662. 320x.

A. Winsor and Newton.

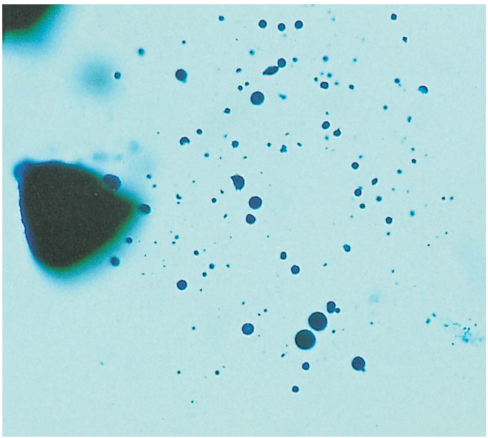


B. Conservation Materials, Ltd.

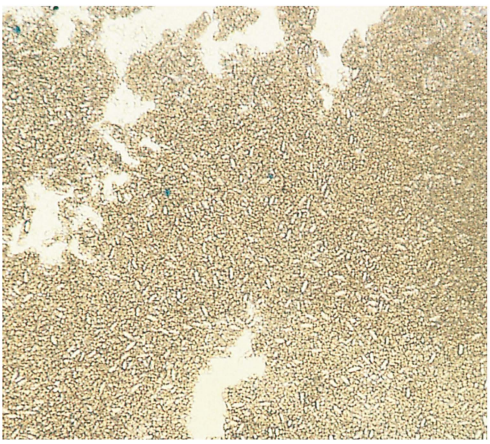
5.0 Identification and Characterization

5.1 Optical and Chemical Microscopy

Prussian blue of all formulations (see section 4.1) is of extremely fine particle size, approximately 0.01 to 0.2 µm in diameter. The shape and size of aggregates of Prussian blue is dependent on the manufacturing process and can vary considerably (fig. 9A–C). It should be emphasized that these are aggregates of submicron particles. The particles smear or clump when dry and are similar to indigo in appearance (De Wild, 1929). Dispersed Prussian blue is transparent and in transmitted light may look like a blue streak or flat flakes; it is blue in reflected light. Clumps or aggregates



C. Aldrich Chemical Company.



D. Scraping of paint made from Cremnitz (lead) white and Prussian blue shown in figure 2L.

of particles are opaque. In this respect, Prussian blue is similar to indigo and phthalocyanine blue. Since Prussian blue is in the cubic crystallographic system, the particles are isotropic and completely extinguished between crossed polars. When pure pigments are examined at 100 to 1,000x magnification, this property distinguishes Prussian blue from indigo and phthalocyanine blue, which both have low birefringence. In practice, the individual particles are too small to resolve and the admixture of other pigments, which are often birefringent, make it extremely difficult to use isotropic behavior to characterize Prussian blue. Figure 9D shows the appearance of a scraping of the pale blue paint, figure 2L, under the optical microscope. The number of blue flakes among the lead white particles is very small.

Welsh (1988) described the differences in the agglomerate shape of Prussian blue prepared according to the original recipes (using cattle blood) and Prussian blue prepared according to more recent recipes. The former consists of angular fragments of varying size. These fragments could easily be confused with natural ultramarine, illustrating the difficulty in identifying Prussian blue using optical microscopy. Prussian blue with large platelike fragments was found in many of J.M.W. Turner's (1775–1851) paintings (Townsend, 1993).

Schilling and Scott (1989) described the use of a Chelsea filter as an aid in distinguishing between ultramarine and Prussian blue.

In pigment mixtures, it can be especially difficult to identify Prussian blue. Prussian blue well dispersed in lead white to give a 5% by volume mixture, resulting in a sky-blue tint when mixed in linseed oil, is not observable at normal magnifications using transmitted light microscopy. Impurities, bulking agents, and extenders (listed in section 4.4) may be birefringent, further confusing the identification.

5.2 Chemical Identification

Prussian blue is most readily distinguished from other blue pigments by its sensitivity to alkali and lack of reaction with acids. When 4M NaOH is added to Prussian blue, it is rapidly converted to a brown compound (fig. 10). The blue color can, in favorable instances, be restored by adding acid to the test mixture (Plesters, 1956). The presence of iron(III) in the alkaline solution may be confirmed by formation of a red color on addition of ammonium thiocyanate. Through these tests Prussian blue may be distinguished from ultramarine (artificial and synthetic), phthalocyanine blue, and indigo. Indigo is affected by dilute alkali only after prolonged heating or exposure and the other pigments are not affected at all.

5.3 Instrumental Methods of Analysis

5.3.1 ***X-ray diffraction.*** Because of the cubic structure of Prussian blue, there are few lines in the x-ray powder diffraction pattern (table 1). The fineness of particle size may sometimes adversely affect the ability to obtain a good diffraction pattern because the colloidal nature of Prussian blue causes rather broad lines. The iron in Prussian blue fluoresces strongly in CuKα radiation, causing darkening of the film. Wilde et al. (1970) stated that there is a small difference in rel-

Table 1 **X-ray Diffraction Data for Prussian Blue CuKα=1.5404 Å, 25°C**[a]

JCPDS 1-0239[b] $Fe_4[Fe(CN)_6]_3$		*Winsor and Newton Alkali Ferric Ferrocyanide (Fig. 11A)*		*Aldrich Chemical Company* $Fe_4[Fe(CN)_6]_3$ *(Fig. 11B)*		*Fezandie and Sperrle Prussian Blue (Fig. 11C)*	
d (Å)	I/I_{max}	*d* (Å)	I/I_{max}	*d* (Å)	I/I_{max}	*d* (Å)	I/I_{max}
5.1	100	5.1	100	5.10	100	5.10	100
3.60	32	3.60	42	3.60	40	3.59	52
2.55	48	2.54	41	2.54	40	2.54	53
2.28	32	2.27	26	2.27	26	2.26	33
2.07	3	2.06	11	2.07	10	2.07	12
1.80	14	1.79	18	1.80	18	1.79	18
1.70	13	1.69	8	1.69	8	1.695	17
1.61	14	1.605	14	1.61	10	1.605	15
1.53	3	—	—	—	—	—	—
1.47	2	—	—	—	—	1.47	<2
1.41	10	1.42	<5	1.41	<5	1.410	<5
1.36	8	1.355	<5	1.36	<5	1.360	<5
and other lines with I/I_{max} <2		1.235	~2			1.235	<2

a. A calibrated rule was used to estimate *d*-values. Intensities of lines were measured using a Hoefer Scientific Instruments gel scanner.
b. Data from *JCPDS Powder Diffraction File, JCPDS* (1982).

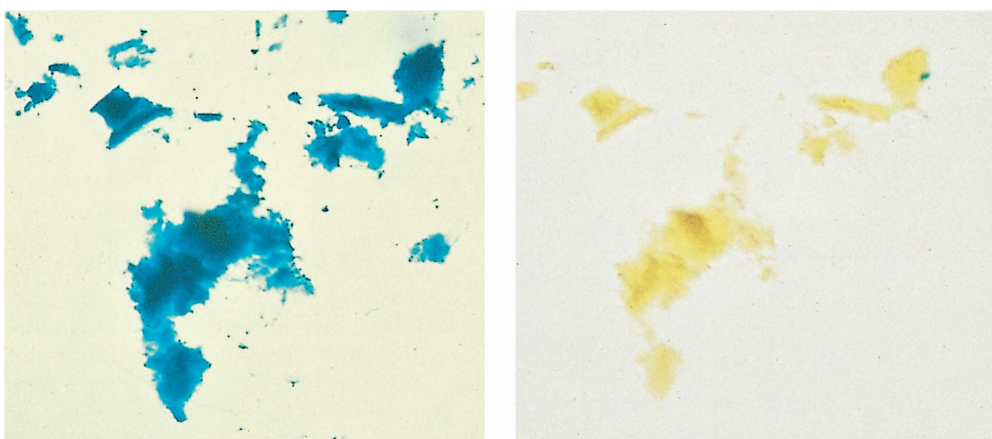


Fig. 10 Photomicrograph of Prussian blue. 520x. A. Before reaction with 4M sodium hydroxide. B. After reaction with 4M sodium hydroxide, which converts Prussian blue to a brown compound.

ative intensities of diffraction lines in insoluble and "soluble" Prussian blue, but the results were not quantifiable. The diffraction patterns of pigments from three sources are indistinguishable despite the differences in formulas. These patterns are shown in figure 11. Line widths are greatest for the Aldrich product (fig. 11B), implying smaller particle size.

When Prussian blue is mixed with other pigments, such as lead white, its tinting strength is so great that very small quantities are necessary and therefore it is often not detectable using x-ray powder diffraction analysis. A relatively high concentration of Prussian blue in mixtures is required for identification using this method. The presence of 10% Prussian blue by weight in lead white

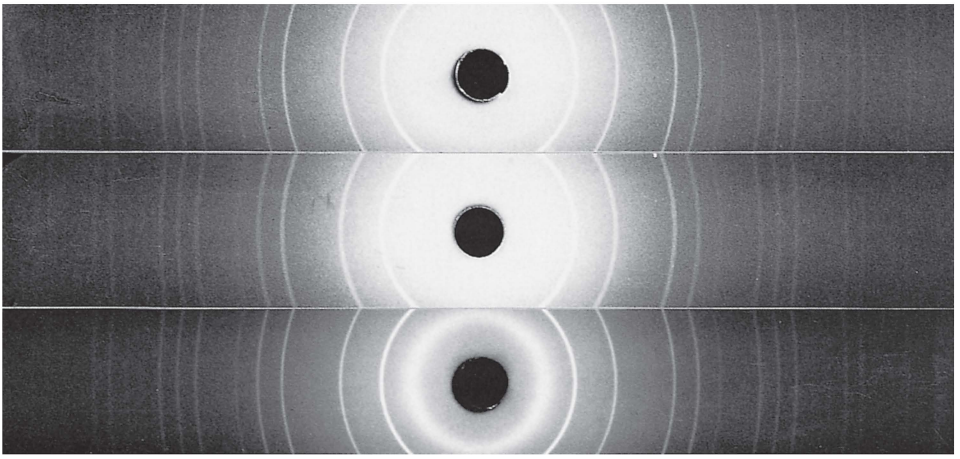


Fig. 11 X-ray diffraction powder patterns for Prussian blue.

A. Winsor and Newton alkali ferric ferrocyanide.
B. Aldrich Chemical Company, $Fe_4[Fe(CN)_6]_3$.
C. Fezandie and Sperrle Prussian blue.

could not be detected using x-ray powder diffraction analysis. Microchemical testing is a more positive method for confirming the presence of Prussian blue (see section 5.1).

Keggin and Miles (1936) first determined the crystal structure of $Fe_4[Fe(CN)_6]_3.14H_2O$. Later refinements were given by Buser and Ludi (1976) and Dix and Rae (1978). Locations of water molecules were determined using neutron diffraction methods (Herren et al., 1980). The overall structure can be described as *Fm3m*. The length of the unit cell (see fig. 7) is 10.166 Å. The calculated density is 1.78 gcm^{-3}, which compares with the measured density of 1.75 to 1.81 gcm^{-3}. Bond lengths are Fe–C: 1.93(3) Å, Fe–N: 2.00(2) Å, Fe–O: 2.14(3) Å, C≡N 1.15(3) Å.

5.3.2 ***Infrared spectroscopy.*** The infrared spectrum of Prussian blue is shown in figure 12A. The absorbance at 2083 cm^{-1} is characteristic of the C≡N stretch (table 2). The fact that the absorbance falls below 2090 cm^{-1} is further evidence that Prussian blue is a ferric ferrocyanide (Nakamoto, n.d.). The presence of an absorbance band at 2083 cm^{-1} in the infrared spectrum of an unknown pigment can be used to infer the presence of the cyanide group, and therefore, Prussian blue. This band was used to identify Prussian blue in a sample containing less than 5% by weight in a green paint (Newman, 1979). Figure 12B shows microreflectance in an infrared spectrum of Prussian blue and titanium white in linseed oil; the cyanide stretch is at 2083 cm^{-1} and is easily discernible. The far infrared spectra of Prussian blue and soluble Prussian blue were described by Wilde et al. (1970). They demonstrated that the infrared spectra of Prussian blue and Turnbull's blue (the easily peptized pigment) are not identical. In this instance, Turnbull's blue is probably the alkali ferric ferrocyanide.

The reaction product between Prussian blue and alkali is generally thought of as a hydrated iron oxide. Figure 12C is the infrared spectrum of the brown compound. The cyanide stretch has moved to a lower wavenumber and is split in three, centered at 2035 cm^{-1}. A new peak at 867 cm^{-1} appears. It seems probable that the reaction product could be similar to $Na_2(Fe^{III}OH)[Fe^{II}(CN)_6]$ or other compounds.

5.3.3 ***Spectrochemical analysis.*** The only element in Prussian blue that can be used for spectrochemical analysis is iron. The other elements certain to be present in the pigment, carbon and nitrogen, may also be present in the binding medium (nitrogen in proteinaceous media). Zinc, aluminum, barium, calcium, potassium, and other elements may be observed.

5.3.4 ***X-ray spectrometry (x-ray fluorescence).*** Using x-ray fluorescence spectroscopy to infer the presence of Prussian blue requires confirmation by other tests since the same spectrum could result from different materials. For example, ultramarine painted over a red iron-earth ground would show the presence of iron and would therefore be indistinguishable

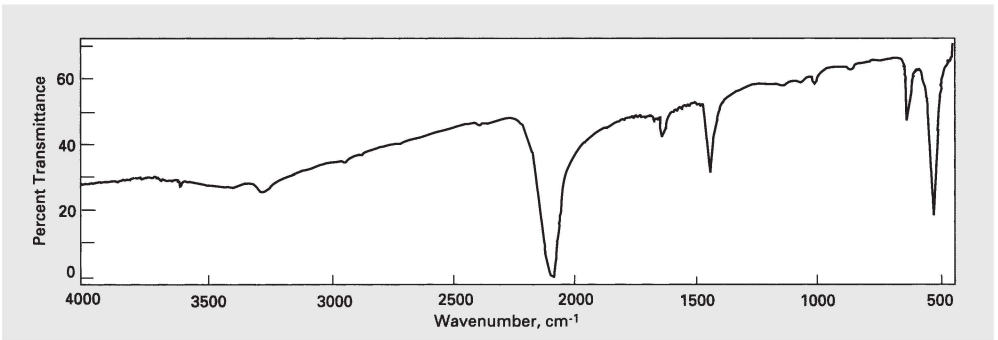
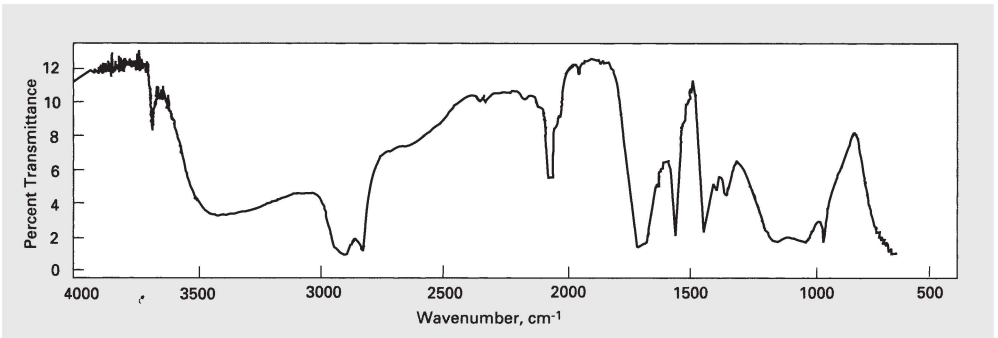
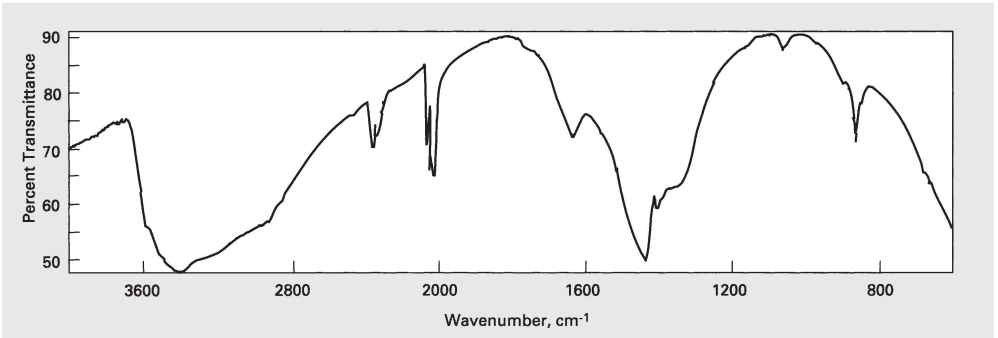


Fig. 12 A. Infrared spectrum of Winsor and Newton Prussian blue. The dry pigment was pressed into a potassium bromide pellet; the spectrum was obtained using a Bio-Rad FTS-60A.



B. Microreflectance infrared spectrum of a paint film made from Prussian blue and titanium white in linseed oil. The sample was laid on a gold slide, the spectrum was obtained using a Bio-Rad FTS-60A with a UMA 300 microscope accessory, resolution=4 cm^{-1}.



C. Infrared spectrum of the brown reaction product of Prussian blue with 4M sodium hydroxide. Obtained by method given in 12A using an Alpha-Centuri spectrometer.

from Prussian blue. Similar problems arise when examining green pigments that might contain Prussian blue. Furthermore, because of its high tinting strength, Prussian blue may be present in very small quantities and therefore difficult to detect.

When exciting atoms in Prussian blue using an instrument designed to examine works of art without removing samples, in this case the Kevex 0750A, the photon energies of the x-ray spectral K lines of iron are the only lines detectable. The energies of these lines for iron are $K\alpha_1$=6.403 keV, $K\alpha_2$=6.390, $K\beta_1$=7.057 keV (Goldstein et al., 1992). Energy-dispersive x-ray fluorescence

Table 2 **Infrared Absorbance Frequencies for Prussian Blue and Their Assignments**

Frequency (cm^{-1})	*Assignment*
3377	Bound water
3256	Bound water
2083	C≡N stretch
1686	
1611	
1414	
1111	
1047	
981	
835	
606	Fe–N stretch
495	Fe–C and C–Fe–C in-plane bend or Fe–C≡N bend

spectroscopy indicating the presence of iron has been used to identify Prussian blue in textiles (Kashiwage & Yahara, 1979).

As mentioned, Prussian blue is frequently admixed with zinc white. Zinc or nickel may also be present in the formulation (see section 4.4) and can be detected using energy-dispersive x-ray fluorescence spectroscopy. The energies, in keV, of the emitted radiation from these elements are zinc: Kα=8.631, Kβ=9.572; nickel: Kα=7.472, Kβ=8.265. Distinguishing the source of zinc as either from ZnO (zinc white) or in the formulation of the Prussian blue is not possible; however, the likely source is zinc white. Sources of nickel are in nickel titanate yellows, nickel azo yellow, and as an impurity in smalt. X-ray fluorescence spectroscopy can provide valuable information when used in combination with other analytical techniques; when used alone, XRF results are inconclusive.

5.3.5 ***Neutron activation.*** None of the major elements of ferric ferrocyanide are suitable for detection using neutron radiation analysis. However, in the formulations containing alkali metals, the sodium and potassium ions may be detected. Many extenders used with Prussian blue cannot be detected using this method of analysis; however, aluminum in alumina, which is often found in the formulation of Prussian blue, may be readily detected if measurements are made immediately following activation (Lechtman, 1966).

5.3.6 ***Mössbauer spectroscopy.*** Iron hexacyanoferrate was one of the first compounds to be studied using Mössbauer spectroscopy (see fig. 6) (Fluck et al., 1963). The results conclusively showed that Turnbull's blue and Prussian blue are identical and the use of $K_4Fe(CN)_6$ with Fe^{3+} salts or $K_3Fe(CN)_6$ with Fe^{2+} salts produces the same compound. From the ratio of intensities of the peaks due to Fe^{3+} and Fe^{2+}, Fluck and colleagues also showed that adjusting the molar ratio of reactants to 1:1 produces the so-called soluble Prussian blue, $KFe[Fe(CN)_6]$.

5.3.7 ***Scanning electron microscopy.*** Prussian blue from Aldrich Chemical Company (fig. 13A) and Conservation Materials (fig. 14A) was examined using this technique. The morphology of the dry pigment varies considerably. The aggregates of particles range in size from 1 to 15 μ and in shape from platy rhombs to spheres. Energy-dispersive spectra obtained simultaneously are shown in figures 13B and 14B.

An example of the difficulty in determining the presence of Prussian blue from elemental analysis using energy-dispersive x-ray spectroscopy is demonstrated by the examination of a Kremer pigment sample of chrome green (fig. 15), using scanning electron microscopy with energy-dispersive x-ray spectroscopy (EDX). No distinctive morphology could be discerned in the scanning electron micrograph. After sixty seconds of collecting, chromium, lead, and potassium only were detected by EDX. Iron was below the detection limit of the instrument. By optical microscopy, there was no difficulty in identifying this sample as a mixture of chrome yellow and Prussian blue.

5.4 Criteria for Identification

X-ray powder diffraction provides certain proof of the presence of Prussian blue if a pattern can be obtained. However, as noted, it is sometimes difficult to acquire a pattern of Prussian blue in mixtures. The cyanide absorbance in the infrared spectrum at 2083 cm^{-1} is diagnostic that a color contains admixed Prussian blue (with the exception of browns and blacks that are calcined Prussian blue). The extreme sensitivity of Prussian blue to alkali differentiates it from other blue pigments; the re-formation of the blue color with acid provides further confirmation (see section 5.2).

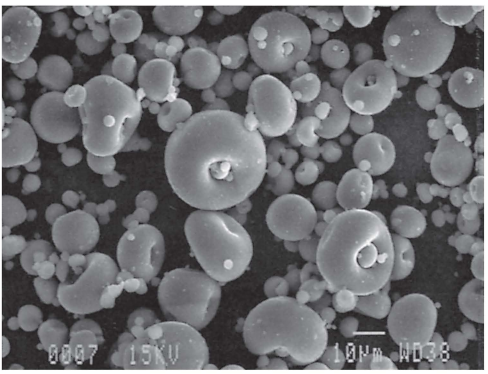


Fig. 13 Prussian blue from Aldrich Chemical Company. A. Scanning electron micrograph obtained using a JEOL 840A SEM showing spherical aggregates of the submicron particles of Prussian blue. Printed at 400x.

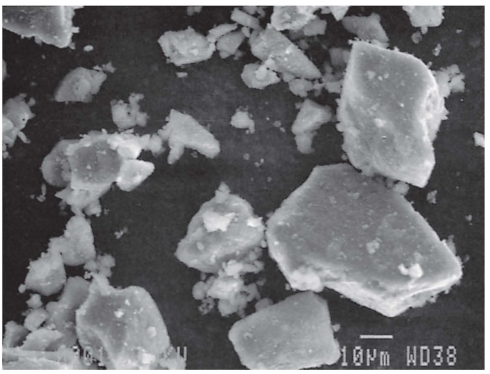
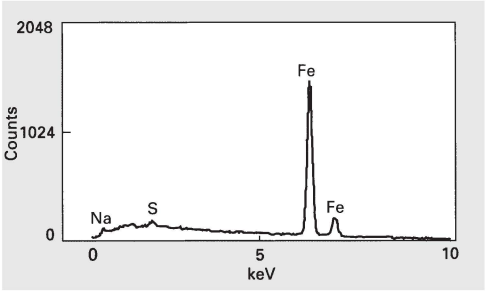
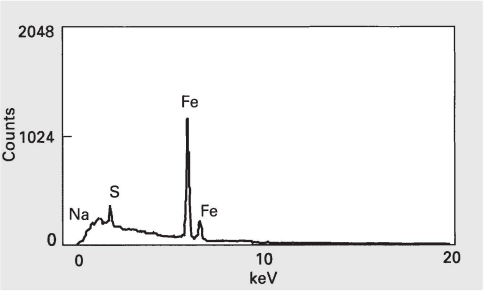


Fig. 14 Prussian blue from Conservation Materials (analyzed using same method given in fig. 13A and B). A. Scanning electron micrograph showing platy aggregates that can be easily broken up. Printed at 400x.



B. Energy-dispersive spectrum of sample shown in 13A obtained using a Tracor Northern Si(Li) detector. The material contains, in addition to iron, traces of sulfur and sodium.



B. Energy-dispersive spectrum of sample shown in 14A contains sulfur and sodium in addition to iron. Accelerating voltage was 20 V live-time 60 s.

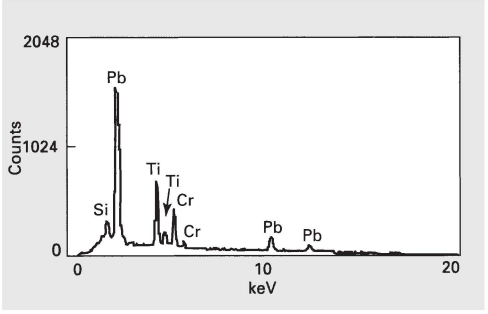


Fig. 15 Energy-dispersive spectrum of dry chrome green, a mixture of Prussian blue and chrome yellow, supplied by Kremer Pigmente. The spectrum was acquired using a Tracor Northern Si(Li) detector on a JEOL 840A scanning electron microscope. The accelerating voltage was 20 V, acquisition live-time 60 s. Under these conditions the only elements detected at 1,800x are silicon, lead, titanium, and chromium; iron is not detected. Figures 13–15 from Melanie Feather, Conservation Analytical Laboratory, Smithsonian Institution.

6.0 **Occurrences**

The following occurrences illustrate the rapid and widespread introduction of Prussian blue following its discovery in the early 1700s.

The earliest examples found in easel paintings are in a Dutch painting, which predates 1722, by Adriaen van der Werff (1659–1722), *Jacob Blessing the Sons of Joseph* (Buck, 1965) and in two Italian pictures of 1719–1723 by Giovanni Antonio Canal (called Canaletto) (1697–1768), *Veduta del Rio dei Menicanti* and *Veduta del Canal Grand da Palazzo Balbi* (L. Lazzarini, personal communication, 1987). Prussian blue was found in a French painting, *Italian Comedians*, by Antoine Watteau (1684–1721) (Fisher, 1984) and is possibly in another painting by Watteau (Bergeon & Faillant-Dumas, 1984). A 1723 receipt for wall paint containing Prussian blue for the Trinity Church, Boston, has been documented (Batcheler, 1981). This is a relatively early occurrence of the pigment in the Western Hemisphere, indicative of the rapid spread of Prussian blue and also that it was economical.

In Italy, the pigment was found in later Canaletto paintings, now in the National Gallery, London, *Venice: The Feastday of St. Roch* dated 1735 (Bomford & Roy, 1982), *Stonemason's Yard* dated 1730, and *San Simeone Piccolo* dated 1738 (Bomford & Roy, 1993). It was also found in Giovanni Battista Tiepolo's (1696–1770) *Salita al Calvario* (dated 1738–1740), using microscopy and microchemical tests (L. Lazzarini, personal communication, 1987) and in his paintings in the Scuola Grande dei Carmini, Venice, commissioned 1739 (Rossi-Manaresi et al., 1990). In a French painting later than Watteau, Prussian blue was used for the sitter's dress and the background in a pastel by Jean Baptiste Perronneau (1715?–1783), *A Girl with a Kitten*, signed and dated 1745, National Gallery, London (A. Roy, personal communication, 1988).

Prussian blue has been identified on several eighteenth-century English paintings. It was used for the blues and mixed with Naples yellow for the greens in William Hogarth's (1697–1764) series *Marriage à la Mode,* c. 1743 (Roy, 1982). It was described by Paul Sandby on the palette of Richard Wilson (1713/1714–1782) (Whitley, 1928). It was also found in a 1740 portrait by Thomas Bardwell (d. 1780), *John Campbell, Second Duke of Argyll, and Duke of Greenwich* (Talley & Groen, 1975). Bomford et al. (1988) identified it in a portrait of *Dr. Ralph Schomberg,* c. 1771, by Thomas Gainsborough (1727–1788), in the National Gallery, London.

In England in the early nineteenth century, A. Maheux identified William Blake's (1757–1827) use of Prussian blue mixed with gamboge for the greens in the paintings *Cain,* 1799–1809; *Job: Behemoth,* 1821; *Job: Last Judgment,* 1821; *Brunelleschi,* 1824–1827; *Lucia Carrying Dante,* 1824–1827; and *Rusticucci,* 1824–1827, all in Harvard University Art Museums (Fogg) (R. Newman, personal communication, 1988). Prussian blue has been found in many paintings by the English artist John Constable (1776–1837), dating from 1802 to 1837; he used it both for blue and in mixtures for green (Cove, 1991).

Several occurrences of the pigment have been reported in American paintings of the last half of the eighteenth century. It was found in the blues and greens (mixed with yellow lakes and ocher in the latter) in *Dorothy Murray,* c. 1760, by John Singleton Copley (1738–1815), Harvard University Art Museums (Fogg). The pigment was also found in *Mrs. Daniel Denison Rogers*, by Copley, which was painted in England in 1783 (Shank, 1983). Bockrath (1988), using polarized light microscopy, identified it in *The Gordon Family,* c. 1760 by Henry Benbridge (1743–1812) in the Pennsylvania Academy of Fine Arts, Philadelphia. Ashworth et al. (1988) described its use by Charles Willson Peale (1741–1827), and it has been found in Peale's *Portrait of Thomas Ringgold*, c. 1773 (Michael Palmer, personal communication, 1990).

The use of Prussian blue continued in nineteenth-century American works of art. It was found in John James Audubon's (1785–1851) hand-colored engravings in *The Birds of America,* 1827 to 1838 (Adair & Young, 1981). Winslow Homer (1836–1910) from the 1870s to 1880s used drawing paper toned with Prussian blue and chrome yellow (Perkinson, 1986). Prussian blue is present in a watercolor pigment box belonging to Homer (Newman et al., 1980). The author identified it mixed with gamboge in another of Homer's watercolor boxes; it is labeled "Prussian green," a term used by Winsor and Newton for this mixture. It was identified in the painting *The Sea* by John Frederick Kensett (1816–1872) (Dwyer, 1985). The pigment was found in the blues in J.A.M. Whistler's (1834–1903) "Peacock Room" painted from 1876 to 1877, now in the Freer Gallery of Art, Smithsonian Institution (Winter & FitzHugh, 1985). The use of Prussian

Fig. 16 Anish Kapoor, *Dragon*, temporary installation, 1992. Approximate room dimensions: 30 x 70 ft. (9 x 21 m). Photo courtesy Art Tower Mito Contemporary Art Gallery, Mito, Japan.

blue by Albert Pinkham Ryder (1847–1917) was discussed by Alexander et al. (1990). It has been found mixed with chrome yellow in Albert Bierstadt's (1830–1902) *Last of the Buffalo,* 1888, in the Corcoran Gallery of Art, Washington (M. Palmer, personal communication, 1986).

Prussian blue was found in the sky and mixed with the greens in *The Northern Drawbridge in Copenhagen* by the Danish painter Christen Købke (1810–1848) (A. Roy, personal communication, 1988). It was used in nineteenth-century Dutch Gothic revival polychrome sculptures (Van Asperen de Boer, 1975).

The pigment has been identified in many impressionist paintings although it is absent in some painters' palettes. For example, it was not found in paintings by Paul Cézanne (1839–1906) (Butler, 1984) or in ten of Georges Seurat's (1859–1891) works (Fiedler, 1984). It was found in several pastels by Edgar Degas (1834–1917), Harvard University Art Museums (Fogg) (DeSantis, 1984). It was used in Claude Monet's (1840–1926) *Bathers at La Grenouillère,* 1869, National Gallery, London (Roy, 1981) and in blue paint in Vincent van Gogh's (1853–1890) *Self-Portrait Dedicated to Paul Gauguin,* 1888 (Jirat-Wasitynski et al., 1984) as well as in *La Mousmé* (see fig. 5). Prussian blue has been identified in many paintings by Pablo Picasso (1881–1973) (Delbourgo, 1981).

In a twentieth-century painting, Prussian blue was identified by polarized light microscopy in the Cleveland Museum of Art *Portrait of Josef May*, 1926, by the German artist Otto Dix (1891–1969) (Miller, 1987).

In Asia, Prussian blue has been found on nineteenth-century Japanese paintings (E. W. FitzHugh, personal communication, 1990) and it was used in the false patina on Chinese bronzes (Gettens, 1969).

In contemporary art Prussian blue has been used in a mixed media sculpture made up of three parts, *A Flower, A Dream Like Death* by the British artist, Anish Kapoor (b. 1954); it is a composition containing polystyrene, cloth, gesso, and raw pigment (Museum of Modern Art, New York, Sid R. Bass Fund) (Eugena Ordonez, personal communication, 1992). It was also found in Kapoor's *Dragon* (fig. 16), which was a temporary installation (1992) comprised of rocks covered with a mixed-media slurry that included dammar resin and Prussian blue pigment. The dry pigment was sprinkled over the surface of the rocks (Jay Krueger, personal communication, 1993).

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8
Emerald Green and Scheele's Green

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1.0 Introduction

1.1 Pigment Definition

Scheele's green, a copper arsenite of varying composition, was the first synthetic green copper arsenic pigment. It is CI Pigment Green 22, no. 77412 in the *Colour Index* (1971b). Pigments known as Scheele's green comprise a group of copper arsenite compounds having widely variable compositions depending on manufacturing methods and the shade desired, with the color ranging from pale yellow-green to deep green. Introduced in 1778, its use as an artist's pigment is little documented.

Emerald green, copper acetoarsenite, $3Cu(AsO_2)_2.Cu(CH_3COO)_2$, also known as Paris green or Schweinfurt green, was discovered as a result of trying to improve Scheele's green (Church, 1915). It is CI Pigment Green 21, no. 77410 in the *Colour Index* (1971b). It has an unusually brilliant blue-green to green hue. It was introduced between 1800 and 1814 and has been available until recently (see section 2.4).

These compounds are no longer available as artists' pigments, at least in the United States and Europe, because of their extreme toxicity. Paris green and its variations were used extensively at one time as insecticides, fungicides, and wood preservatives, as were copper arsenites. Both compounds may still be used for these purposes in some countries.

The naturally occurring copper arsenite mineral, trippkeite, $CuAs_2O_4$, is extremely rare (Winchell, 1933; Zemann, 1951; Palache et al., 1966; Roberts et al., 1974; Pertlik, 1975). It was analyzed and named by Damour and Vom Rath (1881). Its correspondence to Scheele's green or its variants is difficult to ascertain since samples of this mineral were unavailable for comparison. There is no naturally occurring copper acetoarsenite.

1.2 Current Terminology

English: emerald green, Paris green, Veronese green, Schweinfurt green
German: Schweinfurter Grün, Schweinfurtgrün
Russian: изумрудная зелень
French: vert Véronèse, vert Paul Véronèse, vert de Schweinfurt
Italian: verde di Schweinfurt
English: Scheele's green
German: Scheeles Grün, Scheelesgrün
Russian: зелень шила
French: vert de Schéele
Italian: verde di Scheele

The names emerald green and Veronese green are still in use although they now apply to composite pigments that imitate the hue of the original copper acetoarsenite. True emerald green, Paris green, Veronese green, and Scheele's green are no longer being produced, although their names are referred to for historical purposes.

2.0 History

2.1 Archaic and Historical Names

The names given by various sources appear in table 1. Mierzinski (1881) and Eibner (1909) each list over forty; Schaaff and Riederer (1992) compiled a list of eighty-six names. Many synonyms were used interchangeably for both Scheele's and emerald green; inconsistencies in the literature make it difficult to resolve the correct assignment

Table 1 **Other Names for Scheele's Green and Emerald Green**[a]

Scheele's Green

Common names:
Mineral and Swedish green

Less common names:
Ash green

Names incorrectly used by some authors:
Brunswick green, Green verditer

Emerald Green

Common names:
Mitis, Paris, and Schweinfurt green, *vert Véronèse*, *vert* Paul Véronèse

Less common names:
Basel, Beautiful, Braunschweig, Brixen, Deck, Eisleben, Fine, French, Hamburg, Imperial, Jasniger, Kassel, Kirchberg, Lacquer, Leipzig, Lime-arsenic, May, Munich, Moss, Mountain, Neuwied, New, Original, Paper, Parrot, Patent, Persian, Powder, Saalfeld, Soda, Smaragd, Urania, Vienna, Würzburg, and Zwickau green

Names incorrectly used by some authors:
Verditer

Names Applied to Either or Both Pigments (sometimes mixed with other pigments)

Bremen, Copper, Dust, Eisenach, English, Haystack, High, Jasmine, Kaiser, King, Kirchberg, Kurrers, Leobschütz, Mineral, Mitis, Munich, Neuwied, Opaque, Paint, Patent, Pickle, Priming, and Swiss green

a. Data from Mierzinski (1881), Guignet (1888), Eibner (1909), Zerr and Rübencamp (1908), Rose (1916), Kittel (1968), *Colour Index* (1976), Schaaff and Riederer (1992). This list of names is by no means conclusive. Certain names appear in more than one group since some authors list them as referring to one pigment and some to both.

of some terms. Mitis or Vienna green were the original designations for copper acetoarsenite, but these names were superseded by Schweinfurt green when mass production began at Wilhelm Sattler's Farben und Bleiweiss firm in Schweinfurt (fig. 1). Names were derived from the place of origin, such as Würzburg or Bremen, and described various mixtures (lime-arsenic green) or applications (priming green); other more fanciful names such as pickle or May green defined shades (Eibner, 1909; Kittel, 1960; Kühn, 1969). Some of the names were a deliberate attempt to conceal the poisonous nature of the pigments. Guignet (1888) warned that most of the bizarre terms were used to conceal the presence of arsenic. Early nomenclature was ambiguous; a single name might apply to several substances. Mitis green might refer to either pure copper acetoarsenite, a specially prepared Scheele's green, a copper arsenate compound, or a mixture either of emerald and Scheele's green or emerald and imperial green. It is also possible that Mitis green was actually a variety of Scheele's green based on Wurzbach's (1868) description of the pigment. The name Scheele's green was sometimes used interchangeably for emerald green.

Riffault et al. (1874) indicated that green lake was a form of Scheele's green and also claimed that Mitis, Vienna, and Kirchberger greens were copper arsenates. However, Church (1915) used the names Vienna, Mitis, and Veronese green to describe specially prepared copper arsenites. Emerald or Schweinfurt greens could occur as the ordinary or distilled variety, depending on the type of verdigris used in production; Scheele's green existed as an ordinary or a German variety, depending on the production technique used (Zerr & Rübencamp, 1908; Gentele, 1909; Rose, 1916). Neuwied, Braunschweig, Kaiser, Berg, copper, and mountain green refer to copper acetoarsenite lime greens that contain calcium or barium sulfate (Mierzinski, 1881). According to Zerr and Rübencamp (1908), parrot and Persian green were emerald green mixed with chrome yellow and barium sulfate, although Gentele (1909) used the names parrot green and Mitis green for a mixture of copper arsenite and acetoarsenite, while Guignet (1888) designated Scheele's green co-precipitated with calcium sulfate as pickle or Neuwied green.

In France, emerald green was called *vert* Paul Véronèse (or *vert Véronèse*) after the sixteenth-century Venetian painter Paolo Veronese; it is not clear why it was named after this artist since his career predates the pigment. It was probably a proprietary color since authors such as Guignet (1888) and Coffignier (1925) mentioned its beautiful color and special preparation conditions, although the methods were not disclosed. Veronese green was a term also applied to green earth (Toch, 1911; Wehlte, 1975; Grissom, 1986).

Green verditer correctly denotes synthetic copper carbonate while Brunswick green originally referred to copper chloride and, more recently, to a chrome yellow-Prussian blue mixture (Harley, 1982). Mineral green, mountain green, and Bremen green are also used as names for malachite (Heaton, 1956; Gettens & FitzHugh, 1993). There is some confusion between the terms emerald green and the French *vert émeraude*, espe-

Fig. 1 Advertisement for Wilhelm Sattler's *Farben und Bleiweiss Fabrik*, Schweinfurt, Germany. Photo from Erich Schneider, Städtische Sammlungen Schweinfurt.

cially when the latter is translated into English. *Vert émeraude* is a transparent chromium oxide known in English as viridian and has often been incorrectly translated as emerald green.

2.2 Early History

The early history of both pigments concerns their chemical composition, synthesis, and manufacturing methods. The limited historical documentation is the result of trade secrets and possible destruction of records in war time.

2.2.1 ***Scheele's green.*** Scheele's green was discovered in 1775 by Carl Wilhelm Scheele, a Swedish chemist, while he was doing research on arsenic. He presented his discovery to the Royal Academy of Sciences, Stockholm, and published his findings in 1778; he recommended its use as an artist's pigment and described the method of its preparation. Synthesis of the pigment involved mixing solutions of copper sulfate and arsenic trioxide (dissolved with the aid of potassium carbonate) resulting in the precipitation of copper arsenite. Because the color remained unaltered and appeared stable after three years, he suggested its use for oil and watercolor painting. The pigment became known as Scheele's or Swedish green (Kopp 1847; Scheele, 1931; Harley, 1982). It was first made in Sweden and then introduced in Germany where it was manufactured by a different process because exact details of Scheele's method were a trade secret. As a result, two pigments of different composition were produced—the real Scheele's green and the German variety (Zerr & Rübencamp, 1908). As no satisfactory greens were available at this time, this discovery was a welcome addition to the artist's palette.

Few references exist as to actual manufacturers of Scheele's green. A single early citation in George Field's *Practical Journal 1809* includes a sample he obtained from W. Brockedon in Paris (Field, 1809; Harley, 1982). In fact, there were a variety of manufacturing methods for this copper arsenite green that were not necessarily identical to the original. For example, a method was patented by the English color maker William Parker (1812) for improving Scheele's green by

producing a material lower in residual alkali and thereby less reactive with oil media.

Scheele's green, like verdigris (copper acetate), turned out not to be a reliable pigment primarily because of darkening. It came to be considered inferior as a pigment and was gradually replaced by the brighter and less reactive emerald green (Gettens & Stout, 1966).

A pigment named Schweinfurt blue, prepared without heat or by alkali treatment, was said to have the same composition as Scheele's green (Field, 1835).

2.2.2 ***Emerald green.*** Emerald green's discovery is credited to two different sources. In 1808, Wilhelm Sattler began a paint manufacturing business in Schweinfurt, Germany. According to Bechstein (1860), Sattler saw a reference in Crell's *Chemische Annalen* in 1814 stating that verdigris, when combined with an arsenic compound, produced a pleasant green color. Sattler, with the help of pharmacist Friedrich Russ, performed experiments that eventually resulted in a pure and vivid color that kept its brilliance in artificial light. They produced it under the name Schweinfurt green but from 1814 to 1822 kept its composition and manufacturing method a trade secret. This new green pigment became widely available throughout Europe and in North America (Ultsch, 1987; Schneider, 1989) and was a profitable secret for Sattler for many years (Ure, 1847).

Ignaz von Mitis (1771–1842) in Vienna is also credited with the discovery of copper acetoarsenite between 1798 and 1812. According to Tschelnitz (1857), this pigment was produced for the first time by Mitis in 1814 in Vienna and was subsequently manufactured in his chemical factory in Kirchberg, Austria. One of his products was Mitis green, described by Wurzbach (1868) as a "beautiful green" pigment containing copper and arsenic (*Arseniksaurem Kupfer*). This chemical composition of Mitis green appears to refer to Scheele's green, since no acetate is mentioned, but the chemical knowledge of Wurzbach, Mitis' biographer, is unknown. Production of the pigment continued in Kirchberg until 1818. Other sources also gave credit to Mitis as the discoverer of copper acetoarsenite and to Sattler's firm as being the first to produce Schweinfurt green on a large scale in 1814 (Kittel, 1960; Schweizer & Mühlethaler, 1968; Wehlte, 1975). Ehrmann (1834) wrote that Schweinfurt green became commercially available about 1814. Before then, it was produced under the names of Vienna green and Mitis green, with its preparation method known to only a few manufacturers. Bersch (1901) suggested that Mitis and Sattler may have discovered this material simultaneously.

Chemical composition and manufacturing methods of emerald green remained a trade secret until 1820 when the German chemist, Justus von Liebig, received samples of a very expensive pigment known as Vienna green or Mitis green and a much less expensive type named Schweinfurt green. He determined their chemical compositions and a method of synthesis, which he published in July 1822 (Liebig, 1822, 1823). Henri Braconnot also received a sample for analysis from a Mr. Noel, the owner of a wallpaper factory in Nancy, and his results were published a few months after Liebig's analysis (Braconnot, 1822). After this information was made available to the public, emerald green was produced by many firms in Europe and eventually in the United States.

2.3 History of Use

2.3.1 ***Scheele's green.*** Riffault et al. (1874) gave an early reference to Scheele's green as being used "extensively . . . in the manufacture of paper-hangings." However, it is difficult to substantiate the extent of its use because few examples have been reported. Hurst (1892) noted that it was widely used at first because it was the best and most brilliant green available at the time, although with the introduction of emerald green, its popularity gradually declined.

The limited information available about the pigment was primarily concerned with its use as a colorant for fabrics and wallpapers (Ure, 1847; Lynn, 1980, 1980/1981). The *Colour Index* (1971a) indicated it was used in calico printing, fixed with albumen. Parnell (1849) and Ure (1847) described procedures for printing on cotton fabric with Scheele's green whereby the pigment was precipitated within the cloth using double decomposition reactions.

Parker (1812) recommended his improved low-alkali version of Scheele's green for a variety of applications, such as house and ship painting, claiming that it was not likely to be decomposed by salt water. He also suggested it for painting venetian window blinds.

According to Harley (1982), there is little mention of Scheele's green in English literary sources; Field's *Practical Journal 1809* and *Chromatogra-*

phy (1835) and a brief mention in a treatise on oil painting published in 1795 are the exceptions. Thus, there is some question as to the extent of its use as an artist's pigment in Britain. Both Church (1915) and Bearn (1923) considered it to be inferior to emerald green; Church commented that "it should not find a place on the palette of the artist." Bomford et al. (1990) indicated that it was used briefly as a decorator's paint rather than as an artist's pigment and was rarely used by the late 1870s. Although the pigment was still mentioned in 1923, by then its use had become limited. In the United States Scheele's green was listed as a dry color in the F. W. Devoe and Company trade catalogues from 1878 and 1883 and as one of "Eduoard's Celebrated French Oil Colors in Tubes" in an 1898 Frost and Adams catalogue. Scheele's green was never offered by Winsor and Newton in any of their paints (Peter Staples, personal communication, 1989).

Statistics on quantities produced or cost of manufacturing are limited. In 1914 the price of 100 kg of Scheele's green was 350 German marks, compared to technical-grade copper arsenite, which cost 240 marks (Rose, 1916). In addition to its use as a pigment, other applications were as a medicinal intestinal antiseptic, as a wood preservative, insecticide, fungicide, and rodenticide (Curtin, 1927; *Kirk-Othmer*, 1965; *The Merck Index*, 1988).

2.3.2 ***Emerald green.*** Immediately after its discovery, emerald green became popular chiefly because of its appealing brilliant color. Once its composition and methods of manufacture became known in 1822, production rapidly became widespread as shown by the number of names associated with place of origin, with the new colorant finding a wide variety of applications (Zerr & Rübencamp, 1908). Emerald green was soon prepared by many paint firms and offered by most color makers. In Britain, Winsor and Newton introduced emerald green in oil and watercolors in their first catalogue in 1832 (Pavey, 1984).

Carlson and Krill (1978) detected copper and arsenic in two pigments labeled blue verditer and green verditer from a paint box made in 1826 by Osborne and Company, Philadelphia; they suggested that these pigments were probably Scheele's or emerald green. They also found a green pigment containing copper and arsenic on one of a group of early American watercolors, *Mr. Kingsbury and Son* (1780–1830) (Janice Carlson, personal communication, 1991).

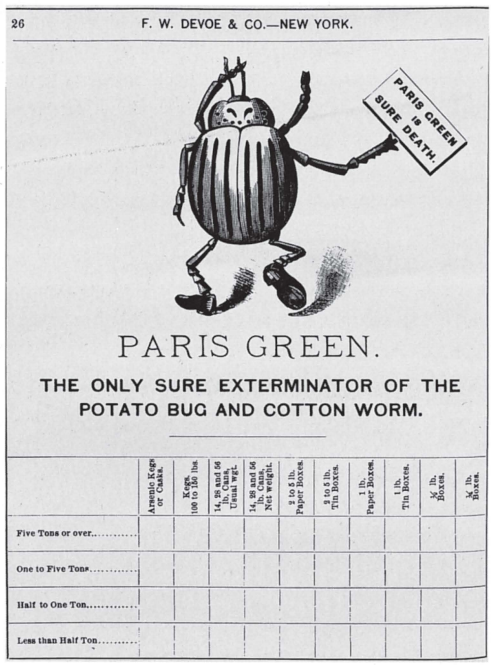

Fig. 2 Illustration from F. W. Devoe and Company, *Trade Catalogue* 1883, New York. Photo from Hagley Museum and Library, Wilmington, Del.

By the late 1800s, despite inherent flaws such as chemical instabilities, incompatibilities with sulfur-containing compounds, and warnings about its poisonous nature, emerald green was being offered by almost all major art supply firms. For example, in their 1883 catalogue, F. W. Devoe and Company listed (under fine greens) both Paul Veronese green and emerald green dry colors; for finely prepared artists' oil colors (under class A) they offered emerald green, Paris green, and Veronese green (Devoe, 1883). Devoe also sold Paris green as a japan finish for coach and car colors, as well as in various grades and quantities for use as an insecticide (fig. 2).

Frost and Adams Company (1898) in Boston, primarily sellers of imported artists' supplies, listed in their catalogue the following manufacturers offering emerald green: Winsor and Newton, George Rowney and Company, James Newman and Company, Dr. Fr. Schoenfeld and Company, L. and C. Hardtmuth, Edouard, Mussini, John W. Masury and Son, E. Faber, and F. W. Devoe and Company. The pigment was available in media such as oil, watercolor, pastels, wax crayons, and pencils. It was also offered by Rowney and Company in moist watercolors made for children.

Emerald green was popular among French

Fig. 3 Paul Gauguin, *Old Women at Arles*, 1888, oil on canvas. Emerald green was used in the grass along the water, in mixtures for the skin and hair of some of the figures, and in the foliage areas. Art Institute of Chicago, Mr. and Mrs. Lewis Larned Coburn Memorial Collection 1934.391.

impressionist and post-impressionist artists and has been identified in many of their works. It is mentioned in contemporary documentation of materials used by many of these artists. When in the South Pacific, Paul Gauguin relied on his friends and dealers in France for most of his art supplies. In a letter of February 1897 to Georges-Daniel de Monfreid, Gauguin requested twenty tubes of "*vert véronèse bonne qualité*" along with other tubes of paint (Joly-Segalen, 1950). An example of Gauguin's use of emerald green can be seen in *Old Women at Arles* (fig. 3). Vincent van Gogh suggested in a letter (no. 475) to his brother Theo in 1886, that he should purchase paints from Tasset and L'Hôte; among the various paints Vincent requested are fifteen double tubes of *vert Véronèse* (Charensol, 1960). Bang (1991) discussed Van Gogh's palette and his use of emerald green in two of his paintings in the Rijksmuseum Vincent van Gogh. The English edition of Van Gogh's letters (Van Gogh-Bonger, 1958) had incorrectly translated *vert Véronèse* as malachite green and *vert émeraude* (viridian) as emerald green. *Vert Véronèse* was among the colors recorded on a note written by Pierre-Auguste Renoir describing his palette (Renoir, 1962). According to Emile Bernard (1925), it was also among the pigments that Paul Cézanne used and *vert Véronèse* can be found in paint lists in Cézanne's sketchbooks and notebooks (Rewald, 1948, 1951). From his writings, we know that the English Pre-Raphaelite artist William Holman Hunt also used emerald green (Hunt 1880, 1969).

Richter and Härlin (1974a) analyzed an early nineteenth-century collection of dry pigments and painting materials (found in a German pharmacy) that included a bottle labeled Schweinfurter Grün; they identified it as emerald green. Pey (1987) researched a Dutch nineteenth-century collection that included several different green pigments, two of which were identified as Schweinfurt green. Pey also analyzed three green pigments labeled "Minraalgroen" and "Papegaaigroen" that were copper arsenic compounds; infrared analysis

indicated these compounds were not Scheele's green or emerald green but may instead be copper formo-arsenite, with the formic group substituting for the acetate group.

Toch (1911) provided an interesting example of the pigment's use:

> Marine painters use it for painting the starboard light, and sometimes produce a most brilliant effect by starting with a hydrated oxide of chromium, then painting a ring of emerald green, and in the center placing a touch of zinc white. This gives the effect of luminosity.

Rose (1916) mentioned that the quantity of copper-containing pigments exported from Germany between 1890 and 1900 was three hundred to five hundred tons, but by 1907 it fell to between thirty-five to fifty tons. In 1914, 100 kg of Schweinfurt green cost 160 German marks. Coffignier (1925) gave statistics concerning trade in the French pigment industry in the early 1900s, pointing out that before World War I trade with Germany was extensive. According to Coffignier, the following are the total French imports and exports for Schweinfurt and related greens and blues:

	Imports in kilos	*Exports in kilos*
1912	17,800	5,400
1918	2,300	1,500
1919	300	1,500
1920	68,700	23,800

(Values for 1912 are for Schweinfurt green, Mitis green, pale greens, and pale blues; the others are solely Schweinfurt green.)

In addition to being sold as an artist's pigment, emerald green was used in the decorative arts for coloring wallpapers, cloth lampshades, decorating domestic furniture and fabrics, coloring linoleum, and as a component in paints for toys (Ure, 1847; Church, 1915; Bearn, 1923; Lynn, 1980/1981). It was also used in exterior and interior house paints, in japan finishes for coach and carriage painting, and for striping and ornamental work on automobiles and sleighs (Uebele, 1913). Pearce (1913), in discussing greens used in house decorating, noted that emerald green is "the finest and brightest green that can be produced, for which there is no substitute."

Gettens (1969) reported it was a commonly used pigment for false patinas and bronze repairs since it had the proper bluish hue that imitated the effect of natural malachite and atacamite corrosion products.

Quantitatively, emerald green's main application was as an insecticide and fungicide marketed as Paris green. By 1942, although it was being replaced by newer and more effective arsenic-based products, Paris green was still being used in the United States at an annual rate of approximately two million pounds (Roark, 1942).

Gardner (1933, 1939) listed four manufacturers of Paris green: Sherwin-Williams Company, Ansbacher-Siegle Corporation, Fred L. Lavenburg Company, and the Ansbacher Color Corporation. The *Colour Index* (1976) listed two manufacturers of emerald green: Resinous Chemicals Ltd. in Durham, England, and Sherwin-Williams Chemical Company.

Kittel (1960) remarked that Schweinfurt green was still in use in the 1950s, despite its toxicity, because of its bright tone and lightfastness. Emerald green was among the artists' pigments listed by the British Standards Institution (1957). Winsor and Newton purchased emerald green from a firm in France that made it primarily for use as a rat poison; the firm could not understand why Winsor and Newton specified strict color requirements (Peter Staples, personal communication, 1989). Winsor and Newton discontinued offering the pigment by the 1960s, replacing it with Winsor emerald, a mixture of azo yellow and phthalo green (Pavey, 1984). Sattler's factory ceased production in 1930, but the Gademann Color Factory, also located in Schweinfurt, produced emerald green until the mid-1950s. In 1989, the city of Schweinfurt held an exhibition commemorating Sattler's historical importance to the city and the pigment that he made famous (Erich Schneider, personal communication, 1989). In the United States, F. W. Weber Company was still offering real emerald green in 1960; the pigment is also listed in their 1974 catalogue, although this may have been an imitation emerald green (Weber, 1960, 1974). By 1984, the Martin/F. Weber Company was supplying a product called emerald green that was a composite of cadmium sulfide, barium sulfate, titanium dioxide, copper phthalocyanine, and chlorinated copper phthalocyanine (Martin/F. Weber, 1984).

2.4 Dates of Use

The exact date when the use of Scheele's green was discontinued is not known. Emerald green was used as a pigment from its first manufacture in the early 1800s until the 1960s in Europe and the United States; its use as an insecticide continued into the early 1980s.

3.0 General Pigment Properties

3.1 Color and Spectral Reflectance

The method of manufacture of Scheele's green determines its color variations. The copper-to-arsenic ratio determines shade, with a higher arsenic value producing lighter colors (Sattler, 1888). Its hue has been described as yellowish green or grass green. Bearn (1923) characterized it as having a pale, yellowish green color.

The color of emerald green ranges from pale to dark green depending on the manufacturing process and the resulting crystal form and perfection. The different shades are due mainly to variation in particle size, with the smaller grains yielding lighter colors. The light absorption path and hence the shade of the pigment is determined by the sizes of the final grains. Emerald green's spherulitic form is responsible for the unusual color and brilliance of this pigment. There is also a secondary effect due to pleochroism, which causes large crystals to favor a blue shade. Batches of various-sized particles can be mixed to create lighter or darker colors; however, size spread influences the shade with a given grain size being darkest and having the most intense color with a narrow distribution. If it is desired to match such a pigment and no material is available with a similar size range, only an approximate match can be accomplished. If large, dark green grains are finely ground, their color lightens to a shade similar to that of the rapidly precipitated variety (Sattler, 1888).

Figure 4 shows a typical reflectance curve of emerald green in parchment size. The dominant wavelength varies slightly from 509.2 nm to 511.9 nm. The purity ranges from 22.8% to 23.2%. With a CIE (*Commission Internationale de l'Eclairage*) illuminant type C, the tristimulus values are: X=22.71, Y=39.12, and Z=31.00 (Barnes, 1939). See section 3.3 for a reflectance curve of emerald green in oil.

3.2 Hiding Power and Tinting Strength

No reliable refractive index information has been published for the group of compounds classified as Scheele's green. De Wild (1929) reported that it has a refractive index between 1.550 and 1.749. Its hiding power and tinting strength have not been reported.

Emerald green has good hiding power due to a combination of a moderately high refractive index (1.71 to 1.78) and reasonable opacity. Some authors (Bearn, 1923; Gettens & Stout, 1966) indicated that it has fair body and covering power; Bersch (1901) stated that because of varying particle sizes, the deeper the shade, the less the covering power, but Toch (1911) reported that emerald green used alone was defective and a weak color.

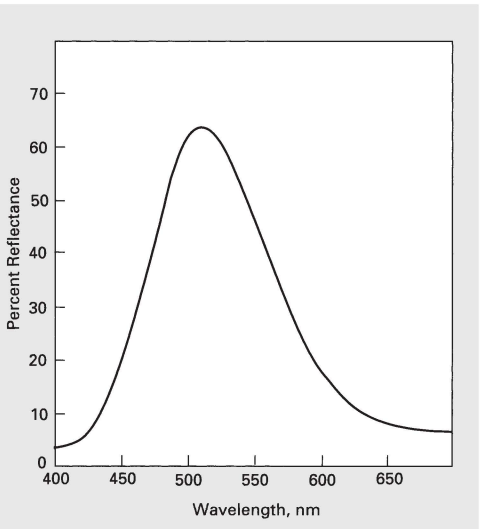

Fig. 4 Spectral reflectance of emerald green in parchment size. Adapted from Barnes (1939).

3.3 Permanence

Bachhoffner (1837) indicated that copper arsenic pigments were not very permanent, although they were superior to other copper greens. Standage (1886) considered emerald green to be the most permanent of the copper greens and not adversely affected by damp or polluted air and that copper arsenite is similar in stability. Bersch (1901) referred to Scheele's green as able to "resist the action of the atmosphere tolerably well." In Field's *Practical Journal 1809* the Scheele's green sample from Paris was described as "browned by damp & foul air but less affected than copper greens in general during the same time" (Harley, 1982). Gettens and Stout (1966), however, wrote that this pigment fades rapidly, possibly because of the presence of copper hydroxide.

An 1888 study by Russell and Abney on the effects of light on watercolors (Brommelle, 1964) showed that after exposure for approximately two years emerald green had turned "very slightly brown," indicating some degree of darkening, although this reaction did not occur in a sealed glass tube exposed to the same illumination. Gen-

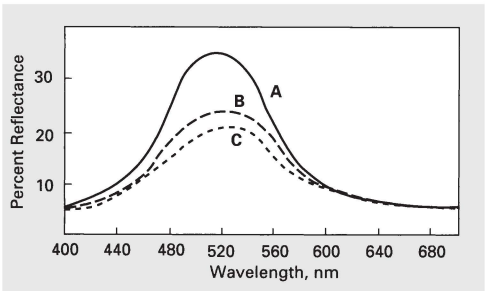

Fig. 5 Spectral reflectance of emerald green showing darkening of the pigment in oil paint after 111 hours of exposure in a fadeometer. (A) unexposed (B) covered by glass and UF-1 filter (C) covered by glass. Adapted from Feller (1968).

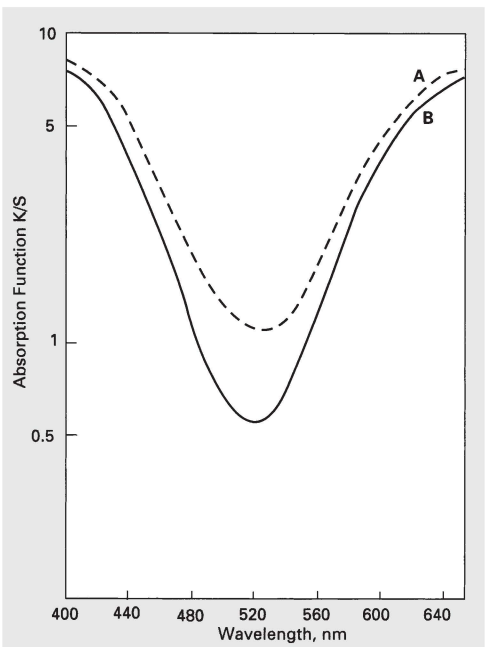

Fig. 6 Spectral absorption of emerald green showing darkening in oil paint. (A) exposed emerald green (B) unexposed emerald green. Adapted from Feller (1968).

tele (1909) stated that emerald green withstands air and light very well, while Bearn (1923) indicated that it is moderately stable to air and light. Wehlte (1975) indicated that emerald green is weatherproof and lightfast.

Using spectrophotometry Feller (1968) studied the darkening of emerald green in oil on exposure to light (expressed in terms of the Kubelka-Munk K/S value), which shows as a decrease in the principal reflectance peak (fig. 5) or increase in the absorption peak (fig. 6). Curve A is the exposed emerald green in both figures. Emerald green at complete hiding in oil (see fig. 5) is darker than emerald green at incomplete hiding in parchment size (see fig. 4). This difference is seen in the spectral reflectance curves in the two figures; the difference could also be partly due to the fact that the emerald green samples used in each case were not the same.

Darkening is caused by hydrogen sulfide from the atmosphere reacting to form black copper sulfide (De Wild, 1929; Gettens & Stout, 1966). The reaction will proceed even with very low concentrations since the solubility product for copper sulfide is low (Mairinger et al., 1980). Church (1915) noted that emerald green is less affected by the presence of hydrogen sulfide than is Scheele's green. As a watercolor, emerald green quickly darkens in impure air, whereas in an oil medium it is practically permanent. According to Eibner (1909), darkening by hydrogen sulfide occurred least in oil medium. Reactions with sulfides are not directly reversible by oxidation and yield soluble copper sulfate that could rapidly lead to weathering.

Banik and Ponahlo (1981) examined the effects of copper-containing pigments, including copper acetoarsenite, on paper and have found that Schweinfurt green did not cause degradation of cellulose.

3.4 **Chemical Properties**

Scheele's green and emerald green are soluble in mineral acids and in sodium, potassium, or ammonium hydroxides. If ammonia is added to acid solutions of the pigments, a light blue precipitate of $Cu(OH)_2$ first forms; excess ammonia then creates the deep blue cuprammonium ion. Concentrated acetic acid will extract the copper from emerald green, producing copper acetate and arsenic trioxide (Ehrmann, 1834; Hurst, 1917; Weast, 1981–1982). Emerald green will give off acetic-acid vapors when dissolved in moderately strong acid (Church, 1915).

Both pigment types are insoluble in water if exposed for short periods, although emerald green will undergo hydrolysis over several days and lose up to 25% of the arsenic, with considerably less of the copper being dissolved. Heat accelerates this hydrolysis. The loss is greater if the material is first ground to reduce particle size and increase surface area. Emerald green will also be decomposed by carbon dioxide in water, with up

to 48% of the arsenic going into solution. With a sufficient excess of water, the pigment will eventually be broken down into its component parts. Heating either pigment results in the formation of black copper oxide (Plesters, 1956). Reaction with hydrogen sulfide and interaction with metallic sulfides cause formation of black copper sulfide. This reaction would be significantly retarded in oil-based paints (Eibner, 1909; Hurst, 1917).

Because impure or adulterated pigments were common, a series of chemical tests were described that determined the purity of emerald green (Hurst, 1892; Bearn, 1923). These tests can be summarized as follows:

A pure sample dissolves completely in hydrochloric acid to form a yellow-green solution that turns blue when diluted with water. If the sample is pure, the addition of barium chloride to this acid solution should produce only a trace of a precipitate that indicates the presence of sulfate. Hydrogen sulfide will precipitate combined copper and arsenic sulfides from the acid solution. After filtering and boiling to remove residual hydrogen sulfide, no iron, zinc, or calcium should be present in this solution, as would be indicated by a precipitate on the addition of ammonia, ammonium sulfate, and ammonium oxalate. Solutions in ammonia appear deep blue and the allowable precipitate of impurities is 0.5%. Solutions in sodium hydroxide appear pale blue and boiling will precipitate red cuprous oxide.

3.5 **Compatibility**

Copper arsenic greens will darken in the presence of sulfur-containing compounds to form black copper sulfide; the most important pigments in this category are cadmium sulfide and its variants. Uebele (1913) and Weber (1923) indicated that emerald green should not be mixed with any pigments containing sulfur, such as ultramarine blue and green, cadmium yellow, vermilion, and lithopones. Gettens and Sterner (1941) studied the compatibility of cadmium sulfide and emerald green in a linseed oil paste by exposing it to a temperature of 40°C and relative humidity of 80% for four months. The mixture darkened and the authors reported that cadmium yellows and reds, and lithopones caused a double decomposition reaction with emerald green. A comparison sample not subjected to elevated temperature and humidity also darkened. Emerald green reacted with cadmium sulfide on a microscale to rapidly produce significant darkening (Fiedler & Bayard, 1986).

Several artists were concerned by the sudden change resulting from mixing emerald green and cadmium sulfides. Camille Pissarro noted "I have tried the mixture of cadmium with red, white, and Veronese green. It becomes black in four or five days from the Veronese green. Even blacker than the chrome yellow mixture" (Rewald, 1943). William Holman Hunt (1880) discussed the darkening of a mixture of emerald green and cadmium yellow to almost black in two weeks on a trial canvas. He also noted that emerald green used alone changed to a deeper tint, but Veronese green was still bright and clear; the latter may have been a differently manufactured copper acetoarsenite or possibly an unrelated compound. Doerner (1949) described a "bright green and very spring landscape which had turned absolutely black, not merely blackish" as a result of mixing cadmium yellow with emerald green.

Gettens and Stout (1966) indicated Scheele's green blackens by association with lead compounds, presumably due to the formation of lead acetate, which then reacts with airborne sulfur compounds to form lead sulfide. Standage (1886) reported Scheele's green is destroyed when mixed with true Naples yellow, which is lead antimonate.

Another incompatibility noted by Weber (1923) was the decomposition of most organic lakes when used with emerald green; Toch (1911) indicated that lake colors were destroyed within a few hours.

Bersch (1901) recommended that emerald green should not be applied to lime, with which it reacts to produce a yellowish green copper arsenite similar to Scheele's green. Rose (1916) also indicated it could not be used in distemper, "and therefore not in fresco painting, since calcium hydroxide extracts acetic acid from it and makes it yellowish-green." Alkalies will change it into cuprous hydroxide. Standage (1886) also wrote it should not be used in fresco but Wehlte (1975) stated that it is fast to lime. Wehlte commented that it should not be used in silicate painting; these silicate media were a form of wall painting using waterglass (sodium or potassium silicate) as a binder and such material would hydrolyze to form various fractions that would be reactive. A disadvantage to the use of sand in the plaster or mortar used in fresco was the presence of impurities in the sand. Gentele (1909) noted emerald green should not be used on fresh whitewash because the calcium hydroxide draws acetic acid out of it, leaving behind yellowish green cupric oxide that has an unpleasant color and little brilliance.

3.6 Oil Absorption and Grinding Properties

No percentage of oil absorption has been reported for Scheele's green. Gentele (1909) noted the pigment is very brittle and difficult to grind when wet, although it is easy to grind when dry.

A wide range of values for oil absorption of emerald greens is reported. Mayer (1971) indicated an absorption of 13% oil by weight (13 lb. oil per 100 lb. pigment), Gardner (1933, 1939) gave 20% oil, and Wehlte (1975) gave a value of greater than 60%. Uebele (1913) was more specific: "Eighty-five parts by weight of French pale Paris green and fifteen parts of clarified poppy-seed oil is the proper proportion for mixing, although it may be necessary to use a little more oil." Gardner (1933) listed the values for four Paris green samples as 6.5%, 10.2%, 13.8%, and 15.0% based on data supplied by manufacturers. Oil absorption will vary with the morphology of the particles; those with compact spheres will have a lower absorption while the exfoliated types with a larger surface area-to-volume ratio will require more oil. Although grinding of emerald green was not generally recommended, Gentele (1909) mentioned that the coarser-grained darker varieties are more difficult to grind.

3.7 Toxicity

Scheele's and emerald green were generically referred to as "poison greens." If these pigments were being synthesized for the first time today, they would probably be only laboratory curiosities because of toxicity due to their arsenic content. Emerald green was referred to by Zerr and Rübencamp (1908) as the most toxic pigment produced in quantity. Toxicity measurement on rats gives an LD_{50} oral of 22 mg/kg (*Kirk-Othmer*, 1978; U.S. *EPA Chemical Profiles*, 1985). The allowable exposure level to humans to arsenic in the air is 0.5 mg/M^3 (Weast, 1981–1982). This is equivalent to about 1.1 mg/M^3 of emerald green. Sources of human contact included wallpapers, wall paints, and calico printing. In 1832 arsenic compounds and lead white used as colorants at wallpaper factories in England caused illness among the workers (Entwisle, 1964; Greysmith, 1976). Arsenic-containing pigments were later banned in England for this use and many wallpaper firms there advertised that their papers did not contain arsenic (fig. 7). Concern about arsenic in American wallpapers was also evident (Nylander et al., 1986).

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Fig. 7 Advertisement for wallpaper c. 1890 by Jeffrey and Company, London. From Entwisle (1964), with permission of A and C Black, Publishers, London.

As early as 1839 the Bavarian government issued a royal proclamation warning of the dangers of such use. Sanger (1893) outlined several instances beginning in 1859 where arsenic was either suspected or found in cases of chronic, low-level poisoning. In 1932, almost a century after the Bavarian government warning, two deaths were attributed to fungal metabolites containing the gas trimethyl arsine (Fleck, 1871; Gosio, 1893a, b; Abel & Buttenberg, 1899; Thom & Raper, 1932).

Bersch (1901) mentioned that emerald green was "fixed" on light fabrics, such as those used for ball gowns, with albumen or dextrine, and then brought into the air by the movements of the dancers, resulting in many illnesses.

By 1882, emerald green was banned in Germany for use in toys, wallpapers, and tableware, and by 1888 the use of all copper-arsenic pigments was restricted to oil paints and lacquers or, when used, they were required to be covered with a coat of varnish (Rose, 1916). Because of the possibility of an arsenical pigment being sold under a different name to a manufacturer of such items, it was recommended that all colors be tested by a chemist to avoid being in conflict with the ordinances (Guignet, 1888).

4.0 **Composition**

4.1 **Chemical Composition**

4.1.1 ***Scheele's green.*** There was a wide range of compositions for Scheele's green because of the different chemical types and the variation in the copper and arsenic content. Under the conditions originally specified by Scheele, neutral copper orthoarsenite was probably the predominant variety (Bornemann, 1922). The formula usually given is $CuHAsO_3$, although this is not chemically the most likely type based on modern synthesis and analysis. Scheele's green has been incorrectly referred to as copper arsenate. Schweizer and Mühlethaler (1968) reported the following formulas:

Sharples (1877) and Bornemann (1922): $Cu_3(As_2O_3).H_2O$

Berzelius (1845): $2CuO.As_2O_3$

Ure (1847): $CuO.As_2O_3$

Miller (1864): $CuHAsO_3$

Bloxam (1862): $CuO+CuHAsO_3$

Within each class of compounds the shade of the pigment was determined by varying the copper-to-arsenic ratios of the starting materials, with a wide Cu:As range of 1:1.3 to 1:3.6 given by Zerr and Rübencamp (1908).

Scheele's green can contain some co-precipitated basic copper carbonate or hydroxide in addition to copper arsenite (Bornemann, 1922; De Wild, 1929). Copper arsenites of variable composition can result from the same method of synthesis (Stavenhagen, 1895). Syntheses by Schweizer and Mühlethaler (1968) indicate that copper diarsenite, $2CuO.As_2O_3.2H_2O$, would form under conditions of cold precipitation. When precipitated hot, the concentration of sodium or potassium arsenite determined the species, with neutral copper orthoarsenite, $3CuO.As_2O_3.2H_2O$, copper diarsenite or copper metaarsenite, $CuO.As_2O_3$, forming as the arsenic content of the starting materials was increased. Schweizer and Mühlethaler found by x-ray diffraction that most copper arsenites are amorphous rather than crystalline, although Pertlik (1977) was able to synthesize the mineral trippkeite ($CuAs_2O_4$) in crystal form. Damour and Vom Rath (1881) determined the crystal structure of the mineral to be tetragonal. Carter et al. (1943) mentioned three copper arsenite salts: $Cu_3(AsO_3)_2.3H_2O$, $CuHAsO_3$, and $Cu(AsO_2)_2$. Saxena and Bhatnagar (1958) mentioned one, $CuAsO_2$. Thermometric and conductometric analyses performed by Bhadraver (1962) disclosed $Cu(AsO_2)_2$ as the most probable compound formed by reacting copper sulfate with sodium arsenite. Gmelin (1961) listed ten possible copper arsenites if states of hydration are included; not all of these are necessarily components of Scheele's green. It would also be possible to produce mixed arsenites in a single batch.

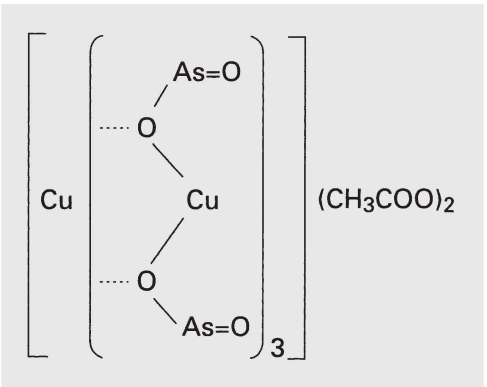


Fig. 8 Structure of emerald green. Adapted from Kittel (1960).

4.1.2 ***Emerald green.*** Emerald green is copper acetoarsenite, $3Cu(AsO_2)_2.Cu(CH_3COO)_2$. It is sometimes incorrectly referred to as copper acetoarsenate. The measured density is 3.25 to 3.27, and the calculated density is 3.34, based on x-ray diffraction. The crystal system is monoclinic with lattice parameters a=9.93, b=9.40, c=5.48, and angle β=102.0° (Pertlik, 1977). The structural formula has six O–As=O groups linked in pairs by three copper atoms coordinated around a central copper atom forming a copper complex. The structure is seen in figure 8.

In the past, the existence of a single compound for emerald green was uncertain; analyses resulted in variations in composition, which were due to retained arsenic trioxide, residual copper arsenite or copper acetate starting materials, or to uncombined copper oxides. Arsenic trioxide, even in carefully made emerald green, can range from trace amounts to a few percent; in improperly prepared material up to 20% arsenic trioxide is common. About 1% to 2% water and up to about 2% sulfate were sometimes present (Parry & Coste, 1902; Heaton, 1956). Some commercial samples taken from products used mainly as an insecticide contained up to 69% arsenic trioxide. This was not deliberate adulteration but resulted from the

need to produce large amounts rapidly (Stillman, 1899).

4.2 Sources

There is no natural source of copper arsenic pigments, although the rare mineral trippkeite exists in a few mineral collections. A copper arsenate mineral olivenite, $Cu_2(AsO_4)(OH)$, also exists. Both pigments are synthetic materials. A few specialty chemical firms currently supply them in laboratory quantities. Commercial sources may exist in countries with less stringent environmental restrictions where the material may still be in use as an insecticide.

4.3 Preparation

Manufacturing Scheele's green did not involve the problems of crystal formation that existed in the making of emerald green, but was complicated by the possible production of several other copper-arsenic compounds. The manufacture of high-quality emerald green was a complicated process; there is extensive literature available that deals with its preparation.

4.3.1 ***Scheele's green.*** The starting materials for Scheele's preparation method were two solutions: one of copper sulfate alone and the other of arsenious acid mixed with potassium carbonate. The solutions were combined and allowed to stand, resulting in the precipitation of the pigment; excess copper precipitated as copper carbonate (Mérimée, 1839; Rose, 1916; Scheele, 1931). Payen's (1835) method called for dissolving arsenic trioxide in boiling water and adding copper sulfate until a sample gave the required color when precipitated with sodium or potassium carbonate. Commercial potassium carbonate varied in alkali content; therefore, a series of test precipitations were performed until the desired color was attained. Sodium or potassium hydroxides caused precipitation of a dark-colored material, which, especially if the alkali was not completely removed, formed a hard mass with glassy fracture that was difficult to pulverize without first saturating it with water and redrying. The darkest shades were made starting with high concentrations of copper sulfate. Lime water could be used as the alkali instead of the carbonates, although a large quantity was required for complete precipitation (Mérimée, 1839; Bersch, 1901; Rose, 1916). In a variation discussed by Church (1915), hot solutions of arsenic trioxide and copper sulfate were mixed together and precipitation resulted when small portions of potassium carbonate were added until the pigment attained its maximum intensity.

The method patented by Parker (1812) consisted of combining potash and white arsenic in water. This combination was gradually mixed cold with a copper sulfate solution; a green oxide (probably copper hydroxide) was produced that changed to Scheele's green. The advantage of this method was the lack of any basic compound that could react with an oil medium.

Zerr and Rübencamp (1908) described commercial preparation using a warm solution of copper sulfate to which was added a solution of sodium hydroxide and arsenic trioxide. The concentration of the latter was varied depending on the shade desired. Additional alkali was introduced until no copper could be detected in the filtrate from the green precipitate. The pigment was allowed to settle and was then washed, filtered, and pressed. A brighter color was obtained if the dry pigment was heated at 60°C to 70°C.

Gentele (1909) outlined processes for the creation of true Scheele's green and the German variety of the pigment. To produce Scheele's green, a solution of potassium carbonate and sodium or potassium hydroxide was added to a solution of copper sulfate. A solution of arsenic trioxide and potassium carbonate was then added to this alkaline mix after it had cooled. The precipitate was allowed to settle, and was then washed, filtered, and dried. A darker, more brilliant green resulted when the precipitate was dried at elevated temperatures.

In the German process, the alkali was dissolved with the arsenic trioxide rather than with the copper salt. A lighter shade could be produced when a boiling solution of copper sulfate was stirred together with a basic solution of arsenic trioxide. The first reaction would produce copper diarsenite while the other would favor copper metaarsenite. Interestingly, the proportions of reactants described for the German variety more closely matched the original directions given by Scheele (Gentele, 1909; Rose, 1916).

Pale yellow-green to dark green colors could be made, the shade being determined by the relative portions of copper to arsenic; the mixtures that contained more arsenic yielded a paler product. The ratios of the starting materials, temperature, and the amount of excess alkali determined the arsenic-to-copper ratio of the final material. In this respect, the formulas for Scheele's green are only approximate (Zerr & Rübencamp, 1908;

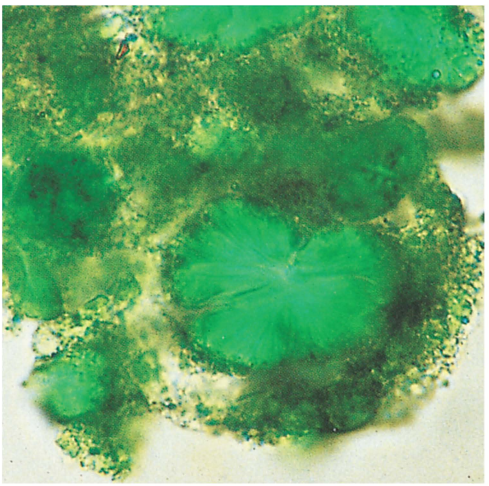


Fig. 9 Photomicrograph by transmitted light of a stage in the acetate method of producing emerald green, illustrating the gelatinous matrix of copper arsenite and arsenic trioxide in which are embedded growing spherulites of emerald green. The acetate process seems to favor coarse spherulitic structure. Sample prepared by Vladimir Shishkov, Guelph, Ontario, Canada, August 1991. Mounted in Aroclor 5442, n=1.66. 1,000x.

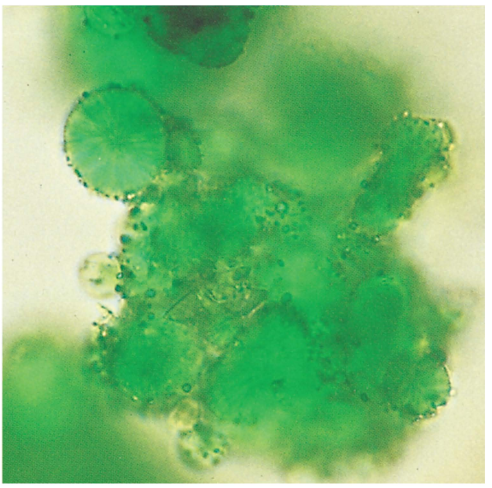


Fig. 10 Photomicrograph by transmitted light of a stage in the sulfate method of producing emerald green showing small spherulites with smooth surfaces composed of fine subunits. The matrix is less pronounced than in the acetate process and the crystallite subunits probably grew more rapidly as is consistent with their small size. Sample prepared by Vladimir Shishkov, Guelph, Ontario, Canada, August 1991. Mounted in Aroclor 5442, n=1.66. 1,000x.

Gentele, 1909). In general, the precipitate did not correspond exactly to the stoichiometry of the starting materials but rather was richer in copper and poorer in arsenic. Some hydroxide, carbonate, and free arsenic trioxide could be present in the final product (Schweizer & Mühlethaler, 1968).

4.3.2 ***Emerald green.*** The two basic preparation methods of historical importance for emerald green are the acetate and sulfate methods. Although there were many variations, the general reactions are:

Acetate method

$$6NaAsO_2+4Cu(CH_3COO)_2 \rightarrow 3Cu(AsO_2)_2.Cu(CH_3COO)_2+6CH_3COONa$$

Sulfate method

$$4CuSO_4+6NaAsO_2+2HCH_3COO+Na_2CO_3 \rightarrow 3Cu(AsO_2)_2.Cu(CH_3COO)_2+4Na_2SO_4+H_2O+CO_2$$

In both methods the reaction proceeds through an intermediary of hydrated basic copper arsenite or similar compound, which is then converted into emerald green; there are variations in the proportion of the ingredients, concentration of solutions, temperature, mixing, reaction time, precipitation time, and rate of crystallization. The time required to make a batch ranges from less than one hour to many days. In order to create a high-quality pigment, the proper crystal size, shape, and state of agglomeration must be achieved and many preparation methods have evolved around these criteria, either intuitively or through precise knowledge. Figures 9 and 10 illustrate intermediate stages in the two processes.

In making the emerald green pigment, it was extremely difficult to achieve a high-quality product. It was necessary to give the precipitate sufficient time to grow undisturbed to form the best crystals, but conversely, sufficient agitation was needed to achieve a uniform product and to disperse the crystallization nuclei and reactants. Both factors were made difficult by the indirect crystallization from a flocculent, and often slimy, intermediate. The amount of agitation used was critical to producing a proper pigment. In cases where reactants were added after crystallization was partially complete, concentration gradients and reaction rates would be changed. Materials had to be of high purity, especially with respect to iron, which was detrimental to the resulting pigment shade. In addition, if any errors were made, such as insufficient water, too high a temperature, too much stirring, or stirring at the wrong time, an

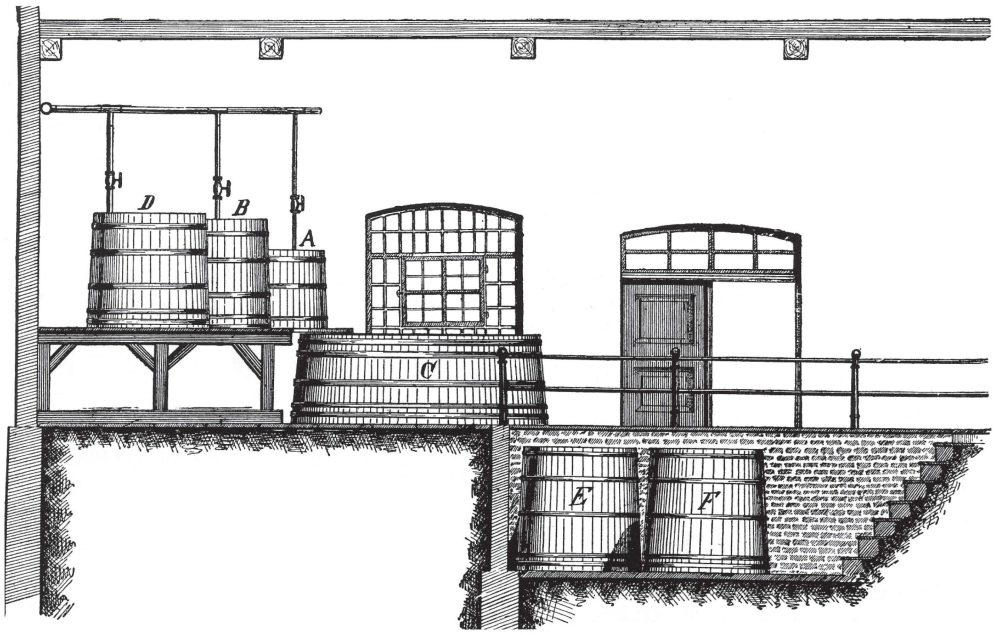


Fig. 11 Diagram of a facility (see also fig. 12) designed specifically for the manufacture of emerald green showing the arrangements of the dissolution and precipitation-crystallization vats.

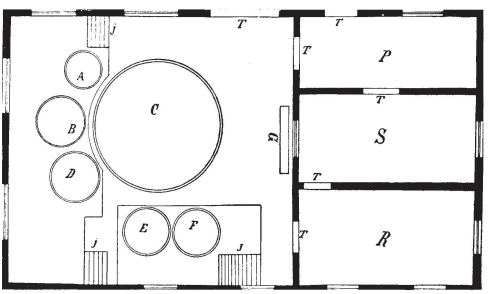


Fig. 12 Floor plan of figure 11. Dissolution of verdigris is carried out in *A*, the arsenic solution is contained in *B*, and *C* is the large, shallow precipitation and crystallization vat where the creation of the pigment actually occurs by both chemical reaction and crystallization. Vessel *D* is not explained in this reference, but it is probably a hot water buffer tank while *E* and *F* are for removal of spent mother liquor. After crystallization, the press *G* is used to expel excess liquid, *R* is the drying room, *S* is the area for sifting and sorting, and *P* is the packing room. *T* indicates the doors and *J* the stairs. From Zerr and Rübencamp (1908).

unsatisfactory whitish green resulted (Zerr & Rübencamp, 1908).

Emerald green can be made from a solution by evaporation, but the crystallization process is completely different, depending on encrustation and chance nucleation events and will result in a poor color because of the absence of the unique uniform spherulitic particles (Sattler, 1888).

Because emerald green was probably the most toxic pigment ever made in any quantity, the preparation and handling areas for its production had to be separate from the rest of the manufacturing facility with provisions for adequate ventilation and housekeeping. Zerr and Rübencamp (1908) illustrated a factory suitable for making emerald green (figs. 11–12).

Crystallization mechanism. The formation of the unusual spherulitic habit of emerald green requires a unique crystallization process, which was outlined by Sattler (1888). His diagram of emerald green crystal growth is shown in figure 13. All the morphologies he described, except the well-formed single crystal or the very unusual forms, can be observed in the photomicrographs and scanning electron micrographs in figures 14–32. Figure 13 (A) shows a very rare sin-

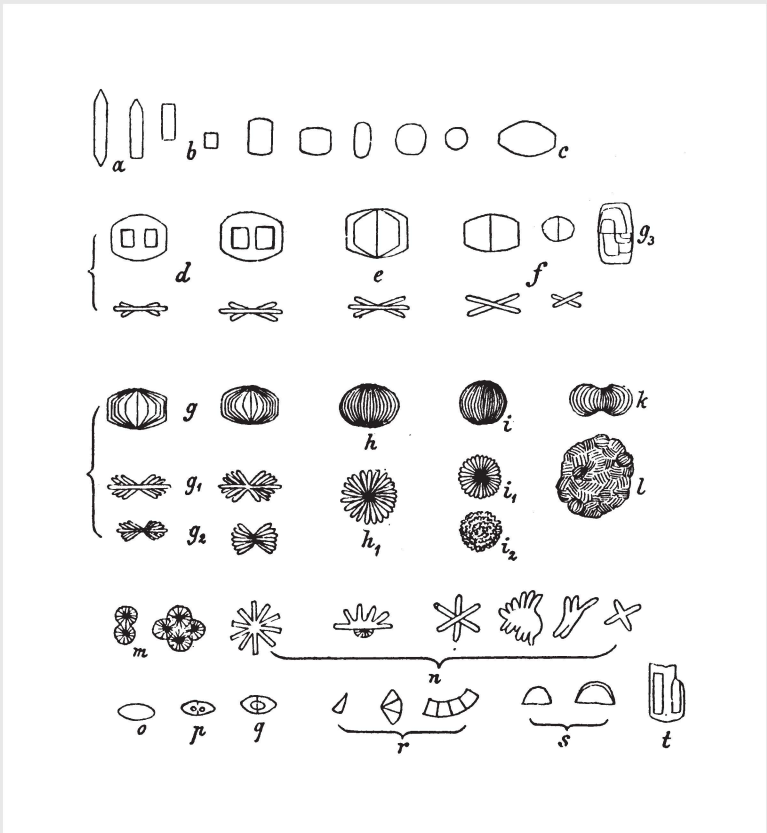


Fig. 13 Emerald green crystal growth diagram from Sattler (1888). Photo from Brown University Graphic Services, Providence, R.I.

gle prismatic crystal that usually has one or both ends blunted as in the forms from (A) to (B); the remainder of the row from (B) to (C) illustrates the rounded ends more commonly found on single crystals, most of which are plates. Simple cases of twinning, viewed from the side and top, are seen in (D) (E) and (F). In (D) there are crystallites near the center of a main crystal, in (E) the secondary crystallites grow at the center, and (F) is the simplest case of interpenetration twinning. These twinned assemblages show the same crystal lattice orientation when viewed from the side and various extinction positions seen from the top. The more complex forms that can be created during crystallization on the same pattern, where more or less similar-sized subunits add on, are seen in (G), viewed from the side (G_1) and top (G_2); when different size plates grow, a form illustrated in (G_3) is created with different sizes of plates. Growth continues by filling in the interstices to generate rounded spherulites as seen in (H and I, side views) and (H_1 and I_1, top views),

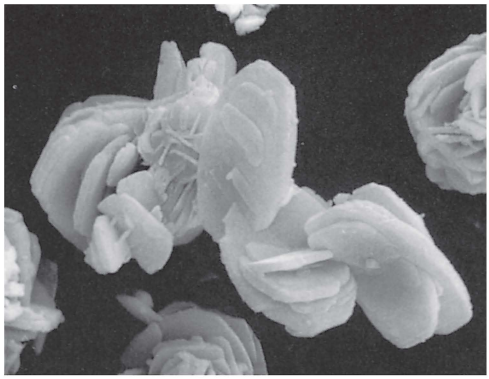
with these having microscopically visible striations corresponding to the crystallites; (I_2) has a smoother surface with very indistinct striations. Sometimes type (H) particles will form with depressions at the poles as seen in (K); (L) shows the incrustations that form on the surface of the liquid, and (M) shows intergrown agglomerates of spheres. Finally, the types labeled (N) are unusual forms, and the rest show various fragments of spherulites as single plates or groups.

The crystal size and state of agglomeration determines the color produced, with slow growth of large entities yielding the most desirable color. In general, the reaction path for the formation of emerald green begins with a form of Scheele's green (copper arsenite) as a gelatinous intermediary that both forms a matrix for arsenic trioxide nuclei and regulates diffusion in spherulite formation.

The sulfate process starts with a blue-green precipitate of basic copper sulfate that in concentrated solutions rapidly becomes thick and yellow-green in color; dilute solutions give a more gradual transition to copper arsenite. If copper acetate is the starting ingredient, the process of formation is similar; the main differences are that the solution is already rich in acetic acid, saturated with copper and arsenic trioxide, and therefore forms the product more rapidly and reliably. If the arsenite is washed and dried it becomes denser and will not readily dissolve to form emerald green. A freshly precipitated amorphous arsenite is needed to allow adequate diffusion of copper and arsenite ions in the formation of spherulites. Uniform diffusion gradients in all three dimensions are necessary for symmetrical particle geometry because it is uniform depletion of ions from the gelatinous solution that results in a spherulite. Another equally important intermediate compound is arsenic trioxide in amorphous particles that act as nuclei in spherulite growth. Small arsenic trioxide particles will form regardless of the conditions of mixing, concentrations, or temperature, but with different distributions. In an ideal situation, the arsenic trioxide nuclei will be evenly interspersed throughout the gelatinous mass of copper arsenite. The size of the initial copper arsenite particles is important as they coalesce into both a reactant and substrate for the arsenic trioxide granules. The more uniform the arsenite, the more probable that the trioxide grains will be evenly dispersed to allow the formation of separate emerald green spheres; if they are too close, multiple particles will intergrow. Variations in local density of nuclei yield a mixed precipitate with both isolated spheres and multiple spherulites. The nuclei convert to small emerald green plates and/or needles on the addition of acetic acid in the sulfate process or spontaneously with copper acetate. As these nuclei grow into the final pigment, the copper arsenite precipitate is slowly dissolved to generate emerald green. The growth mechanism may start out with a few plates forming a framework within which additional plates crystallize or, more commonly, many crystals will grow simultaneously to form a sphere. Some samples can show the entire series of formation stages while others have only the complete spherulites. Variations in the final product can be seen in figures 14 and 15. The relative uniformity of the grains depends on the precipitation mechanism of the copper arsenite, while stirring will influence the absolute size of the grains. More agitation results in rapid saturation of the precipitate and its removal from the solution by the growing particles of emerald green that, in turn, increases the crystallization rate and, hence, favors smaller grains. The physical conditions of precipitation (that is, temperature, concentration, amount of time for the formation of amorphous arsenic trioxide in the initial material, the method of addition of components, nucleation dispersal and number, combined with the amount of agitation) determine most of the pigment properties; the types of starting chemicals for the two processes are of lesser importance.

Acetate method. Liebig (1822, 1823) first described this process that was started by mixing verdigris (copper acetate, see Kühn, 1993) dissolved in hot vinegar with a solution of arsenic trioxide. A dirty-green precipitate formed, which was redissolved by the addition of more vinegar; the mixture was then boiled until emerald green with a bluish tint precipitated. If a darker, more yellow color was desired, the initial precipitate was heated in water containing potassium carbonate; however, if the heating continued too long, a color similar to Scheele's green formed.

The method originally used at the Schweinfurt plant was described by Kastner (1922). A small amount of vinegar was added to a slurry of verdigris in water that became a soft blue-green mass of gelatinous dibasic copper acetate; water was then added to precipitate light blue flakes. This precipitate was then gradually added to a boiling solution of arsenic trioxide (Rose, 1916). Ehr-



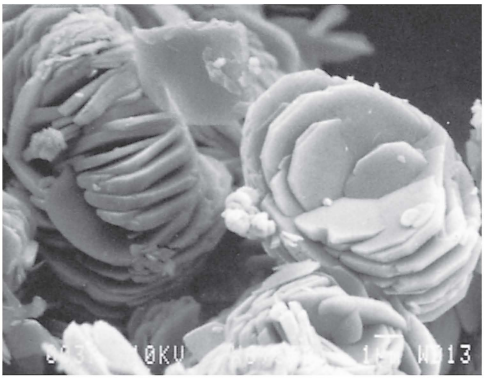
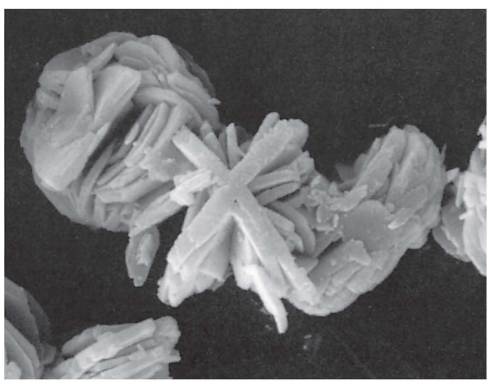
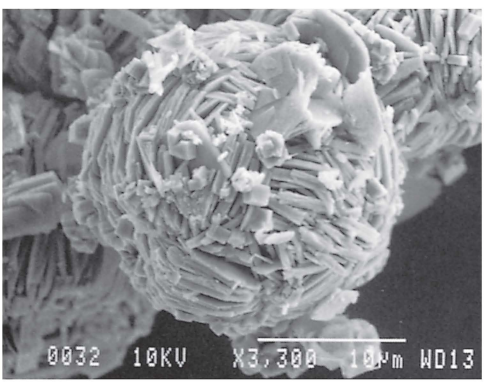


Fig. 14 Scanning electron micrographs of emerald green, labeled Scheele's green, Fezandie and Sperrle (August 1936) in the Forbes Collection, Art Institute of Chicago (AIC).

A. Small structures with few crystals are common in some samples; the center plate shows the beginnings of secondary twinning crystals while the others are in more advanced stages of growth. 2,900x.

C. The interpenetration twin-growth mechanism with the structure to the right displaying the relative arrangement of the individual crystal plates is evident. The grain on the upper left, seen from the edges of the crystallites, is more completely formed. Printed at 2,900x.





B. The center grain has two main sets of relatively thick intersecting crystals with the interstices in the process of filling in by the growth of secondary crystallites. The grain to the lower right is similar although it is shown at a different orientation. 2,900x.

D. This grain has an overall spherical form with the crystallites arranged in groups or as single entities with different orientations. The cubic crystals are probably As_2O_3. Printed at 1,800x.

mann (1834) recommended making a thin slurry of basic copper acetate in warm water, which was added while warm to a boiling solution of arsenic trioxide. The pigment formed in the boiling mixture after several minutes. A variation of this method called for mixing while at a boil the acetate and arsenic trioxide in the same vessel; a dirty-green precipitate formed, which changed to emerald green when cooled, sometimes after adding an equal volume of cold water.

Later variations of the acetate method also started with copper acetate and arsenic trioxide (Sattler, 1888; Bersch, 1901; Gentele, 1909). If neutral copper acetate (distilled verdigris) was substituted for basic copper acetate (ordinary verdigris) a deeper color formed, which has been sometimes incorrectly described as distilled emerald green (Bersch, 1901).

Sulfate method. Braconnot (1822) was the first to refer to the sulfate method of preparation. Copper sulfate was dissolved in a small amount of water; arsenic trioxide was boiled separately with potassium carbonate until no more carbon dioxide was given off; this hot arsenic-containing solution was

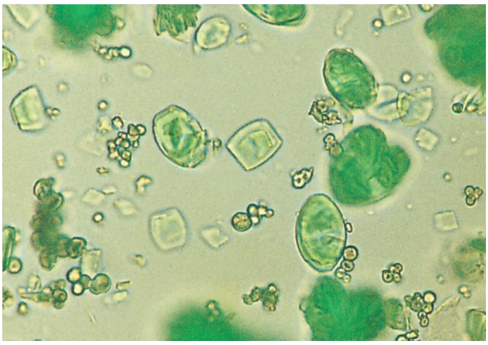
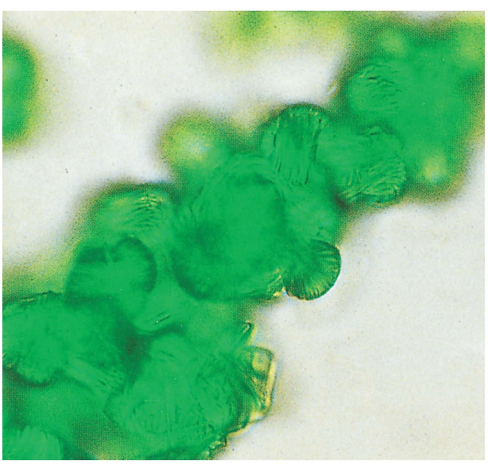


Fig. 15 Photomicrographs by transmitted light of emerald green no. 284, in the Martin J. Fischer Collection (MJF). Samples provided by Ron Harvey, Milwaukee Public Museum. The material from the Fischer Collection had a variety of types ranging from single crystal plates to complex agglomerated spherulites; these clearly show the stages of growth. The crystallites were large enough to be readily seen by the limited resolution of the optical microscope.

A. The starting point in the formation of spherulites with multiple radiating plates is shown. There are single plates and interpenetration twinned structures of a few crystallites with opposite pairs of sides either curved or straight. Absorption color for individual plates is minimal. The rounded colorless agglomerates are unreacted arsenic trioxide. Mounted in Canada balsam, n=1.52. 820x.



B. The complex structures illustrated are composed of many intergrown spherulites with various sizes and orientations representing the final stages of crystallization; these are common especially with grains composed of coarse plates. The various degrees of attachment between spherulites and different internal arrangements of plates within individual spheres are shown. Mounted in Canada balsam, n=1.52. 950x.

mixed slowly with the sulfate solution until the effervescence ceased and a dirty, greenish yellow precipitate formed. A slight excess of acetic acid was added, resulting in the lightly crystalline-green powder of emerald green separating out at the bottom of the vessel. The process was accelerated by the addition of a small amount of Scheele's green to the mixture before the emerald green appeared. Sattler (1888) described a similar method. Two variations of this scheme were listed by Hurst (1892) who also described a method in which a solution of arsenic trioxide in water was mixed with verdigris and allowed to stand until emerald green developed.

There were two major variations of the sulfate method. In one, the sulfate could be first mixed with sodium or calcium acetate to form copper acetate, or copper arsenite could initially be precipitated from the sulfate and reacted with acetic acid or acetate. The choice would largely depend on the cost of an acetate compared to acetic acid. In some cases, it was economical to make sodium acetate from calcium acetate and sodium sulfate, although this resulted in residual gypsum being precipitated from unreacted calcium acetate along with the emerald green (Gentele, 1909). A commercial process in 1923 used copper sulfate, arsenic trioxide, sodium carbonate, and sodium acetate. The sodium carbonate and arsenic trioxide were dissolved in water by heating that resulted in the formation of sodium arsenite with the release of carbon dioxide. The boiling sodium arsenite solution was rapidly introduced into a copper sulfate solution maintained at 90°C and then dilute sodium acetate (or an equivalent amount of acetic acid) was stirred into the mixture until emerald green precipitated (Bearn, 1923).

Recent methods. Several preparation methods for emerald green have been patented in the twentieth century. A solution of copper amino acetate can be reacted with powdered arsenic trioxide for a cyclic method of preparation. Acetic acid is set free and is neutralized by the ammonium ion; when the precipitate is filtered, the liquid is charged with copper or copper oxide to regenerate the copper amino acetate that is then reacted with more arsenic (Krefft, 1941). Another patent uses ammonium and copper acetates generated by the action of acetic acid and ammonia on copper and arsenic trioxide or an alkali-arsenic salt to produce a high yield of emerald green (Serciron, 1939). Webster (1933) outlined a method that involves the rapid addition of sodium arsenite to

copper sulfate, followed by acetic acid to produce a low-density Paris green.

There are several unusual methods used to produce emerald green: in a reaction between two solids, copper oxide and arsenic trioxide in acetic acid are ground together, which usually results in an impure product, or solid calcium arsenite is added to a hot or boiling solution of copper acetate and allowed to stand for approximately six hours. This product is also generally impure and is olive or dark green in color (Luchinski & Churilkina, 1940a).

Another method reacted a solution of copper acetate with solid arsenic trioxide. The solution was boiled and then held at 90°C; the arsenic trioxide gradually converted to emerald green in from one to six hours (Luchinski & Churilkina, 1940b).

4.4 Adulteration and Sophistication

Emerald green was mixed with barium sulfate, calcium sulfate, or chromium pigments to produce less costly or modified shades, either during washing or after drying. Dry mixing was accomplished in a rotary drum, rather than by conventional grinding, in order not to destroy the crystal structure of the green (Zerr & Rübencamp, 1908). Poor manufacturing in many cases lead to excessive free arsenic trioxide, sometimes over 20%. Clay, lead sulfate, calcium carbonate, copper carbonate, aluminum oxide, and magnesium carbonate were added in amounts sometimes exceeding 40% (Böckmann, 1893; Haywood, 1900). Green aniline colors were sometimes added to emerald green to give better staining power (Toch, 1911).

Mixed pigments were also made by co-precipitation or sequential precipitation using calcium hydroxide. Lime green was produced by boiling calcium hydroxide with excess arsenious acid to produce a solution of calcium arsenite; copper sulfate solution was added until precipitation was complete with the resulting mixed pigment being comprised of calcium sulfate and copper arsenite. Patent green was made by sequentially precipitating emerald green and gypsum. A calcium acetate solution was made by reacting quicklime or limestone with acetic acid, copper sulfate was then added to precipitate gypsum, leaving copper acetate in solution. Hot arsenious-acid solution was added, thus precipitating emerald green mixed with the calcium sulfate (Bersch, 1901). Imperial green was another type of lime green made by adding pure Vienna lime to the blue liquor remaining from emerald green manufacture, with part or all of the initial copper acetoarsenite sometimes incorporated into the final product. Calcium hydroxide could be used to neutralize the spent mother liquor to create a pigment with a blue shade that contained considerable calcium orthoarsenite. With the addition of dolomitic hydroxide, the pigment was called Kaiser green (Rose, 1916). Soda green, a finely divided emerald green, was similarly made by neutralizing with sodium carbonate (Zerr & Rübencamp, 1908).

A pigment called meadow green (*Wiesengrün*) was a mixture of copper arsenite, copper phosphate, and copper carbonate (Rose, 1916). A bluish mixture of copper arsenite, copper hydroxide, and calcium sulfate was referred to as Brunswick green or green verditer, although these names usually have other meanings (see 2.1). There were two varieties of Neuwied green, one being similar to this Brunswick green. The other variety started with copper acetate to precipitate emerald green instead of Scheele's green. An alternative Neuwied green combined the extender and pigment by physical mixing. In many cases barium sulfate was added to the less costly varieties (Bersch, 1901; Zerr & Rübencamp, 1908).

Parrot greens, sometimes used for wallpaper, were made by precipitating lead chloride with potassium bichromate to form lead chromate in the washing tank that contained emerald green. The amount added was determined by whether a green or blue shade was desired. As much as 30% barium sulfate could be added as an extender (Zerr & Rübencamp, 1908).

Mineral green was copper hydrate brightened with copper arsenite (Bearn, 1923). Potassium zincate could be used to precipitate a particularly bright green from a solution of copper sulfate and arsenic trioxide (Bersch, 1901). A light green pigment, similar in color to Scheele's green, referred to as Mitis, Vienna, or Kirchberger green was a copper arsenate made by dissolving potassium arsenate in hot water and stirring this mixture into a solution containing copper sulfate. As with preparation of the arsenites, the shade was determined by the proportions of copper and arsenic (Riffault et al., 1874). Coffignier (1925) also discussed a copper arsenate pigment named Mitis green. The term Mitis (or parrot) green could apply to a mixture of emerald and Scheele's (or imperial) greens (Gentele, 1909).

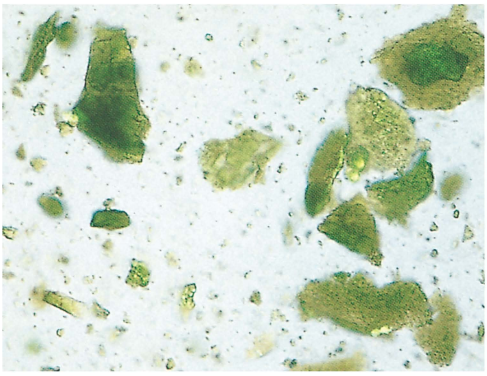


Fig. 16 Photomicrograph in partially crossed polars of copper arsenite labeled Scheele's green?, in the Forbes Collection, Freer Gallery of Art, Smithsonian Institution. Birefringence is practically nonexistent in this sample, which consists of nodules or flakes and small fragments. The larger particles have a mottled appearance and are either amorphous or composed of many very small crystallites. Mounted in Aroclor 5442, n=1.66. 350x.

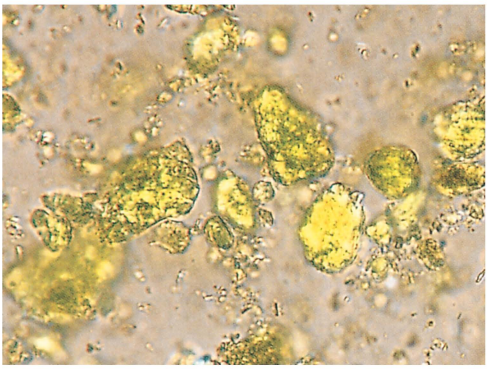


Fig. 17 Photomicrograph in partially crossed polars of cupric arsenite, sample no. 7200, from ICN Pharmaceuticals, Inc. (1983). The sample consists of small isolated crystals and agglomerated multicrystalline nodules. Many of the single crystals are acicular with parallel extinction. The yellow coloration is due to a combination of polarization and absorption colors. In transmitted light the material is a dull yellow-green. Mounted in Aroclor 5442, n=1.66. 780x.

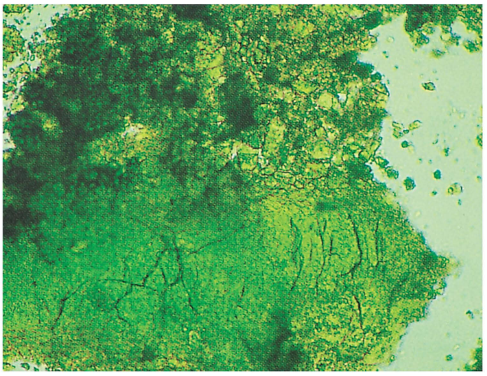


Fig. 18 Photomicrograph by transmitted light of Scheele's green from W and J George and Becker Ltd., London, c. early twentieth century. Mounted in polystyrene and dibutyl phthalate, n=1.57. Photo by Ashok Roy, National Gallery, London. 450x.

5.0 Identification and Characterization

5.1 Optical and Scanning Electron Microscopy

Scheele's green occurs in flakes of variable size that are slightly transparent, of irregular shape, and have a high refractive index (De Wild, 1929). Laurie (1914) described it as noncrystalline. Samples of copper arsenite disclose both an isotropic material with a wide size distribution and a birefringent type. In the isotropic sample (fig. 16), the larger particles are flakes with irregular outlines. Both surface topography and internal structure give the particles a mottled appearance. The birefringent type (fig. 17) forms as very small, equant to needle-shaped, crystals, and as rounded polycrystalline nodules; no isolated large crystals were observed. Birefringence of this sample is moderate and extinction of the needle-shaped particles is parallel. The sample in figure 18 was supplied as Scheele's green and its optical appearance and infrared spectrum are consistent with that designation; however, its x-ray diffraction pattern is similar to that of emerald green, indicating that some emerald green is evidently present in the sample. This Scheele's green sample must be in an amorphous form and thus does not give an x-ray diffraction pattern (see sections 5.3.1 and 5.3.2).

Scheele's green was not examined by scan-

ning electron microscopy because of its nondescript nature and lack of adequately documented samples.

Single crystals of emerald green are prisms with parallel sides and pyramid angles of 52°. The crystal system is monoclinic (Sattler erroneously called it orthorhombic). The refractive indices are α=1.71 to 1.72, β=1.77 to 1.78; birefringence is moderate at 0.06 to 0.07. The crystals have negative elongation and close to parallel extinction. Weak pleochroism is present, with $n\alpha'$=bright blue-green and $n\beta$=pale light green (Gettens & Stout, 1966; Pertlik, 1977; McCrone et al., 1979).

Isolated crystals of emerald green are rare; most grains are an assemblage of plates or acicular crystals organized as rosettes or spherulites that can vary from sample to sample and sometimes within a sample (Sattler, 1888). The simplest assemblage is two plates grown together or interpenetrating at an acute angle, with the plates either similar or different in size. More plates are usually present to fill in the interstices and create structures ranging from open rosettes to dense spherulites. Outer edges of the plates often curve to conform to the outline of the sphere or rosette. With compact spherulites, the outer surface may show parallel striations viewed from the side or crystals radiating from the center if seen from the top; other samples have a more random arrangement of the crystals. Plates can be relatively coarse and easy to visualize or can be at the limit of resolution of the optical microscope. Rosettes, which can be considered coarse or incomplete spherulites, show thin plates intersecting at the center when viewed from the top; if seen from the side, there are flat, overlapping or intersecting crystals with more or less parallel orientations. Other rosettes display a circular, irregular, or exfoliated plate pattern (fig. 19). There are also incomplete structures that have an irregular X-shape when viewed from the top. The center of a sphere may clearly show the origin of the radiating plates or appear dark because of total internal reflection, especially in compact spheres. This dark spot can be circular or irregularly shaped and often causes the particle to resemble a doughnut (fig. 20).

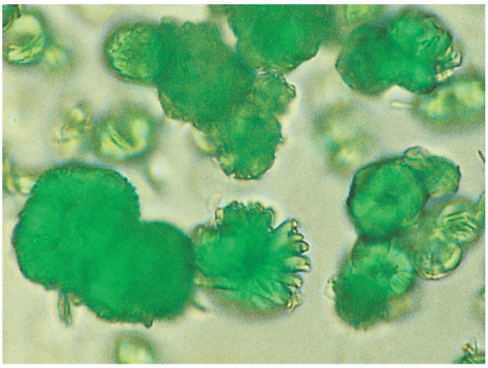


Fig. 19 Photomicrograph by transmitted light of emerald green labeled Fezandie (May 1936) in the Forbes Collection (AIC), shows a variety of grain types, some having relatively smooth surfaces and compact, fine crystallites and others having rough surfaces due to an exfoliated coarse-plate morphology. The large grain to the lower left is an agglomerate of two well fused spherulites while to the right is a more loosely bound agglomerate. The centers of the spheres are dark in the latter and indistinct in the former. The upper agglomerate has poorly formed subunits with random orientation. Absorption colors are different depending on thickness and crystal compactness. Mounted in Canada balsam, n=1.52. 880x.

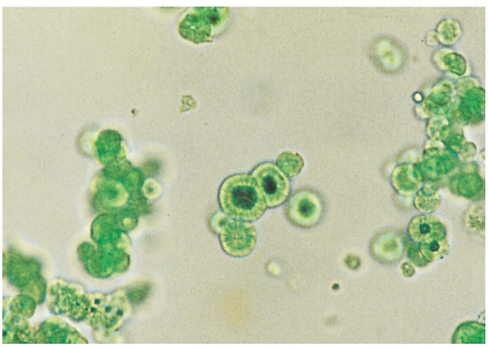


Fig. 20 Photomicrograph by transmitted light of emerald green, labeled Weber, Forbes Collection (AIC). Internal reflections in the initial growth zone at the centers of spherulites could cause a dark or light center depending on exact position of focus. The center zone probably has different crystallites. Mounted in Canada balsam, n=1.52. 740x.

It is common for spheres to grow together in a dumbbell-shaped habit or as multiple intergrowths consisting of several to dozens of spheres. In some cases, the outlines of the individual spherulites and plates are distinct, in others they are very faint. The way the individual crystals are arrayed may follow the original spheres or may conform to the agglomerate. Single spherulites have a diameter range of 8 to 40 µm while multiple spheres can be up to a few hundred micrometers across. Individual plates forming the associations are from 2 to 20 µm wide and can be

Fig. 21 Scanning electron micrographs of emerald green no. 284 (MJF).

A. The upper right exhibits a few intergrown plates and in the upper left a more complex structure is seen. The large agglomerate consists of some open or exfoliated spherulites along with more completely filled-in structures and random plates. 900x.

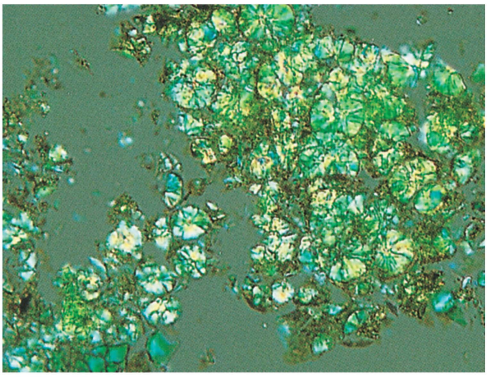
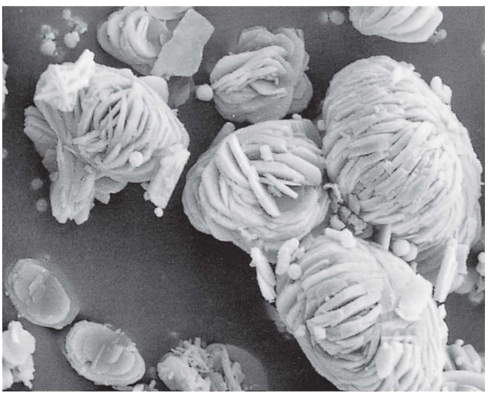


Fig. 22 Photomicrograph in partially crossed polars of emerald green from the dark green grass area in *A Sunday on La Grande Jatte, 1884*, by Georges Seurat, Art Institute of Chicago 1926.224. Intact spheres and fragments are shown; some radiate extinction patterns are present along with anomalous blue polarization colors. Viridian, zinc yellow, and some organic binder are also present. Mounted in Aroclor 5442, n=166. 370x.



B. A few small groups of crystal plates can be seen in the lower left. In the crystallization process, these plates would grow by the addition of solute to the existing plates and also by filling in the interstices of the resulting open structure by more crystallites to reach an end point such as the large grain with minimal spaces between subunits on the right. Several intermediate forms are also present. Although not analyzed, the small structureless spheres are probably remnants of copper arsenite and arsenic trioxide. 1,100x.

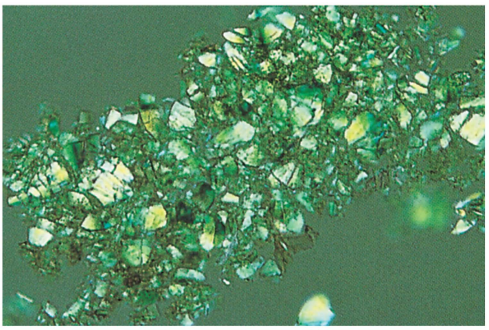


Fig. 23 Photomicrograph in partially crossed polars of emerald green from *Still Life: Apples and Grapes* by Claude Monet, Art Institute of Chicago 1933.1152. Many fan-shaped fragments of spherulites, some with linear or curved extinction patterns are shown. Several grains also show anomalous blue polarization colors. Mounted in Aroclor 5442, n=1.66. 310x.

submicrometer in thickness. Some crystallization conditions will result in a variety of morphologies, while others will yield a single type, with or without interpenetrated associations (fig. 21).

Manufacturing, handling, mixing with paint media, or preparation for microscopy can easily break the fragile particles into partial spheres, chains or groups of plates, wedge-shaped sectors, or single, isolated plates (figs. 22–23). In this respect, it is best to use sample preparation methods that produce a minimum of shear forces; the use of a medium of high viscosity or excessive

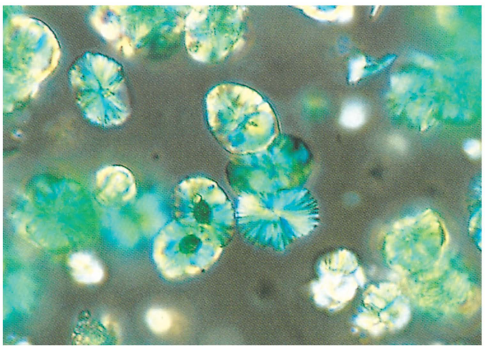


Fig. 24 Photomicrograph in partially crossed polars of Schweinfurt green, Kremer Pigmente, 1989. A variety of structures are seen: a pair of fused spherulites near the center show dark internal reflection structures while to the right of these is a grain oriented to display radiating crystal plates. The elipitical particle above the radiate is a partially filled-in spherulite viewed from the side. Several other spherulites and agglomerated plates are also present. Mounted in Aroclor 5422, n=1.66. Sample from Rainer Richter, Staatliche Kunstsammlungen Dresden. 740x.

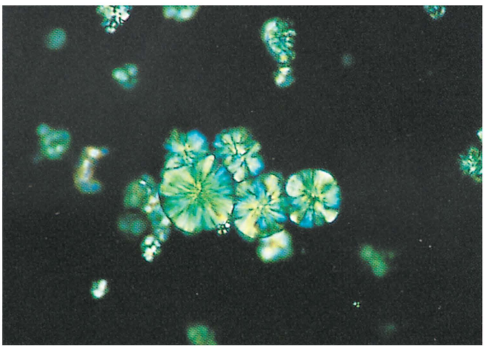


Fig. 26 Photomicrograph in crossed polars of emerald green from F. Weber Company, Forbes Collection (AIC). These spherulites show radiate extinction symmetry and some anomalous blue polarization colors. Mounted in Aroclor 5442, n=1.66. 540x.

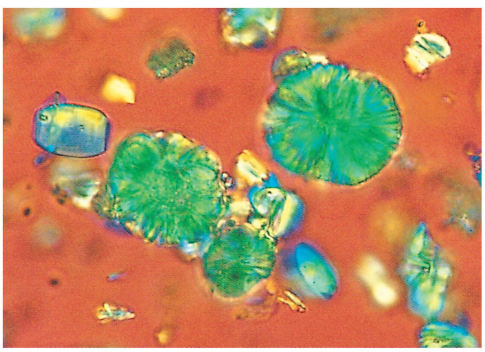


Fig. 25 Photomicrograph with first-order red plate of emerald green no. 284 (MJF) shows single crystal interaction with the isolated plates and more complex multiple interactions with the spherulites. When viewed from the side, the polarization effect of the large grains is the cumulative interaction of many more or less random plates; viewed from the top along the central axis, the radiating crystallites display slight changes in orientation from plate to adjacent plate resulting in radiate extinction. Absorption color overlaps the polarization colors. Mounted in Canada balsam, n=1.52. 740x.

dispersion can destroy much of the morphology. Separated plates can have parallel sides and prismatic outlines, a wedge shape, two opposite sides curved and two parallel, a needle shape, or a rounded-to-irregular outline. While the spheres are an intense green, most of the detached plates are nearly colorless because of the short absorption path. Extreme instances were noted in which grinding between microscope slides quickly reduced the pigment to submicrometer particles; when the particles are this small, emerald green can be very difficult to identify optically.

Polarization phenomena in spherulites usually result from the additive or subtractive birefringence of overlapping crystals (figs. 24–26). Small spheres, ranging from a creamy yellow to a blue-gray, will be seen in crossed polars, although polarization colors can be masked by absorption with large particles appearing as various levels of green in all orientations. Anomalous blue may be present with grains of proper thickness. In certain orientations, a few spherulites will show a cross similar to that seen with starch; in other positions, the cross can be indistinct or nonexistent depending on how many crystallites are present and their individual orientations. Sometimes individual areas, curved lines, plates, or sectors will go to extinction; other spheres, especially those

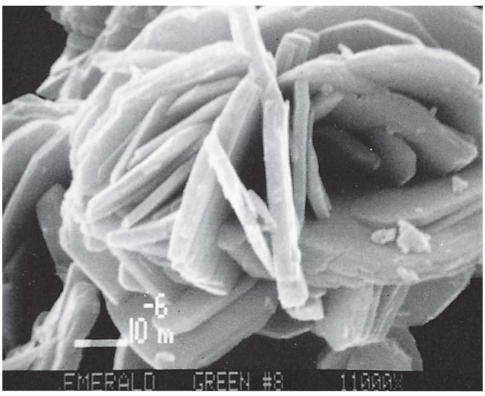


Fig. 27 Scanning electron micrograph of emerald green labeled Fezandie (May 1936), Forbes Collection (AIC), is a good example of an open or exfoliated crystal structure with intergrown crystallites in many orientations. Printed at 6,400x.

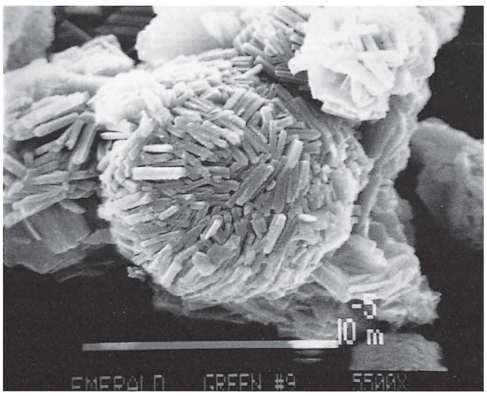


Fig. 29 Scanning electron micrograph of emerald green, F. Weber Company, Forbes Collection (AIC). A spherulite like this would appear quite smooth seen by optical microscopy (see fig. 20); here, the small crystal plates and their interlocking arrangement can be seen. Printed at 3,200x.

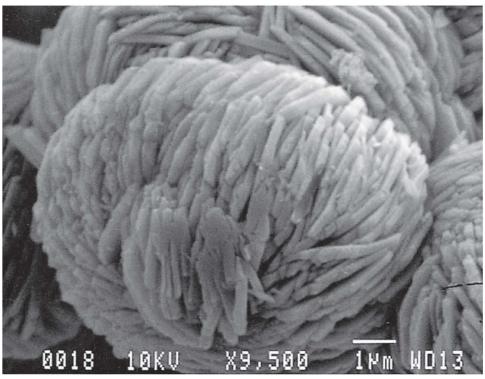


Fig. 28 Scanning electron micrograph of Paris green. The structure of these dense, well-formed spherulites is made up of parallel or close-to-parallel groups of plates with the overall organization radiating from a common central axis; in this case, the background grain shows the top view along the axis with sets of plates radiating in opposite directions while the foreground view is from the side direction. The radiate structure is not perfect since there are many secondary crystallites that fill in the gaps between the original plates. These spherulites have a denser crystallite packing than other samples. Sample from Max Saltzman, University of California at Los Angeles. Printed at 6,000x.

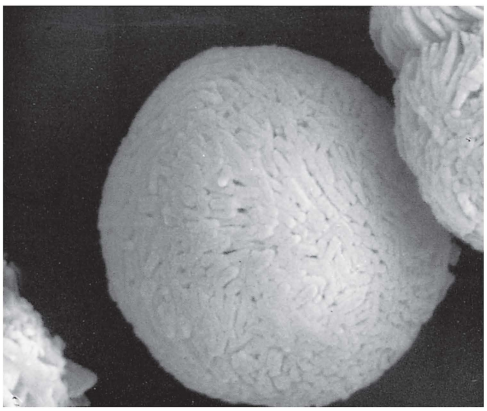


Fig. 30 Scanning electron micrograph of emerald green, F. Weber Company, Forbes Collection (AIC), shows an unusually smooth spherulite with very fine crystal grains. The internal structure causing the "doughnut" effect does not show in scanning electron micrographs. 6,000x.

large or complex, show incomplete extinction phenomena, again because of overlapping plates with a multiplicity of orientations. Plates will have first-order gray-to-white colors with parallel, undulose, irregular, or inclined (up to 10°) extinction. Refractive index measurements can yield intermediate values when the measurement is being performed on many thin crystallites in different overlapping orientations. Butler (1973a) described the grains as radial, usually with a dark spot in the center, breaking into rounded or wedge-shaped flakes and with undulose extinction.

The morphologies present can give some information as to the type of manufacturing conditions. The presence of well-formed plates or prisms indicates that the material was crystallized in undis-

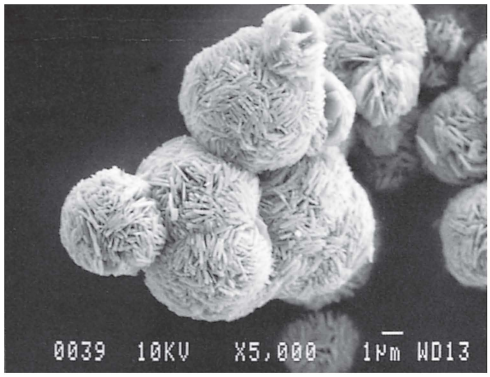


Fig. 31 Scanning electron micrograph of emerald green (labeled German emerald green-Scheele's green), F. Weber Company, Forbes Collection (AIC), with agglomerates of well-formed spherulites, which are common in some samples. The formation mechanism involves outward growth of each sphere in the gelatinous copper arsenite matrix until the peripheries make contact. Bonding strength is variable depending on area of contact and amount of interlocking or fusing of the small plate-shaped crystallites. Printed at 2,800x.

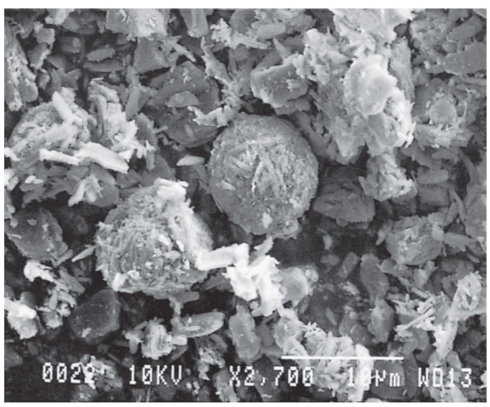


Fig. 32 Scanning electron micrograph of veronite green (labeled *veronite vert*), from Lefranc (1927) in the Forbes Collection (AIC). The relatively imperfect morphology with very poorly formed or damaged spherulites and irregular plates caused either by the precipitation process or by subsequent handling can be observed. Printed at 1,500x.

turbed conditions. If clear, high-index octahedra of arsenic trioxide crystals are found, it indicates that the process used started with copper acetate. The size of the spherulites indicates the rate of crystal formation, with the large spherulites having formed more slowly (Sattler, 1888).

When examined by scanning electron microscopy, emerald green discloses a range of morphologies (figs. 27–32). The simplest is a few intersecting plates with either straight or rounded edges, which represent interpenetration twinning. More complex assemblages of plates are seen as exfoliated radiating structures or rosettes, again with either straight or curved edge crystallites. Spherulites with both rough and smooth surfaces constitute the endpoint of compact crystalline growth. These are composed of plates with curved edges or curved needles. In addition to isolated spheres or radiates, some crystallization conditions favor multiple growth with a few-to-many interpenetrated spherulites or radiates.

5.2 Chemical Microscopy and Spot Tests

A number of chemical tests can be applied to Scheele's green and emerald green by chemical microscopy or as spot tests.

Scheele's green dissolves in 3N HCl to give a green solution, in 4N NaOH to give a pale blue precipitate of $Cu(OH)_2$ and in concentrated HNO_3 to give a blue solution. Emerald green produces similar reactions except that the HCl solution is almost colorless. Heating of both materials results in a black residue of CuO (Plesters, 1956).

The presence of copper can be determined microchemically by various tests. The reaction with potassium mercuric thiocyanate produces yellow-green dendrites, boat-shaped crystals, or acicular prisms of copper mercuric thiocyanate (Short, 1931; Chamot & Mason, 1960). The triple nitrate test produces dark brown to black squares, rectangular plates and cubes (Chamot & Mason, 1960). Spot tests can be carried out with 2,2'-diquinolyl (cuproin), phosphomolybdic acid, or Alizarin Blue (Feigl & Anger, 1972), and with sodium diethyldithiocarbonate to give an orange spot test on a filter membrane or with rubeanic acid (dithiooxamide), which gives a greenish black spot test for copper (Plesters, 1956).

There are several tests for arsenic. The reaction with ammonium molybdate results in the formation of yellow isotropic granules, octahedra, trisoctahedra, and cubes (Short, 1931). The test with stannous chloride produces blackish brown elemental arsenic. Silver nitrate reacts to form a red-brown precipitate of silver arsenate (Plesters, 1956). The arsine test also determines the presence of arsenic (Chamot & Mason, 1960).

To differentiate between arsenite and arsenate the following tests can be done: for arsenite, nitric acid will give octahedra of As_2O_3, or, as an alternative ammoniacal silver nitrate will give a lemon

Table 2 **X-ray Diffraction Data for Trippkeite and Copper Arsenite**

Trippkeite[a] $CuAs_2O_4$ *JCPDS 31-0451*		*Cupric Arsenite*[b] *ICN Pharmaceuticals July 1983*		*Copper Arsenite*[c] *Scheele's Green(?)*		*Trippkeite*[a] $CuAs_2O_4$ *JCPDS 31-0451*		*Cupric Arsenite*[b] *ICN Pharmaceuticals July 1983*		*Copper Arsenite*[c] *Scheele's Green(?)*	
d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
6.07	55	6.07	60	—	—	1.95	35	1.95	60	—	—
—	—	—	—	4.61	30	1.92	7	—	—	—	—
4.30	14	4.33	40	—	—	1.82	3	—	—	—	—
—	—	4.11	40w	4.18	20	1.81	2	—	—	—	—
—	—	—	—	4.03	30	1.72	1	—	—	—	—
3.84	8	3.85	?	—	—	1.70	11	1.70	1	—	—
—	—	3.69	?	—	—	1.68	<1	—	—	—	—
3.40	3	—	—	—	—	1.67	14	1.67	30w	1.67	50
3.16	100	3.16	100	—	—	1.64	25	1.64	30	—	—
—	—	3.11	100	3.11	100	1.58	1	1.60	20w	1.60	40
3.04	45	—	—	—	—	1.53	1	—	—	1.55	20
—	—	2.89	?	—	—	1.52	1	—	—	—	—
2.79	6	2.78	?	2.79	10	1.47	10	1.47	20w	1.47	20
2.72	35	2.71	50	2.69	?	1.46	4	—	—	—	—
—	—	2.59	20	2.62	?	1.44	14	1.44	10w	—	—
2.53	15	2.49	60w	2.49	70	1.43	4	—	—	—	—
2.44	1	—	—	—	—	1.42	3	—	—	—	—
2.38	<1	2.40	60w	2.39	60	1.41	6	—	—	—	—
2.34	35	2.33	50	2.31	10	1.39	16	1.39	20w	—	—
2.26	15	2.25	30	—	—	1.38	1	—	—	—	—
2.19	3	—	—	—	—	1.37	1	—	—	—	—
2.15	1	—	—	2.13	?	1.36	1	—	—	—	—
2.08	2	2.08	20w	2.08	30	1.34	2	—	—	—	—
2.05	2	—	—	—	—	1.33	2	1.33	30	1.33	30
2.02	1	—	—	—	—	+8 lines below *I*=7					
2.00	7	2.00	?	—	—						

?=Very faint line
w=Wide line
a. *JCPDS Powder Diffraction File* (*JCPDS*, 1990).
b. Art Institute of Chicago Pigment Collection. Data for samples of cupric arsenite and copper arsenite from Arthur M. Sackler Gallery and Freer Gallery of Art, Department of Conservation and Scientific Research, Smithsonian Institution, Washington.
c. E. W. Forbes Pigment Collection, Arthur M. Sackler Gallery and Freer Gallery of Art.

yellow precipitate; ammoniacal magnesium acetate will give a precipitate with arsenate (Chamot & Mason, 1960).

The presence of acetate may be detected with silver nitrate to generate pearly scales and long, thin plates of silver acetate; mercuric nitrate will give colorless plates or prisms; and uranyl formate will cause the formation of isotropic tetrahedra of sodium uranyl acetate (Chamot & Mason, 1960).

5.3 Instrumental Methods of Analysis

5.3.1 ***X-ray diffraction.*** The crystal structure of Scheele's green is not known because the samples synthesized by Schweizer and Mühlethaler (1968) were amorphous. The Scheele's green shown in figure 18 gave an x-ray diffraction pattern similar to that of emerald green, thus underlining the uncertainty of the relationship between the two pigments; there is probably some emerald green mixed with amorphous copper arsenite in this sample. Pertlik (1977) published data for synthetic trippkeite, but the mineral's relevance to the identification of Scheele's green is uncertain. Two samples labeled copper arsenite gave different patterns (fig. 33A–B and table 2). The data for cupric arsenite from ICN Pharmaceuticals matched that of the mineral trippkeite, with a few additional lines. These additional lines were the major features of the sample from the Freer

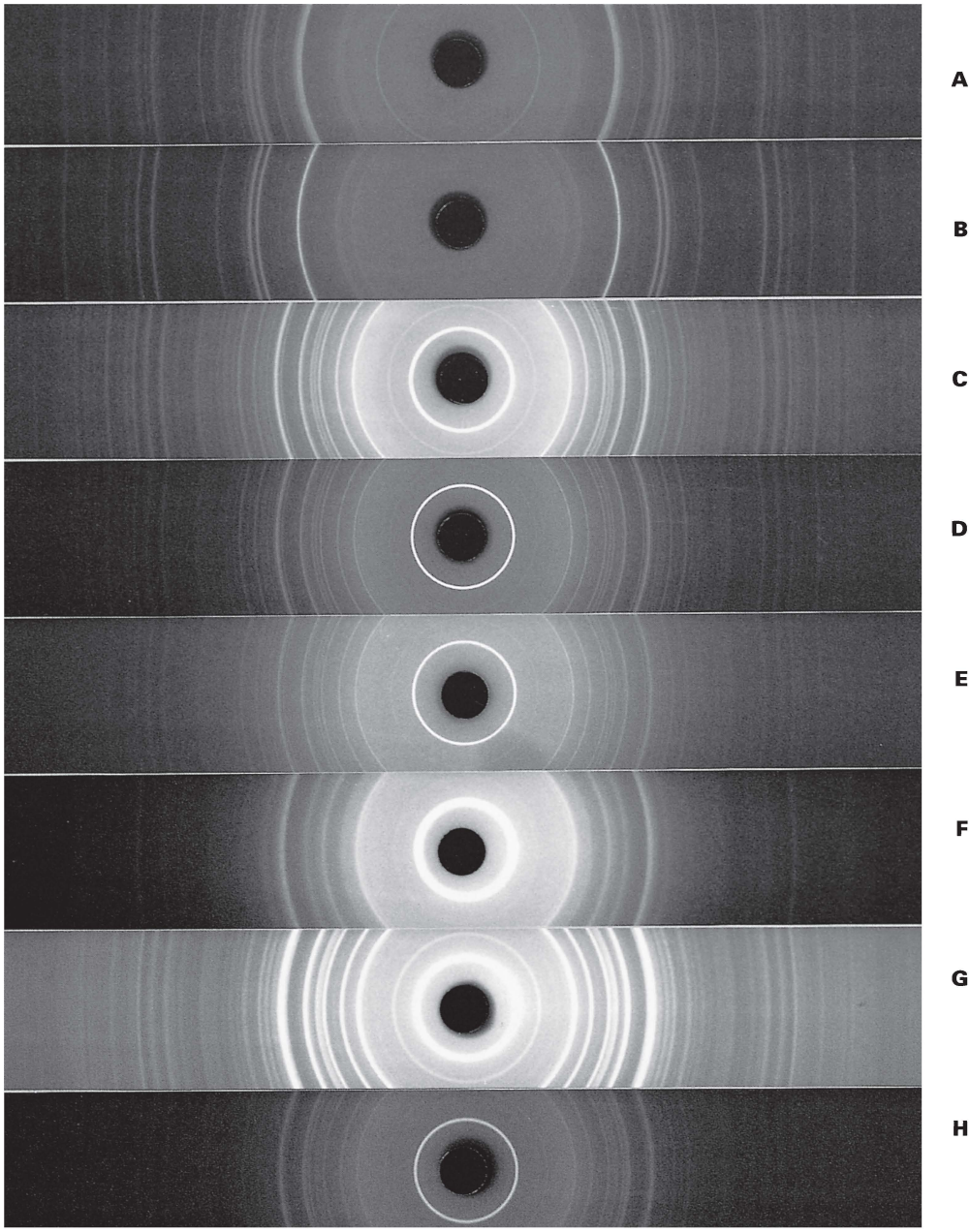


Fig. 33 X-ray diffraction powder patterns of copper arsenite and emerald green. Films from the Department of Conservation and Scientific Research, Arthur M. Sackler Gallery and Freer Gallery of Art, Smithsonian Institution, Washington. Camera diameter 114.6 mm, Debye-Scherrer camera with Gandolfi mount. Photographs not to be used for measurement purposes.

A. No. 7200 cupric arsenite, ICN Pharmaceuticals, Inc. (22 July 1983), Art Institute of Chicago Pigment Collection. This pattern corresponds to published values for trippkeite with some unidentified lines.

B. Copper arsenite, labeled Scheele's green?, Forbes Collection, Freer Gallery of Art. The unidentified lines in A are the dominant lines in this sample.

C. Emerald green, Roberson 9-27, Forbes Collection (AIC).

D. Emerald green, labeled Scheele's green, Fezandie and Sperrle (August 1936), Forbes Collection (AIC).

Table 3 **X-ray Diffraction Data for Emerald Green**

Copper Acetoarsenite JCPDS 1-0051[a]		*Copper Acetoarsenite JCPDS 31-0448*[a] *(Pertlik, 1977)*		*Emerald Green*[b] *Roberson, 9-27*		*Copper Acetoarsenite JCPDS 1-0051*[a]		*Copper Acetoarsenite JCPDS 31-0448*[a] *(Pertlik, 1977)*		*Emerald Green*[b] *Roberson, 9-27*	
d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
10.0	100	9.71	1000	9.72	100	—	—	2.58	20	—	—
—	—	6.76	25	6.71	40	—	—	2.55	35	2.56	30
—	—	5.36	5	5.47	?	—	—	2.49	25	2.51	20
—	—	4.86	9	4.87	10	—	—	2.48	25	2.48	20
—	—	4.70	11	4.70	10	—	—	2.46	9	—	—
—	—	4.66	13	—	—	—	—	2.43	5	—	—
4.55	12	4.53	110	4.55	70	2.40	4	2.41	60	2.42	50
3.99	12	3.93	95	3.97	60	—	—	2.38	12	—	—
—	—	3.71	5	3.71	?	—	—	2.36	6	—	—
3.48	8	3.48	80	3.51	60	—	—	2.31	7	2.33	10
—	—	3.38	55	3.38	50	—	—	2.26	14	—	—
3.30	4	3.28	70	3.29	50	—	—	2.25	65	2.25	50
—	—	3.18	8	—	—	—	—	2.18	17	2.20	30
—	—	3.09	45	3.11	?	—	—	2.15	5	—	—
—	—	3.07	60	3.07	70	—	—	2.12	10	2.14	20
3.06	20	3.06	80	—	—	—	—	2.11	16	—	—
—	—	2.98	10	2.98	?	—	—	2.07	12	2.06	10
—	—	2.73	55	2.77	50	—	—	2.00	16	—	—
—	—	2.71	80	2.71	70w	1.69	8	—	—	—	—
—	—	2.69	19	—	—	1.62	4	—	—	—	—
2.68	24	2.68	155	2.66	70w	1.55	8	—	—	—	—
—	—	2.67	20	—	—	1.45	4	—	—	—	—
—	—	2.63	9	—	—			lines above *I*=5			
—	—	2.62	40	2.60	?						

?=Very faint line
w=Wide line
a. *JCPDS Powder Diffraction File* (*JCPDS*, 1990).
b. E. W. Forbes Pigment Collection, Art Institute of Chicago.

Data from Arthur M. Sackler Gallery and Freer Gallery of Art, Department of Conservation and Scientific Research, Smithsonian Institution, Washington.

E. Veronite green, Lefranc (1927), Forbes Collection (AIC). The scanning electron micrograph of this sample showed poorly formed crystals (see fig. 32).

F. Emerald green, F. Weber Company, Forbes Collection (AIC). This sample had significant line broadening due either to small crystallites or poorly formed lattice structure. Examination by optical microscopy and scanning electron microscopy indicated small crystallites. Also, the reflective cores seen optically could represent a slightly different or distorted crystal form of emerald green.

G. Emerald green, Masury, Forbes Collection, Freer Gallery of Art. An intermediate level of line broadening occurs in this sample.

H. Stone green no. 2, Karwak Gallery, Toronto (June 1979), Art Institute of Chicago Pigment Collection.

Table 4 **X-ray Diffraction Data for Samples of Emerald Green from Paintings in the Collection of the Art Institute of Chicago**[a]

Paul Gauguin The Big Tree[b]		*Paul Gauguin* Old Women at Arles[c]		*Fernand Léger,* Follow the Arrow[d] *Light Green*		*Bright Green*	
d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
7.655	35*	7.622	10	—	—	7.654	<1
E 6.676	5	6.752	10	—	—	6.726	3
4.831	1	4.818	5	—	—	—	—
E 4.691	3	4.691	5	4.679	1	4.703	<1
E 4.548	75	4.537	50	4.525	50	4.536	40
—	—	—	—	—	—	4.424	1
4.267	50*	4.267	5	4.329	1	4.328	3
4.139	5	—	—	—	—	4.246	1
E 3.957	50	3.957	30	3.957	10	3.965	25
—	—	—	—	3.888	10	3.896	25*
—	—	—	—	3.573	5	3.579	25*
E 3.477	40	3.477	30	3.483	15	3.483	20
—	—	—	—	3.437	30	3.430	40
E 3.367	20	3.367	10	—	—	—	—
E 3.294	25	3.294	15	3.299	75	3.305	50
—	—	—	—	—	—	3.275	30*
E 3.103	10	3.103	1	3.087	100	3.091	100
3.061	100	3.061	80	—	—	—	—
—	—	2.981	<1	—	—	2.971	<1
2.864	20*	2.864	<1	2.825	15	2.833	10
E 2.753	10	2.753	10	2.748	1	2.756	1
E 2.704	10	2.700	15	2.712	25	2.716	30
E 2.680	75	2.677	100	2.677	25	2.684	30
2.646	1	2.638	1	—	—	2.623	10
2.601	1	—	—	—	—	—	—
2.554	1	2.551	5	2.558	<1	2.561	3
2.503	1w	2.499	1	—	—	—	—
—	—	2.473	1	2.476	<1	2.479	8
E 2.402	10	2.402	10	2.406	<1	2.411	5
2.241	5	2.244	5	2.322	<1	2.319	1
—	—	—	—	—	—	2.274	<1
—	—	—	—	—	—	2.228	<1
—	—	—	—	2.205	40	2.207	1
—	—	2.187	<1	—	—	—	—
—	—	2.123	<1	—	—	2.115	40*
—	—	2.063	<1	2.097	40	2.099	40*
—	—	1.998	<1	2.045	<1	2.049	5
—	—	1.907	1	1.850	5	1.854	10
—	—	1.814	<1	—	—	—	—
—	—	1.723	<1	—	—	—	—
1.694	5	1.694	1	—	—	—	—
1.619	5	1.622	1	—	—	—	—
1.562	3	1.561	3	—	—	—	—
1.550	<1	—	—	—	—	—	—
1.453	1	1.454	1	—	—	—	—

*=Non-emerald green lines, *I*=20 or above

E=Emerald green lines *I*=10 or above (*JCPDS Powder Diffraction File* 31-0448, see table 3)

a. Samples analyzed by McCrone Associates, Westmont, Ill., using a 57.3 mm diameter powder camera, nickel-filtered copper radiation, 40 kV at 25 MA.

b. Art Institute of Chicago acc. no. 1949.513.

c. Art Institute of Chicago acc. no. 1934.391.

d. Art Institute of Chicago acc. no. 1953.341.

Table 5 **X-ray Diffraction Data for Samples of Emerald Green from Paintings in the Collection of the Art Institute of Chicago**[a]

Georges Seurat A Sunday on La Grande Jatte, 1884[b]		*Claude Monet* Rocks at Belle Isle[c]		*Frédéric Bazille* Self-Portrait[d]	
d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
—	—	7.495	10	—	—
E 6.780	1	—	—	—	—
—	—	6.728	10	—	—
—	—	4.832	<5	—	—
—	—	4.668	<5	—	—
E 4.538	25	4.538	75	4.548	50
—	—	4.278	10	—	—
4.228	<1	—	—	—	—
E 3.940	25	3.949	30	3.947	30
E 3.491	10	3.471	30	3.476	25
E 3.374	<1	3.368	25	3.379	5
E 3.276	100	3.288	25	3.281	15
E 3.067	75w	3.062	100w	3.060	100
2.753	<1	2.757	10	2.756	5
E 2.681	75w	2.681	50w	2.676	90w
2.628	50	—	—	—	—
2.559	<1	2.555	10	2.554	1
2.486	<1	2.467	5	—	—
E 2.403	5	2.406	25	2.405	5
2.231	1w	2.242	5	2.252	3
—	—	2.185	<5	—	—
2.107	<1	2.116	<5	—	—
2.050	<1	2.963	<5	—	—
—	—	1.898	5	—	—
1.854	1	—	—	—	—
1.696	5	1.697	10	—	—
1.612	<1	1.617	10	—	—
1.561	<1	1.561	10	—	—
1.530	<1	1.529	5	—	—
1.453	<1	1.454	10	—	—

E=Emerald green lines *I*=10 or above (*JCPDS* 31-0448, see table 3)
w=Wide lines
a. Samples analyzed by McCrone Associates, Westmont, Ill., using a 57.3 mm diameter powder camera, nickel-filtered copper radiation, 40 kV at 25 MA.
b. Art Institute of Chicago acc. no. 1926.244.
c. Art Institute of Chicago acc. no. 1964.210.
d. Art Institute of Chicago acc. no. 1962.336.

Gallery of Art, E. W. Forbes Pigment Collection, labeled "Scheele's green?" It appears that there may be two crystalline forms of copper arsenite in the ICN sample. It is possible that both amorphous and crystalline forms coexist. To date there is no reference material available documenting Scheele's green.

The standard x-ray diffraction data for emerald green are given in table 3 and patterns are shown in figure 33C–H. Data from emerald green pigments from several paintings are shown in tables 4 and 5, where the strong emerald green lines are indicated. In the data from two samples (table 4) there are strong lines not attributable to emerald green; the source of these lines has not been identified.

5.3.2 ***Infrared spectroscopy.*** The infrared spectrum of copper acetoarsenite (emerald green) is shown in figure 34. Strong peaks are observed at 1557, 1454, 820, 768, 647, and 641 cm^{-1}. Weaker absorbances are found in the regions of 3500 to 3200, 3200 to 2900, and 600 to 430 cm^{-1}. The weaker absorbances at 3200 to 2900 cm^{-1} are due to the C—H stretches in methyl group of acetate present in emerald green. The signals at 1557 and 1454 cm^{-1} can be assigned to the carboxylate group. In comparing the infrared spectrum of emerald green to that of copper arsenite (labeled Scheele's green?) (fig. 35), the signals at 820, 768, 647, and 641 cm^{-1} can be attributed to the As—O bond. Moisture is evident in the infrared spectrum due to the absorbances at 3500 to 3200 cm^{-1} and the shoulder near the 1557 cm^{-1} absorption. The origin of the water is speculative; it can be due to the hygroscopic nature of the pigment and the matrix materials of the infrared pellet (Barbara Berrie, personal communication, 1992). The spectrum of the Scheele's green, W and J George and Becker sample (fig. 36), is very similar to the Forbes copper arsenite sample; the main difference appears to be the singlet versus the doublet absorption bands near 1000 to 1100 cm^{-1}. This may be due to the variability of copper arsenites (Mary Miller, personal communication, 1995). McCawley (1975) published a spectrum for Scheele's green; he used a diamond cell method amenable to samples as small as four micrograms. Szymanski et al. (1968) and Nyquist and Kagel (1971) discussed some of the more detailed aspects of the infrared spectra of arsenites and arsenates.

5.3.3 ***Electron beam microprobe.*** Electron beam microprobe analysis, using either crystal spectrometers or an energy-dispersive detector can determine elemental composition of copper arsenite greens. The analytically useful x-ray lines are $K\alpha_{1,2}$ at 8.04 keV for copper and $L\alpha_{1,2}$ at 1.28 keV and $K\alpha$ at 10.53 keV for arsenic. With an energy-dispersive unit, overlaps can occur with arsenic L and magnesium K (1.25 keV), or alu-

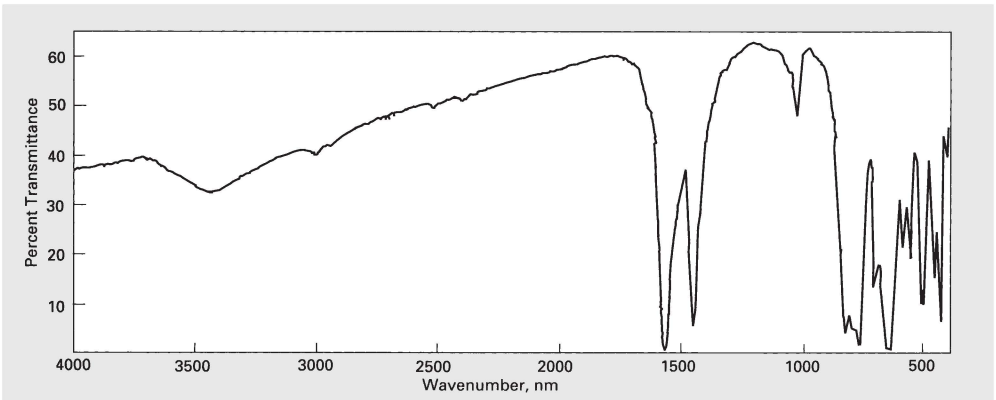


Fig. 34 Infrared spectrum of copper acetoarsenite (emerald green) lot no. 02142 from Dixon Fine Chemicals, Alberta, Canada (August 1987), Art Institute of Chicago Pigment Collection. Data from Conservation Division, National Gallery of Art, Washington.

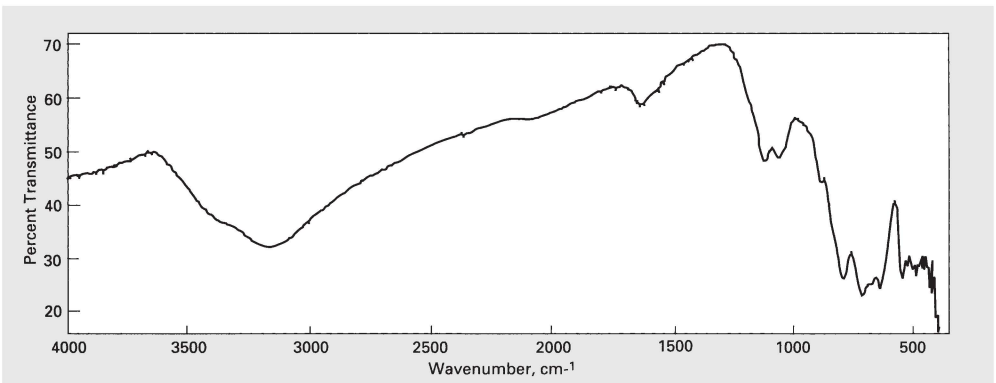


Fig. 35 Infrared spectrum of copper arsenite labeled Scheele's green?, Forbes Collection, Freer Gallery of Art. Data from Conservation Division, National Gallery of Art, Washington.

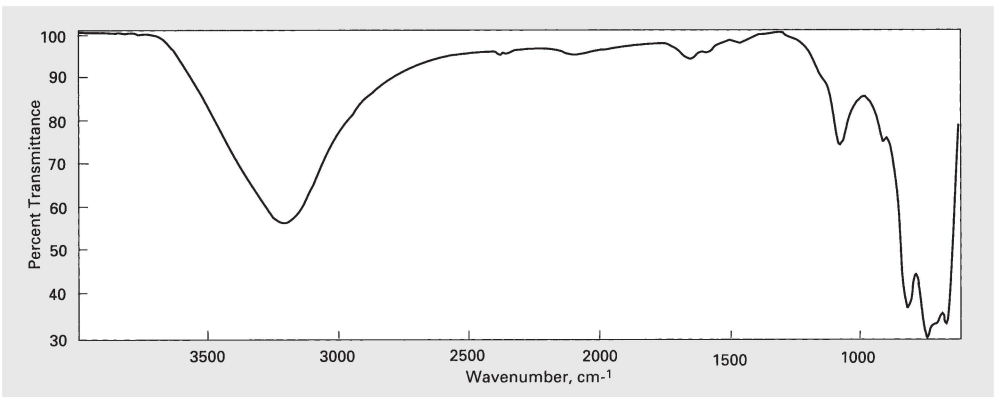


Fig. 36 Infrared spectrum of Scheele's green from W and J George and Becker, Ltd., London, c. early twentieth century. Sample from Ashok Roy, National Gallery, London. Data from Mary Miller, McCrone Associates, Westmont, Ill.

minum K (1.49 keV) lines, and with arsenic K and lead L (10.55 keV) (White et al., 1965; see also Goldstein et al., 1992). Emerald green contains 25.1% copper and 44.3% arsenic or an arsenic-to-copper weight ratio of 1.76. The acetate group would have enough carbon (4.6%) to be analyzed semiquantitatively by a dispersive detector; however, analysis could only be done in the absence of any carbon contribution from an organic medium. Depending on composition, the calculated elemental ranges for Scheele's green are 22.9% to 50.6% for copper and 29.8% to 54.1% for arsenic, with arsenic-to-copper ratios from 0.59 to 2.36. It would be possible to find a Scheele's green with a similar elemental ratio to that of emerald green; as ratios are sometimes the only quantitation available with small particles where geometry and electron diffusion zone uncertainties prevent more accurate values, such data would not differentiate these materials (Bayard, 1973). In this case, carbon content could be used to differentiate the two if no matrix interference is present.

Eighteen samples from reference collections were analyzed by electron beam microprobe with 30 kV accelerating potential and a takeoff angle of 50° (table 6). In most cases, two values are given that represent the analytical spread for several areas. Corrections were made to the data for atomic number, absorption, and fluorescence (ZAF). Quantitation in this instance did not yield the composition of emerald green; this is partially due to uncertainties in particle geometry affecting the ZAF corrections and the possibility of changes such as loss of acetate due to electron bombardment. The data also indicate real variations in the copper-to-arsenic ratio beyond those caused by geometry and in some instances it was possible to see small arsenic trioxide crystals associated with emerald green using scanning electron microscopy with x-ray fluorescence. Samples 2, 4, 5, 6, 7, 12, and 17 had uniform composition from grain to grain while samples 3, 9, 10, 11, 13, 14, 15, and 16 were variable. Iron was found in all samples, although the source of this signal could be from the instrument.

5.3.4 ***Neutron activation.*** Neutron activation analysis was performed on ten samples at the Ford Nuclear Reactor-Phoenix Memorial Laboratory Facility at the University of Michigan (tables 7 and 8). Immediate, one-hour, one-week, and four-week decay time counts were evaluated. The immediate and one-hour analyses were difficult to perform because of the high radioactivity of arsenic and the fact that its intense gamma radiation masks gammas from other elements. Sample sizes ranged from 6.2 to 93.3 mg. Quantitation on copper is slightly high and arsenic slightly low when compared to stoichiometry. Antimony, an element commonly associated with arsenic, was seen in all samples (Reed Burn, personal communication, 1987).

5.4 Criteria for Identification

Emerald green can be readily identified by optical microscopy when the unique spherulitic morphology is intact. However, particle shape can be altered by manufacturing methods, subsequent handling, mixing with media, or improper sample preparation. Sample dispersion for examination should involve minimal shear forces. By microscopy the samples of copper arsenite disclose variable shape, size, birefringence, and refractive index. If identification by optical microscopy is unsuccessful, analysis by microchemical tests for copper, arsenic, and acetate would then be indicated, if there is sufficient sample. Electron beam microprobe analysis readily discloses the presence of copper and arsenic but may not differentiate between the two pigments if the elemental ratios are similar to emerald green and the chemically associated carbon cannot be measured because of interference from organic matrices. X-ray diffraction will positively identify emerald green but may be of little value for Scheele's green because of variations in crystal structure of copper arsenites or the possibility of an amorphous sample. Infrared spectroscopy will detect the acetate group in emerald green and can differentiate between the two pigments.

Table 6 **Analysis of Copper Arsenic Pigments by Electron Beam Microprobe by Weight Percent**[a]

Sample No. and Name	*Copper*	*Arsenic*	*Arsenic/ Copper*	*Iron*	*Silicon*	*Calcium*	*Potassium*	*Magnesium*	*Sulfur*
1. Emerald green, copper acetoarsenite Fezandie and Sperrle 1936[b]	23.1	43.6	1.88	0.2	2.2	0.2	0.1	—	—
2. Emerald green	27.2	49.5	1.81	0.5	—	—	—	—	—
Fezandie, May 1936[b]	27.8	49.0	1.79	0.5	tr	—	—	—	—
3. Veronite green	16.4	37.4	2.28	0.6	8.2	0.3	0.4	—	—
Lefranc, 1927[b]	21.5	44.4	2.05	0.3	4.4	0.3	0.3	—	—
4. Veronite vert	26.7	50.0	1.86	0.5	—	—	—	—	—
Lefranc, 1927[b]	27.0	49.8	1.86	0.4	—	—	—	—	—
5. Emerald green	28.1	48.6	1.73	0.6	—	—	—	—	—
Roberson, 9-27[b]	28.2	48.4	1.73	0.7	—	—	—	—	—
6. Emerald green	26.2	50.3	1.92	0.4	—	—	—	—	—
Rowney[b]	26.6	50.0	1.92	0.7	—	—	—	—	—
7. Emerald green	28.1	48.7	1.73	0.4	—	tr	—	—	—
F. Weber[b]	28.7	48.0	1.67	0.6	—	—	—	—	—
8. Emerald green-Scheele's green*	22.9	48.2	2.10	0.2	1.3	—	—	—	—
F. Weber, Philadelphia[b]	24.2	47.0	1.94	0.4	2.3	0.3	0.1	—	—
9. Scheele's green*	23.8	43.2	1.82	0.5	5.7	0.1	—	—	—
Fezandie and Sperrle, August 1936[b]	27.3	49.3	1.81	0.6	—	—	—	—	—
10. Stone green no. 2	20.6	34.3	1.67	0.4	3.0	0.1	—	11.7	—
Karwak Gallery, Toronto (from China) June 1979[c] (dolomite/magnesite, calcite, and silicate mix)	—	—	—	0.4	0.8	42.5	—	20.5	—
11. No. 1 from set of Chinese pigments (Peking [Beijing] 1949)[d]	15.1	27.8	1.84	0.9	20.2	—	—	—	—
	27.8	48.7	1.75	0.7	—	—	—	—	—
12. No. 1 from set of modern Persian pigments, Tehran, 1954[d]	25.6	48.0	1.88	0.6	—	2.7	—	—	—
	26.3	50.0	1.90	0.8	—	—	—	—	—

*Although labeled Scheele's green, these samples are emerald green by analysis. Several copper acetoarsenite samples in the E. W. Forbes Collection at the Art Institute of Chicago are labeled Scheele's green or include both names.

tr=Trace

a. Samples analyzed by McCrone Associates, Westmont, Ill.

b. Edward W. Forbes Collection, Art Institute of Chicago.

c. Art Institute of Chicago Pigment Collection.

d. Arthur M. Sackler Gallery and Freer Gallery of Art, Department of Conservation and Scientific Research, Smithsonian Institution, Washington, pigment collection.

e. Martin J. Fischer Collection, Milwaukee Public Museum.

f. Edward W. Forbes Collection, Arthur M. Sackler Gallery and Freer Gallery of Art, Smithsonian Institution, Washington.

g. Sample from Ashok Roy, Scientific Department, National Gallery, London.

Table 6 Continued

Sample No. and Name	*Copper*	*Arsenic*	*Arsenic/ Copper*	*Iron*	*Silicon*	*Calcium*	*Potassium*	*Magnesium*	*Sulfur*
13. Emerald green	21.3	54.4	2.55	0.2	—	—	—	—	—
no. 284, M. J. Fischer Collection[c]	23.2	49.9	2.15	0.2	0.6	tr	tr	—	—
14. Emerald green	20.9	53.2	2.54	0.5	11.8	—	—	—	—
Masury[f]	30.5	69.5	2.28	—	—	—	—	—	—
15. Copper aceto-	15.9	48.9	3.08	0.4	16.2	—	—	—	—
arsenite, lot	27.5	65.5	2.38	0.2	3.1	—	—	—	—
no. 02142, Dixon Fine Chemicals, Canada, 1987[c]									
16. Cupric arsenite	31.3	36.0	1.15	0.3	1.6	0.2	1.6	—	—
no. 7200, ICN	33.1	36.1	1.09	0.5	1.3	0.2	1.4	—	—
Pharmaceuticals, July 1983[c]									
17. Copper arsenite	40.9	34.8	0.85	0.3	—	—	—	—	2.6
(Scheele's green?)[f]	39.4	35.3	0.90	0.7	—	—	—	—	2.2
18. Scheele's green	31.7	33.7	1.06	0.4	—	—	—	—	0.3
W and J George	35.3	36.1	1.02	0.6	—	—	—	—	0.6
and Becker Ltd., London[a,g]									
Theoretical Composition									
Emerald green:									
copper, 25.1									
arsenic, 44.3									
arsenic/copper, 1.76									
Scheele's green:									
copper, 22.9–50.6									
arsenic, 29.8–54.1									
arsenic/copper, 0.59–2.36									

Table 7 **Elements Detected by Neutron Activation Analysis in Pigments in the Edward W. Forbes Collection, Art Institute of Chicago**[a]

Element and Measurement Method	*Emerald Green, Fezandie and Sperrle, 1936*	*Veronite Vert, Lefranc 1927*	*Emerald Green, Roberson 9-27*	*Emerald Green Rowney*	*Emerald Green Weber*
Aluminum, ppm	207	105	146	189	139
Antimony, ppm	3786	1496	148	3275	261
Arsenic, percent	38.7	41.2	39.1	37.9	39.3
Calcium, ppm	8718	—	—	—	—
Chlorine, ppm	—	—	—	500	—
Cobalt, ppm	6.4	11.3	11.0	10.1	12.0
Copper, percent	26.6	29.3	27.4	26.7	27.7
Erbium, ppm	3017	—	—	—	—
Gallium, ppm	0.80	0.83	0.92	0.96	0.83
Germanium, ppm	—	1.19	0.41	—	—
Iron, percent	—	0.60	0.48	—	0.25
Nickel, ppm	364	—	132	—	—
Potassium, ppm	—	—	—	—	4583
Praseodymium, ppm	—	3.61	—	—	—
Rubidium, ppm	160	—	121	179	—
Silver, ppm	—	—	—	43	—
Sodium, ppm	3701	1298	3108	9399	806
Tin, ppm	—	—	—	—	37
Zinc, ppm	—	188	117	132	85
Zirconium, ppm	479	—	—	—	—

a. Data from Reed R. Burn, Ford Nuclear Reactor, Phoenix Memorial Laboratory, University of Michigan.
Searched for, not detected: Barium, Cerium, Magnesium, Manganese, Neodymium, Niobium, Ruthenium.

Table 8 **Elements Detected by Neutron Activation Analysis in Pigments**[a]

Element and Measurement Method	*Emerald/ Scheele's Green F. Weber*[b]	*Scheele's Green Fezandie and Sperrle August 1936*[b]	*Cupric Arsenite No. 7200 ICN 1983*[c]	*Paris Green*[d]	*Stone Green No. 2 Canada, June 1979*[c]
Aluminum, ppm	197	136	231	621	846
Antimony, ppm	280	3828	478	1382	214
Arsenic, percent	39.8	40.7	30.7	49.9	29.6
Barium, percent	—	—	—	2.77	—
Cerium, ppm	—	—	—	139	—
Cobalt, ppm	14.8	7.2	8.8	146	10.2
Copper, percent	27.5	28.5	37.0	31.0	19.4
Erbium, ppm	—	—	1519	—	—
Gallium, percent	0.79	0.88	1.02	0.57	0.75
Germanium, ppm	—	0.53	—	—	—
Iron, percent	0.47	—	—	2.15	0.56
Magnesium, ppm	—	—	—	—	8546
Manganese, ppm	—	59	—	—	120
Neodymium, ppm	—	—	—	1123	—
Nickel, ppm	—	—	1035	1367	185
Niobium, ppm	—	—	—	205	—
Potassium, ppm	—	—	9726	—	—
Praseodymium, ppm	—	1532	—	—	—
Rubidium, ppm	—	—	—	—	1.5
Ruthenium, ppm	—	—	—	2622	—
Silver, ppm	—	—	92	—	—
Sodium, ppm	1805	5403	—	—	4175
Tin, ppm	113	—	—	1015	0.35
Zinc, ppm	112	—	124	1157	1123

a. Data from Reed R. Burn, Ford Nuclear Reactor, Phoenix Memorial Laboratory, University of Michigan.

b. Edward W. Forbes Pigment Collection, Art Institute of Chicago.

c. Art Institute of Chicago Pigment Collection.

d. Sample (1960s) from Max Saltzman; Art Institute of Chicago Pigment Collection.

Searched for, not detected: Calcium, Chlorine, Zirconium.

6.0 **Occurrences**

Many identifications of emerald green are available, but documentation of Scheele's green is limited. Ashok Roy, National Gallery, London, identified both Scheele's green and emerald green in Edouard Manet's *Music in the Tuileries Gardens*. They occur together in a matrix of yellow lake admixed with small amounts of ivory black and yellow ocher as a transparent glaze and also as an opaque mixture with white and yellow ocher painted over the glaze in some foliage areas (Bomford et al., 1990). Copper arsenite was used by Edwin Landseer in *Queen Victoria at Osborne*, which was painted in 1866 (A. Roy, personal communication, 1990).

Townsend (1993a, b) noted that J.M.W. Turner used Scheele's green from c. 1806–1807. He substituted emerald green for Scheele's green by the 1830s, and when viridian became available the artist used a mixture of the two in paintings dated from the 1840s. Townsend's study indicates that Turner used many pigments soon after they were commercially available. Another early finding of emerald green was on John Constable's palette, c. 1835–1837 (Southall, 1982; Cove, 1991). It was also identified on an 1860 signed and dated canvas on which William Holman Hunt painted experimental color patches (A. Roy, personal communication, 1990); the canvas was possibly part of Hunt's studies in pigment compatibility (see also section 3.5). Church (1915) listed the English painter Samuel Palmer (1805–1881) as using emerald green.

The palettes of the impressionists and post-impressionists were complex and included an extensive variety of pigments that in many cases only became commercially available in the middle-to-late nineteenth century. Emerald green had an obvious appeal to these artists, who were striving for brilliant, pure spectral colors. Although industrialization created many new pigments, such as the coal-tar derivatives, the unique color of emerald green was difficult to duplicate, and it remained in use for some time. Based on the number of occurrences found, it can be concluded that it was a favorite color among artists such as Paul Cézanne, Paul Gauguin, Vincent van Gogh, and Claude Monet.

Clapp (1963) was one of the first to report Cézanne's use of emerald green. An in-depth study by Butler (1973a) on Cézanne's painting materials indicated that emerald green was used in nearly every tone sampled from *Chestnut Trees at Jas de Bouffan*. Cézanne's mixtures varied from a few particles in the yellow sky to over 75% in the medium-yellow-green grass and 90% in the yellow-green grass. Emerald green was identified in all of the ten Cézanne paintings analyzed at the Philadelphia Museum of Art (Butler, 1984). Butler reported it was one of the four pigments (the others being lead white, vermilion, and ultramarine) that was used most frequently and in "significant proportions." Delbourgo and Rioux (1974) reported finding greens containing copper and arsenic (probably emerald green) in paintings by Monet and Cézanne.

In a letter dated February 1898 to his friend, de Monfreid, Gauguin discussed his large canvas, *Where Do We Come From? What Are We? Where Are We Going?* (Museum of Fine Arts, Boston). He described in some detail its composition and the placement of some of the colors and noted, "although there are different shades of color, the landscape constantly has a blue and Veronese green hue from one end to the other" (Guérin, 1978). The use of emerald green in this painting was corroborated in a study of Gauguin's technique and materials by Christensen (1993). She has also reported the pigment was used in fifteen of his other paintings, which included twelve works in the National Gallery of Art, Washington. In a study of Gauguin's materials, emerald green has been identified on the eight Gauguin paintings in the collection of the Art Institute of Chicago (see list of Occurrences).

Research conducted by Harriet Stratis at the Art Institute of Chicago on the technique and materials of several pastels by the French symbolist artist Odilon Redon has disclosed his use of emerald green. One such example can be seen in Odilon Redon's pastel *Sîta* (fig. 37).

The green labeled "*Verones grün*" in the pigment collection of the Swiss artist Arnold Böcklin was identified as emerald green by Richter and Härlin (1974b). Kühn (1969) reported emerald green on two of Böcklin's works and on four other late nineteenth-century paintings in the Schack Galerie, Munich. The pigment was also identified on four paintings by the German artist Karl Hagemeister dating between 1875 and 1908 (Schaaff & Riederer, 1992).

In paintings by the Spanish Forger both copper and arsenic have been detected by neutron autoradiography and neutron activation analysis. Strong arsenic activity associated with the green pigment was noted in all of the Spanish Forger works ana-

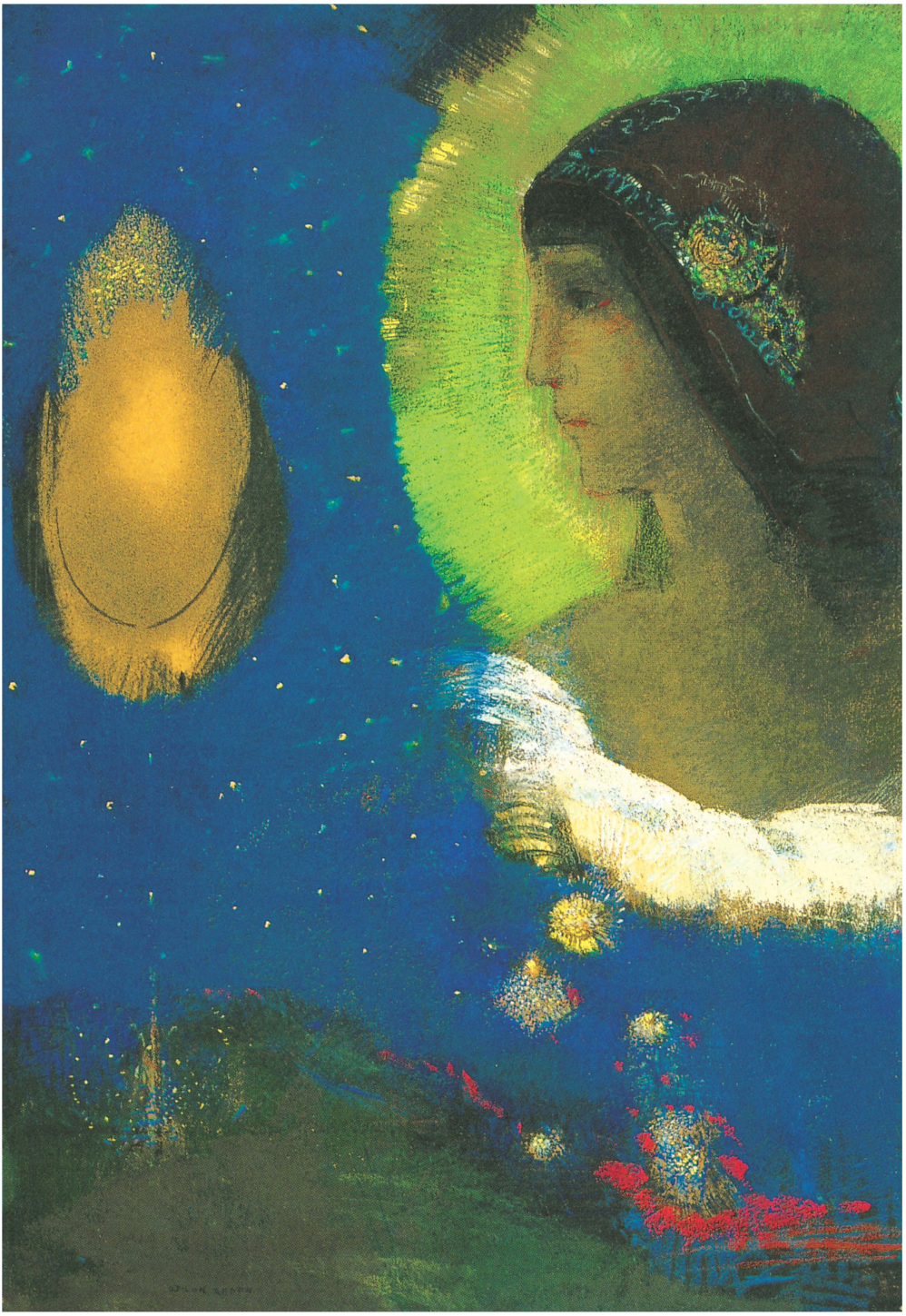


Fig. 37 Odilon Redon, *Sîta*, pastel over charcoal on paper, c. 1893. The yellow-green halo around the face seen in profile is a mixture of emerald green, chrome yellow, and calcium carbonate. Art Institute of Chicago, Joseph Winterbotham Collection 1954.320.

lyzed (Muether et al., 1978; Cotter, 1981). This artist, whose identity is still unknown, is believed to have been active in Paris toward the end of the nineteenth century and the beginning of the twentieth century. Lawrence Majewski, Institute of Fine Arts, New York University, identified emerald green by optical microscopy in the miniature *Exorcism of Mary Magdalene* by this artist (Voelkle, 1978).

Emerald green was used to decorate an early nineteenth-century animal skin coat in the collection of the Canadian Museum of Civilization, National Museums of Canada, Ottawa (no. 83/3/1), made by the Red River Métis People, early settlers of Manitoba. The pigment on the coat was analyzed by Elizabeth Moffatt at the Canadian Conservation Institute, Ottawa, using x-ray diffraction and Fourier transform infrared spectroscopy (Marilyn Laver, personal communication, 1987).

Although the number of documented occurrences of emerald green in Asia is limited, a few examples have been reported. It has been found in *Landscape of the Season: Spring*, acc. no. 98.123, a painting by the Japanese ukiyo-e artist, Andō Hiroshige (1797–1858), in the Freer Gallery of Art, Smithsonian Institution, Washington (FitzHugh, 1979) and *Nadirshah*, acc. no. S1986.439, an Indian painting of c. 1900 in the Arthur M. Sackler Gallery, Smithsonian Institution, Washington (FitzHugh, 1988).

Emerald green and quartz were identified by optical microscopy, x-ray powder diffraction, and x-ray fluorescence as the components of a Chinese ink cake (no. 42.232) in the collection of the Cleveland Museum of Art. The original date of the mold for the ink cake is 1623, although reusing such molds was not uncommon (Bruce Christman, personal communication, 1988). Emerald green was used in the false patina on a modern repair of a twelfth century B.C. Chinese Shang dynasty bronze vessel in the Freer Gallery of Art (Gettens, 1969).

Occurrences of Scheele's Green

Date	*Artist, Country, Title or Description, Collection or Location*	*Analyst and Method of Identification*
c.1805	Joseph M. W. Turner, British, Oil sketch on panel, *Guildford from the Banks of the Wey,* Tate Gallery London N02310	Townsend (1993b) EDX
1862	Edouard Manet, French, *Music in the Tuileries Gardens*, National Gallery London 3260	Bomford et al. (1990) micr., EDX
1866	Edwin Landseer, British, *Queen Victoria at Osborne*, Royal Collection England	Burnstock[a] micr., EDX

EDX=Energy-dispersive x-ray fluorescence
micr.=Light microscopy
a. Ashok Roy, personal communication, 1990.

Occurrences of Emerald Green

Date	*Artist, Country, Title or Description Collection or Location**	*Analyst and Method of Identification*
c.1832	Joseph M. W. Turner, British, *Going to School,* Watercolor on paper Tate Gallery, London D27715	Townsend (1993b) micr., EDX
c.1832	Joseph M. W. Turner, *Rouen Looking Down River*, Watercolor and gouache on paper, Tate Gallery, London D24673	Townsend (1993b) micr., EDX
c.1860	Moritz von Schwind, German(?) *The Morning Star*, Schack Galerie Munich	Kühn (1969)
1860	William Holman Hunt, British Experimental color patches painted out by the artist on a signed and dated canvas, Scientific Department National Gallery, London	Roy[b] micr., LMA
1860	L. J. Kleyn, Dutch, *A View of the Hague*, Gemeentemuseum The Hague, Netherlands	De Wild (1929)
1862	Edouard Manet, French, *Music in the Tuileries Gardens*, National Gallery London 3260	Bomford et al. (1990) micr., EDX
c.1865	Frédéric Bazille, French, *Self-Portrait* Art Institute of Chicago 1962.336	Fiedler micr., XRD[a]
1866	Arnold Böcklin, Swiss, *Amaryllis* Schack Galerie, Munich	Kühn (1969)
1868	Claude Monet, French, *On the Seine at Bennecourt (Au Bord de l'eau, Bennecourt)*, Art Institute of Chicago 1922.427	Fiedler micr.
1869	Claude Monet, *Bathers at La Genouillère*, National Gallery London 6465	Roy (1981) LMA
1871	Arnold Böcklin, *Italian Villa* Schack Galerie, Munich	Kühn (1969)

*All works are oil on canvas unless indicated otherwise
chem.=Chemical or microchemical test
EDX=Energy-dispersive x-ray fluorescence
EBM=Electron beam microprobe
ES=Emission spectroscopy
FTIR=Fourier transform infrared spectroscopy
LMA=Laser microprobe analysis
micr.=Light microscopy
XRF=X-ray fluorescence spectroscopy
XRD=X-ray diffraction
a. Analysis by McCrone Associates, Westmont, Ill.
b. Ashok Roy, personal communication, 1990.
c. F403, F405, F499, F532, and F555 are numbers assigned by J.-B. de la Faille in the catalogue raisonné, *The Works of Vincent van Gogh: His Paintings and Drawings*, Amsterdam, 1970.
d. Harriet K. Stratis, associate conservator of prints and drawings, Art Institute of Chicago.
e. Marilyn Laver, personal communication, 1987.

Occurrences of Emerald Green Continued

Date	*Artist, Country, Title or Description Collection or Location**	*Analyst and Method of Identification*
1871	Camille Pissarro, French, *The Avenue Sydenham*, National Gallery London 6493	Bomford et al. (1990) micr., EDX
1873	Claude Monet, *Monet's House at Argenteuil*, Art Institute of Chicago 1933.1153	Fiedler micr.
1875	Pierre-Auguste Renoir, French, *Lady at the Piano*, Art Institute of Chicago 1937.1025	Butler (1973b) micr.
1876–1877	Pierre-Auguste Renoir *The Café Concert*, National Gallery London 3859	Bomford et al. (1990) micr., EDX
1877	Paul Cézanne, French, *Plate of Apples* Art Institute of Chicago 1949.512	Fiedler micr.
1877	Claude Monet, *The Gare Saint Lazare* National Gallery, London 6479	Roy (1985) XRD, LMA
1877	Camille Pissarro, *The Côte des Boeufs at L'Hermitage*, National Gallery London 4197	Bomford et al. (1990) micr., EDX
1877–1879	Paul Cézanne, *Saint-Henri and the Bay of L'Estaque*, Philadelphia Museum of Art 200-1979-1	Butler (1984) micr., EBM
1877–1879	Edgar Degas, French, *Portrait After a Costume Ball (Portrait of Mme. Dietz-Monnin)*, Gouache, charcoal pastel, metallic paint, and oil on canvas Art Institute of Chicago 1954.325	Fiedler micr.
1878–1879	Edouard Manet, *At the Café*, Walters Art Gallery, Baltimore 37.893	Gifford (1984/1985) micr.
1878–1879	Edouard Manet, *The Beer Waitress* Musée d'Orsay, Paris	Rioux (1989) micr., XRF
1878	Edouard Manet, *The Waitress* National Gallery, London 3858	Roy (1983) XRD, LMA
1879	Berthe Morisot, French, *Summer Day* National Gallery, London 3264	Bomford et al. (1990) micr., EDX
1879	Camille Pissarro, *Rabbit Warren at Pontoise, Snow*, Art Institute of Chicago 1964.200	Fiedler micr.
1879–1882	Paul Cézanne, *Landscape at Pontoise* Philadelphia Museum of Art 127-1980-1	Butler (1984) micr., EBM
1879–1883	Paul Cézanne, *Bay of L'Estaque* Philadelphia Museum of Art 63-116-21	Butler (1984) micr., EBM
1880	Paul Cézanne, *Flowers in an Olive Jar* Philadelphia Museum of Art 63-116-2	Butler (1984) micr., EBM
1880	Claude Monet, *Still Life: Apples and Grapes*, Art Institute of Chicago 1933.1152	Fiedler micr.

Occurrences of Emerald Green Continued

Date	*Artist, Country, Title or Description Collection or Location**	*Analyst and Method of Identification*
1881	Claude Monet, *Lavacourt under Snow* National Gallery, London 3262	Bomford et al. (1990) micr., EDX
1881	Pierre-Auguste Renoir, *Fruits from the Midi*, Art Institute of Chicago 1937.1176	Butler (1973b) micr.
1881	Pierre-Auguste Renoir, *On the Terrace* Art Institute of Chicago 1933.455	Butler (1973b) micr.
c.1881–c.1886	Pierre-Auguste Renoir, *The Umbrellas* National Gallery, London 3268	Bomford et al. (1990) micr., EDX
1882	Claude Monet, *Cliff Walk at Pourville* Art Institute of Chicago 1933.443	Fiedler micr.
1882	Gustave Moreau, French, *The Sirens* Watercolor and gouache, Harvard University Art Museums (Fogg) Cambridge 1943.392	Weston (1977) XRF
1882–1885	Paul Cézanne, *The Pool at the Jas de Bouffan*, Albright-Knox Art Gallery Buffalo	Clapp (1966) micr., chem.
1882–1885	Paul Cézanne, *The Viaduct at L'Estaque,* Allen Art Museum Oberlin, Ohio	Clapp (1966) micr., chem.
1883	Paul Cézanne, *View of the Bay Marseilles with the Village of Saint-Henri*, Philadelphia Museum of Art 63-116-3	Butler (1984) micr., EBM
1883	Claude Monet, *Etretat*, Art Institute of Chicago 1964.204	Fiedler micr.
1884	Claude Monet, *Bordighera*, Art Institute of Chicago 1922.426	Fiedler micr.
1884	Georges Seurat, French, *Oil Sketch for La Grande Jatte*, Oil on panel Art Institute of Chicago 1981.15	Fiedler (1984) micr.
1884	Georges Seurat, *The Island of La Grande Jatte*, Mrs. John Hay Whitney Collection, New York	Fiedler (1989) micr.
1884–1886	Georges Seurat, *A Sunday on La Grande Jatte—1884* Art Institute of Chicago 1926.224	Fiedler (1984, 1989) micr., XRD,[a] EBM[a]
1885	Claude Monet, *Boats in Winter Quarters*, Art Institute of Chicago 1922.428	Fiedler micr.
1885	Claude Monet, *Boats in Winter Quarters, Etretat*, Art Institute of Chicago 1947.95	Fiedler micr.
c.1885–1887	Paul Cézanne, *Chestnut Trees at Jas de Bouffan*, Minneapolis Institute of Art 49.9	Butler (1973a) micr.
c.1886	Paul Cézanne, *Hillside in Provence* National Gallery, London 4136	Roy (1985) micr., XRD, LMA

Occurrences of Emerald Green Continued

Date	*Artist, Country, Title or Description Collection or Location**	*Analyst and Method of Identification*
c.1886	Vincent van Gogh, Dutch, *Montmartre* Art Institute of Chicago 1926.202	Engel (1975) micr.
1886	Claude Monet, *Rocks at Belle-Isle* Art Institute of Chicago 1964.210	Fiedler micr., XRD,[a] EBM[a]
1886–1887	Paul Cézanne, *Portrait of Madame Cézanne*, Philadelphia Museum of Art 67-30-17	Butler (1984) micr., EBM
1886–1887	Vincent van Gogh, *Fishing in Spring* Art Institute of Chicago 1965.1169	Engel (1975) micr.
1886–1887	Vincent van Gogh, *Self-Portrait*, Oil on artist's board, Art Institute of Chicago 1954.326	Engel (1975) micr.
c.1887	Vincent van Gogh, *Still Life: Fruit* Art Institute of Chicago 1949.215	Engel (1975) micr.
1888	Paul Gauguin, French, *Old Women at Arles*, Art Institute of Chicago 1934.391 (see fig. 3)	Fiedler micr., XRD[a]
1888	Paul Gauguin, *Portrait of Vincent van Gogh Painting Sunflowers* Rijksmuseum Vincent van Gogh Amsterdam	Newton (1991) micr.
1888	Vincent van Gogh, *The Bedroom* Art Institute of Chicago 1926.417	Engel (1975) micr.
1888	Vincent van Gogh, *The Garden of the Poets*, Art Institute of Chicago 1933.433	Engel (1975) micr.
1888	Vincent van Gogh, *Gauguin's Armchair with Candle and Books*, Rijksmuseum Vincent van Gogh, Amsterdam F499[c]	Farrell and Newman (1984) ES, XRD
1888	Vincent van Gogh, *The One-Eyed Man* Rijksmuseum Vincent van Gogh Amsterdam F532[c]	Farrell and Newman (1984) ES, XRD
1888	Vincent van Gogh, *Pear Tree in Blossom*, Rijksmuseum Vincent van Gogh, Amsterdam F405[c]	Farrell and Newman (1984) ES, XRD
1888	Vincent van Gogh, *The Pink Orchard* Rijksmuseum Vincent van Gogh Amsterdam F555[c]	Hofenk de Graaff et al. (1991) micr., LMA
1888	Vincent van Gogh, *Self-Portrait Dedicated to Paul Gauguin*, Harvard University Art Museums (Fogg) Cambridge	Farrell and Newman (1984) XRD
1888	Vincent van Gogh, *The White Orchard* Rijksmuseum Vincent van Gogh Amsterdam	Hofenk de Graaff et al. (1991) micr., LMA, FTIR
1889	Vincent van Gogh, *A Cornfield, with Cypresses*, National Gallery London 3861	Roy (1987) micr., LMA

Occurrences of Emerald Green Continued

Date	*Artist, Country, Title or Description Collection or Location**	*Analyst and Method of Identification*
1889	Vincent van Gogh, *Madame Roulin Rocking the Cradle (La Berceuse)* Art Institute of Chicago 1926.200	Engel (1975) micr.
1889–1890	Paul Cézanne, *Millstone in the Park of the Chateau Noir*, Philadelphia Museum of Art 63-116-4	Butler (1984) micr., EBM
c.1890	Edgar Degas, *Dancers*, pastel on paper, National Gallery of Canada Ottawa 6090	Maheux et al. (1988) micr.
1890	Paul Gauguin, *Portrait of a Woman, with Still Life by Cézanne* Art Institute of Chicago 1925.753	Fiedler micr.
1890	Vincent van Gogh, *The Drinkers* Art Institute of Chicago 1953.178	Engel (1975) micr.
1890	Vincent van Gogh, *The Oise at Auvers* Gouache on paper, Tate Gallery London T4714	Roy[b] micr., LMA
1890–1891	Claude Monet, *Poppy Field (Giverny)*, Art Institute of Chicago 1922.4465	Fiedler micr.
c.1890, reworked c.1893	Odilon Redon, French, *Sîta*, Pastel over charcoal on paper, Art Institute of Chicago 1954.320 (see fig. 37)	Stratis[d] micr., EBM
1891	Paul Gauguin, *The Big Tree (Te raau rahi)*, Art Institute of Chicago 1949.513	Fiedler micr., XRD[a]
1891	Claude Monet, *Grainstacks (Snow Effect, Overcast Day)*, Art Institute of Chicago 1933.1155	Fiedler micr.
1891	Claude Monet, *Grainstacks (End of Day, Autumn)*, Art Institute of Chicago 1933.444	Fiedler micr.
1892	Paul Gauguin, *The Burao Tree (Te Burao)*, Art Institute of Chicago 1923.308	Fiedler micr.
1893	Paul Gauguin, *Ancestors of Tehamana* Art Institute of Chicago 1980.613	Fiedler micr.
c.1893–1895	Paul Gauguin, *Mahna No Varua Ino* Woodcut with hand coloring, from suite of woodcut illustrations for *Noa Noa*, Art Institute of Chicago 1948.263	Stratis[d] micr.
c.1893–1895	Paul Gauguin, *Noa Noa*, Woodcut with hand coloring, from the suite of woodcut illustrations for *Noa Noa* Art Institute of Chicago 1948.255	Stratis[d] micr.
1894	Paul Gauguin, *Day of the Gods (Mahana No Atua)*, Art Institute of Chicago 1926.198	Fiedler micr.

Occurrences of Emerald Green Continued

Date	*Artist, Country, Title or Description Collection or Location**	*Analyst and Method of Identification*
1895	Claude Monet, *Sandvika, Norway* Art Institute of Chicago 1961.790	Fiedler micr.
1895–1900	Edgar Degas, *Racehorses*, Pastel on paper, National Gallery of Canada Ottawa 5771	Laver[e] XRF
1895–1905	Edgar Degas, *Woman at Her Toilette* Pastel on paper, Art Institute of Chicago 1937.1033	Fiedler micr.
1896	Paul Gauguin, *Why Are You Angry? (No Te Aha Oe Riri)*, Art Institute of Chicago 1933.1119	Fiedler micr.
1897	Claude Monet, *The Customs House at Varengeville*, Art Institute of Chicago 1933.1149	Fiedler micr.
c.1898	Odilon Redon, *Portrait of Ari Redon* Pastel on paper, Art Institute of Chicago 1950.130	Stratis[d] micr., EBM[a]
1899	Winslow Homer, American, *After the Tornado, Texas*, Watercolor, Art Institute of Chicago 1933.1235	Fiedler micr.
1901	Paul Gauguin, *Tahitian Woman with Children*, Art Institute of Chicago 1927.460	Fiedler micr.
1902–1906	Paul Cézanne, *Mont Sainte-Victoire* Philadelphia Museum of Art E36-1-1	Butler (1984) micr., EBM
1902–1906	Paul Cézanne, *Mont Sainte-Victoire* Philadelphia Museum of Art 1977-288-1	Butler (1984) micr., EBM
1905	Odilon Redon, *Still Life with Flowers* Art Institute of Chicago 1988.141.22	Fiedler micr.
1906	Paul Cézanne, *The Large Bathers* Philadelphia Museum of Art W37-1-1	Butler (1984) micr., EBM
1906	André Derain, French, *The Dance* Tate Gallery, London, on loan	Burnstock[b] micr., EDX
1917	Childe Hassam, American, *White Mountains Poland Springs* Watercolor, Harvard University Art Museums (Fogg) 1942.73	Weston (1977) XRF, micr.
1919	Fernand Léger, French, *Follow the Arrow,* Art Institute of Chicago 1953.341	Fiedler micr., XRD[a]

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9
Chromium Oxide Greens

Chromium Oxide and Hydrated Chromium Oxide

RICHARD NEWMAN

1.0 **Introduction**

Chromium oxide (Cr_2O_3) and hydrated chromium oxide ($Cr_2O_3.2H_2O$) are the only common green pigments based on the element chromium; they are collectively referred to as chromium oxide greens. Both were introduced during the first half of the nineteenth century. They are among the most permanent of artists' pigments, although neither has been widely used. Each of these pigments has a distinctive appearance; chromium oxide is a dull, opaque olive green, while hydrated chromium oxide is an intense, transparent, somewhat bluish green. Chromium oxide is listed as CI Pigment Green 17, no. 77288 in the *Colour Index* (1971). Hydrated chromium oxide is listed as CI Pigment Green 18, no. 77289.

Two other rarer chromium-containing green or blue-green pigments have also been noted. One, a blue or blue-green pigment, consists of fused chromium, cobalt, and aluminum oxides of the approximate composition $Cr_2O_3.CoO.Al_2O_3$ (Kühn, 1969). Wehlte (1975) called it *chromblaugrün* (blue-green chrome). Pamer (1978) identified a similar pigment in certain modern acrylic paints referred to as cerulean blue and reported an unindexed x-ray powder diffraction pattern for it. To date its only reported occurrence is in an 1862 painting by Eduard Schleich the Elder, Schack Galerie, Munich (Kühn, 1969).

The second pigment, a green chromium phosphate, was mentioned by Church (1915) and Coffignier (1924) as usually a basic hydrated chromium phosphate of variable composition. Church called it Arnaudon's chrome green and Mathieu-Plessy's green; Coffignier called it Mathieu-Plessy's green, *vert* Arnaudon, *vert* Schnitzer, and *vert* Dingler. The manufacturing process and possibly the specific chemical composition of these various pigments were in some cases different (Champetier et al., 1956). Hurst (1913) described the precipitation of chromium phosphates from chromium chloride solutions, or in a mixture of potassium dichromate and sodium phosphate. Windholz (1983) gave the composition of Arnaudon's green or Plessy's green as the hemiheptahydrate of $CrPO_4$. Arnaudon's chrome green is listed with similar composition and the same number as chromium oxide in the *Colour Index* (1971). No chromium phosphate pigments have been identified on paintings.

1.1 **Current Terminology**

English: chromium oxide, chromium oxide-opaque
French: oxide verte de chrome opaque
German: Chromoxidgrün

English: hydrated chromium oxide, transparent chromium oxide, viridian
French: vert émeraude
German: Chromoxidhydratgrün

1.1.1 ***Chromium oxide,*** the name that will be used in this chapter, is usually known by its chemical names or some obvious variation such as chrome oxide or chrome sesquioxide. Because of its high refractive index of 2.5, it is also known as chromium oxide-opaque to distinguish it from the hydrated chromium oxide. Robinson (1974) noted *vert émeraude*-dull as another synonym, a term derived from the French name for the hydrated oxide.

1.1.2 ***Hydrated chromium oxide.*** The name viridian, derived from the Latin name *viridi*(s), meaning green, was apparently first applied to the pigment in England in the 1860s (Maerz & Paul, 1950). The French name *vert émeraude* dates to about the mid-nineteenth century.

2.0 History

2.1 Archaic and Historical Names

2.1.1 ***Chromium oxide.*** The earlier nomenclature for this pigment is comparatively straightforward and unambiguous. Names such as chrome oxide, oxide of chromium, and green oxide of chromium opaque are among those most commonly encountered in English catalogues in the late nineteenth and early twentieth century. Church (1915) noted that the pigment was sometimes called true chrome green, a term that can be a source of confusion as chrome green (and Brunswick green) often refers to a mixture of chrome yellow and Prussian blue. Vergnaud (1831) and Lefort (1855) referred to the pigment as *vert de chrome*. Reading green is a name that has been applied to chromium oxide (Wehlte, 1975).

2.1.2 ***Hydrated chromium oxide.*** This pigment was initially referred to as Pannetier's green (*vert* Pannetier), after the Parisian color maker who, along with his assistant Binet, first prepared it about 1838 (Church, 1915). Later it was, and occasionally still is, called Guignet's green (see Patton, 1974), after the French chemist who in 1859 patented the method still generally used for its manufacture. Guignet's (1888) manufacturing method of 1859 produced a more affordable pigment.

English names for the pigment in early twentieth-century catalogues are emeraude green, emerald oxide of chromium, and oxide of chromium transparent. Emeraude first appeared in the English language as a name for the pigment in the 1860s (Maerz & Paul, 1950).

Unfortunately the terms emeraude and emerald have been used to describe hydrated chromium oxide and cause confusion with emerald green, which is the common name for copper acetoarsenite. *Vert émeraude* is still the common French name for hydrated chromium oxide, which undoubtedly is the source of some of the confusing English terms. Church (1915) gave Mittler's green as another name for the pigment.

In their 1910 catalogue, James Newman, a London color manufacturer, described Veronese green and Prussian green as pigments based on chromium oxide, possibly meaning hydrated chromium oxide. Prussian green, however, generally refers to the rare pigment that is chemically similar to Prussian blue, or to a mixture of a yellow pigment and Prussian blue (Harley, 1982), while Veronese green usually refers to emerald green (copper acetoarsenite). Toch (1916), in a confusing description of the chromium oxide greens, indicated that Veronese green was hydrated chromium oxide. It would appear that viridian and Veronese green were used interchangeably by some color manufacturers during the last quarter of the nineteenth century, if not earlier (Carlyle, 1991).

Eibner (1909) noted that *Permanentgrün* and *Viktoriagrün* were mixed colors comprised of hydrated chromium oxide with zinc yellow and sometimes barium sulfate. Coffignier (1924) listed *verts solides* as another name for such a mixed color prepared in Germany. Kittel (1953) described cadmium green as a mixture of hydrated chromium oxide and cadmium yellow.

2.2 History of Use

The element chromium was discovered by Louis-Nicolas Vauquelin in 1797 in "Siberian red lead," the mineral now known as crocoite, lead chromate (Vauquelin, 1798a). Chromium was so named because of the many colored compounds it produced, including chromium oxide, which Vauquelin (1798–1799) predicted, "on account of the beautiful emerald color which it communicates, . . . will furnish painters in enamel with the means of enriching their pictures, and of improving their art." He expressed doubts about the pigment's usefulness in the arts, however, because chromium-containing mineral sources were rare, but in his *Mémoire* Vauquelin (1809) noted chromium oxide was being used as a colorant at porcelain factories at Sèvres and Limoges, and that other ceramic manufacturers were beginning to use it. He once again noted that the color provided by the material produced a very beautiful enamel; his discussion implied, however, that it had not been used in this way at the time and he did not describe its use as a painting pigment.

2.2.1 ***Chromium oxide.*** Laurie (1935), as well as Gettens and Stout (1966), wrote that chromium oxide was not introduced as a pigment until about 1862 but it quite possibly was used earlier. It has tentatively been identified on an 1812 paint-

ing by J.M.W. Turner, *Somer Hill*, in the National Galleries of Scotland, Edinburgh (J. Townsend, personal communication, 1994). George Field, in an entry after 1815 in his *Practical Journal 1809,* included an example of chromium green of his own manufacture, presumably the opaque variety (Field, 1809; Harley, 1982). Vergnaud (1831) described two different preparation methods, and noted that in practice it was rarely used because of its high price. A Winsor and Newton c. 1840s catalogue listing of green oxide of chromium is presumed to be chromium oxide (Harley, 1982). In a book on artists' pigments Lefort (1855) described several methods of preparation.

Kühn (1969) identified chromium oxide in three paintings dating from 1845 to 1850 (see Occurrences). Documents indicate the pigment was most likely used for painting before 1845; future analyses may reveal more conclusive evidence.

Kuovo and Vuorelainen (1958) discovered a mineral form of Cr_2O_3 (eskolaite), a very rare mineral structurally identical to chromium oxide.

2.2.2 ***Hydrated chromium oxide.*** In a discussion of the properties of newly discovered chromium metal, Vauquelin (1798b) described a beautiful green color produced by heating the metal with a blowpipe and borax. This material may have been chemically similar to hydrated chromium oxide pigment, although this possibility was not pursued until later. According to Church (1915), hydrated chromium oxide was first prepared by the color maker Pannetier and his assistant Binet in Paris about 1838. Lefort (1855) noted that of all the "chrome greens," the best and most beautiful is "*vert émeraude*," or "*vert* Pannetier," but that it was prepared by a secret process and its price was so excessive that it could not often be used in painting. At that time, it cost about 140 francs/kg, over one-hundred times as much as chromium oxide, which also was an expensive pigment. In 1859, four years after Lefort's account, Guignet (1859) patented a method for manufacturing the pigment, and probably shortly thereafter it would have been available for use by artists at a more affordable price.

Laurie (1935) indicated that viridian was not available until about 1862, a date that Gettens and Stout (1966) noted in *Painting Materials,* but the pigment was certainly available earlier than this. Viridian has been identified in paintings by J.M.W. Turner as early as 1840, both alone and mixed with emerald green (Townsend, 1993). Winsor and Newton included "transparent oxide of chromium" among oil colors in an 1849 catalogue (Harley, 1982).

In Field's (1835) first edition of *Chromatography* he noted that although chrome green referred to a mixture of lead chromate and Prussian blue, there was a true chrome green that could be made in various degrees of transparency or opacity. A sample of oxide of chromium was included in the publication. Harley (1982) noted that it is not as brilliant or transparent as modern viridian, but neither is it as dull or opaque as chromium oxide. Field did not make a clear chemical distinction between the transparent and opaque varieties, and without analysis it is not possible to determine whether his sample is an early example of a hydrated chromium oxide pigment.

In a 1930 catalogue, Winsor and Newton noted that their house originally introduced viridian, a pigment popularized by the English watercolorist Aaron Penley (1807–1870) (Harley, 1982).

Two paintings dated 1863 and 1863–1864 are the earliest recorded occurrences of hydrated chromium oxide (see Occurrences and Kühn, 1969). However, the Winsor and Newton catalogue listed the pigment as commercially available at least fourteen years earlier, although expense probably precluded its wide use, and, if Church's date for Pannetier's invention is accepted, it could have been available twenty-five years earlier.

2.2.3 ***Popularity of the chromium oxide greens.*** Both chromium oxide greens were available before the middle of the nineteenth century, with chromium oxide almost certainly in use before hydrated chromium oxide. Figure 1 shows a histogram of 160 analyses, carried out by Kühn, of green colors from German paintings, mostly from 1840 to 1886. About 70% of the greens are mixtures of yellow and blue pigments, predominately chrome green (lead chromate yellow and Prussian blue); chromium oxide greens made up 11% of the samples, with ten occurrences of chromium oxide and eight occurrences of hydrated chromium oxide. Although once it became available hydrated chromium oxide may have immediately replaced the poisonous emerald green for commercial and printing purposes (Gettens & Stout, 1966), the histogram suggests that both pigments were used by artists with about the same frequency into the 1880s but were less popular than the mixed "chrome greens." Chromium oxide was about as common as green earth,

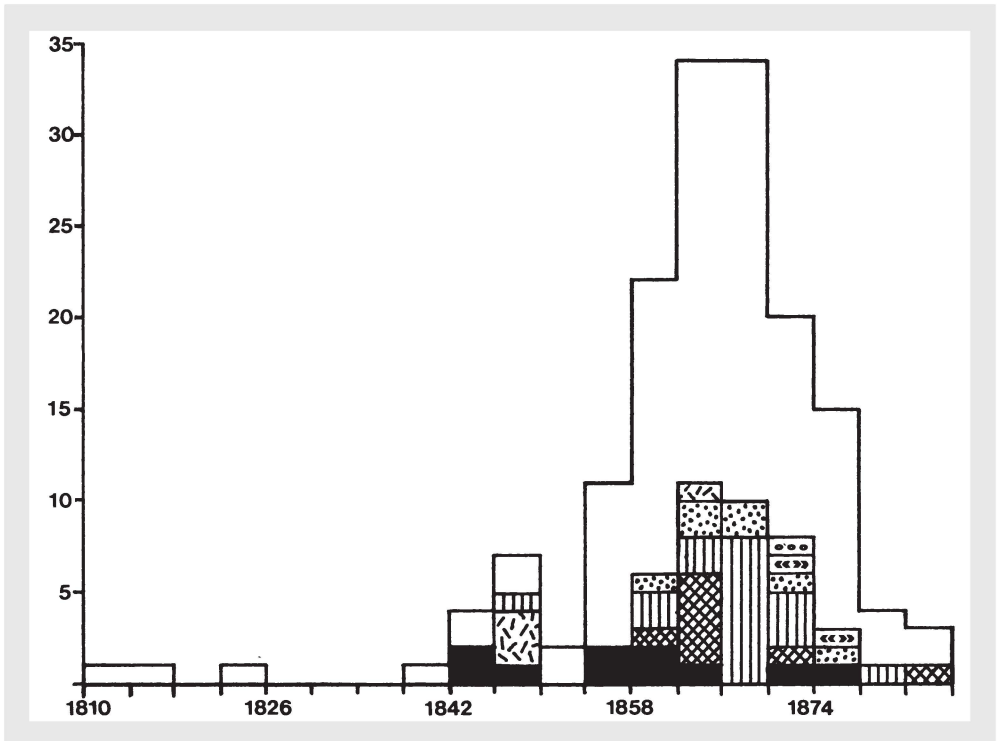


Fig. 1 Histogram of green samples from nineteenth-century paintings in the Schack Galerie, Munich (Kühn, 1969).

the traditional pigment that it most resembles in color. A survey by Russell and Abney (1888) of forty-six watercolorists indicated that they used chromium oxide greens (under several names) less frequently than emerald green and green earth. However, materials of the same probable composition, such as viridian and transparent oxide of chromium, were also reportedly used with the same frequency as emerald green and green earth by those surveyed. Mixed greens were not included in this survey. Published analyses of late nineteenth-century paintings (see Occurrences) indicate that hydrated chromium oxide was still less common than mixed greens or emerald green.

A major reason for the limited use of the chromium oxide greens was probably economic. Early twentieth-century catalogues of artists' pigments list both chromium oxide greens as two to three times more expensive than emerald green and at least three to four times more expensive than chrome greens. The price differences were probably even greater in the late nineteenth century.

Since the 1950s in comparison to the cost of chrome greens, chromium oxide was about the same; hydrated chromium green cost about two and one-half times more (Robinson, 1974). Chromium oxide green pigments accounted for less than 1.5% of total chromium products in 1968. At present, chromium oxide, the most permanent commercially available green pigment, is used when a dull green, highly inert pigment is required, such as in ceramics, highly alkaline masonry mixes (Portland cement), and in rubber compositions (Robinson, 1974). At one time hydrated chromium oxide was used in bank notes (Bearn, 1923), and it is used in mixtures with aluminum flakes to pigment metallic automotive finishes (Patton, 1974). Occasionally it is used in mixtures with yellows for lightfast paints. By 1972, it was considered a very minor pigment, displaced by synthetic organic greens such as phthalocyanine green.

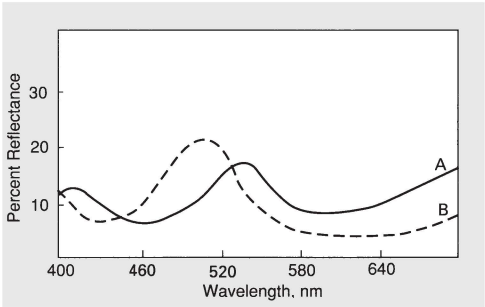


Fig. 2 Spectral reflectance. (A) chromium(III) oxide (Hatfield), (B) hydrated chromium oxide (F. Weber and Company). From Robert Feller, Research Center on the Materials of the Artist and Conservator, Carnegie Mellon Research Institute, Pittsburgh.

2.3 Dates of Use

Both chromium oxide greens were in use by the mid-nineteenth century. They are currently available from several manufacturers in the United States and are sold in prepared artists' colors in all media. They are both recommended as artists' pigments (Wehlte, 1975).

3.0 General Pigment Properties

3.1 Color and Spectral Reflectance

3.1.1 ***Chromium oxide*** is a dull olive green. Light and dark shades of the pigment differ in density with the darker being denser. Other general properties are virtually identical. The pigment has a low overall spectral reflectance; one lighter shade reflected a maximum of 18% (at 540 nm) in masstone (Robinson, 1974). Levison (1976) gave CIE (*Commission on Illumination Internationale de l'Eclairage*) tristimulus values for a 5/95 (volume) reduction with titanium oxide/zinc oxide/barium sulfate that plot very close to neutral in the CIE chromaticity diagram.

A representative reflectance spectrum is shown in figure 2(A). The characteristic broad pair of absorption maxima, at about 460 and 600 nm, is typical of chromium(III) in octahedral coordination in several substances (Neuhaus, 1960). Green minerals containing chromium(III) such as emerald (Wood, 1965; Wood & Nassau, 1968) and chromium glass, as well as chromium oxide, typically contain two such maxima at 580 to 650 nm (orange-red) and 420 to 460 nm (blue-violet). Absorption in these two areas arises from splitting of the *d*-orbitals by the octahedral field. The other major absorption band arising from the splitting occurs in the ultraviolet range (at about 265 nm in emerald).

3.1.2 ***Hydrated chromium oxide*** is a bright green. Its reflectance spectrum generally shows a much higher reflectance than chromium oxide, with a strong peak in the green range (maximum at about 510 nm), approximately 30 nm lower than for chromium oxide, and a weak peak in the violet-blue range (410 nm). A representative spectrum is given in figure 2(B). Levison (1976) reported CIE tristimulus values for viridian (5/95 by volume with white) that fall in the blue-green area of the CIE chromaticity diagram.

3.2 Infrared Reflectography

3.2.1 ***Chromium oxide.*** The chromium oxide greens are unusual among artists' green pigments because of their high reflectance in the near infrared region. Chromium oxide is used for camouflaging since it is the only common green pigment with an infrared energy reflectance that approaches the same level as that of chlorophyll in plants (Robinson, 1974). Farnsworth (1938) noted that chromium oxide absorbs only about 25% of incident radiation in the infrared region, whereas emerald and chrome green absorb almost completely and green earth absorbs about 75%.

3.2.2 ***Hydrated chromium oxide.*** The infrared reflectance of hydrated chromium oxide is slightly lower than that of chromium oxide (Kodak, 1970) but much higher than those of other green pigments such as emerald green and chrome green.

3.3 Hiding Power and Tinting Strength

3.3.1 ***Chromium oxide.*** The hiding power of chromium oxide is good in all media because of its high refractive index of 2.5, which is somewhat higher than that of mixed chrome greens and considerably higher than those of other green pigments (see Gettens & Stout, 1966).

Its tinting strength is high (Wehlte, 1975). However, its dull color and low overall reflectance limit its applications, although it can be used as a substitute for green earth, which is similar in color but much lower in tinting strength.

3.3.2 ***Hydrated chromium oxide.*** Because of its comparatively low refractive indices, the hiding power of hydrated chromium oxide is only moderately good, about one-fourth that of chromium oxide (Patton, 1974). Its brilliant green hue compares favorably with modern organic pigments such as phthalocyanine green. The tinting

strength is good. It is often extended with barium sulfate for easier grinding and dispersal. This does not significantly affect its overall transparency in oil media, where it is a deep blackish green in thick films.

3.4 Permanence

3.4.1 ***Chromium oxide.*** From the time of its discovery, chromium oxide's permanence has been consistently noted as one of its principal strengths. During the nineteenth century, it was one of the few green pigments (and sometimes the only one) given the highest rating for permanence (for example, Russell & Abney, 1888; Vibert, 1892). Levison (1976) showed that it does not change perceptibly under accelerated light aging. Robinson (1974) noted that chromium oxide withstands temperatures up to 1,000°C (1,832°F). The compound has a melting point of about 1,246°C (2,275°F), but it begins to decompose below that temperature (Rollinson, 1973).

3.4.2 ***Hydrated chromium oxide*** is not as stable overall as chromium oxide, but as an artist's pigment is considered very permanent. Levison (1976) rated it as very lightfast. Patton (1974) indicated that it is unaffected by temperatures up to approximately 260°C (500°F), making it unsuitable for use in ceramic glazes. One form of this pigment is an intermediate in the manufacture of chromium oxide, to which it is altered by calcining (Church, 1915). Coffignier (1924) reported Guignet's green decomposes at 250°C to 500°C (482°–932°F).

3.5 Chemical Properties

3.5.1 ***Chromium oxide.*** Bearn (1923) noted the pigment is resistant to boiling acids and alkalies. Tests on the mineral form of chromium oxide indicated it is resistant to a variety of etching chemicals such as acids, bases, and oxidants (Kuovo & Vuorelainen, 1958). Church (1915) noted it is unaffected by ammonium sulfide.

3.5.2 ***Hydrated chromium oxide.*** Bearn (1923) noted that if it is properly prepared hydrated chromium oxide is resistant to alkalies and acids. Coffignier (1924) wrote that it is affected by hot concentrated acids such as hydrochloric acid. Apparently, its overall solubility can be affected by an improper manufacturing process (Hurst, 1913); Church (1915) noted that some pigments not washed thoroughly enough during manufacture caused metal tubes of watercolor to corrode and fall apart in a few months.

Hydrated chromium oxide is not affected by hydrogen sulfide (Church, 1915).

3.6 Compatibility

Chromium oxide and hydrated chromium oxide are compatible with all pigments in all media.

3.7 Oil Absorption and Grinding Properties

3.7.1 ***Chromium oxide.*** Robinson (1974) reported the oil absorption to be low—typically 14 lbs. of oil/100 lbs. of pigment for light shades, 12 lbs./100 lbs. for dark shades; Eibner (1909) and Wehlte (1975) gave a figure of 30% (30 lbs./100 lbs.). Although it is a hard, abrasive material, the pigment is readily dispersed; Kuovo and Vuorelainen (1958) gave a Vickers microhardness for mineral crystals of 3,200 kg/mm^2.

3.7.2 ***Hydrated chromium oxide.*** The very high oil absorption of hydrated chromium oxide, reported by Patton (1974) as 80 to 110 lbs./100 lbs. and by Wehlte (1975) as 50% to 100% (50–100 lbs./100 lbs.) depending on specific gravity, is one of the major deficiencies of this pigment. Its hardness makes it difficult to grind with a glass muller (Wehlte, 1975). It disperses with difficulty, and pure pigment formulations may separate in tubes. The addition of even a small amount of barium sulfate makes the pigment easier to grind and disperse.

3.8 Toxicity

3.8.1 ***Chromium oxide.*** Robinson (1974) and Wehlte (1975) described it as substantially nontoxic. McCann (1979) gave its skin and inhalation toxicity as moderate, its ingestion toxicity as slight. It is a suspected carcinogen, however, and in the dry state may cause skin and respiratory irritation and allergies. It should be handled with care.

3.8.2 ***Hydrated chromium oxide.*** Wehlte (1975) reported hydrated chromium oxide to be nonpoisonous. In general, chromium(III) compounds are of low toxicity (Sittag, 1985), but because its properties are similar to chromium oxide, the dry pigment should be handled with care.

4.0 Composition

4.1 Chemical Composition and Crystal Structure

4.1.1 ***Chromium oxide.*** The pure pigment is Cr_2O_3, 68.4% chromium and 31.6% oxygen by weight. The compound has the same structure as α-Fe_2O_3 (the mineral hematite) and α-Al_2O_3 (corundum) and is identical to the rare mineral eskolaite (Kuovo & Vuorelainen, 1958). The ideal density, calculated from the lattice determined by the National Bureau of Standards, now National Institute for Standards and Technology (Swanson et al., 1955), is 5.245 g cm^3 (26°C). Superficially, the structure consists of oxygen atoms in hexagonal close packing, with chromium atoms in octahedral coordination; two-thirds of the octahedra are occupied and one-third are vacant. Each chromium atom is surrounded by six oxygen atoms in a roughly octahedral array, and each oxygen atom is surrounded by four chromium atoms in a grossly distorted tetrahedral array (Beattie & Gilson, 1970). The compound belongs to the hexagonal-scalenohedral class of the rhombohedral division of the hexagonal system, with symmetry $\bar{3}\frac{2}{m}$. Six Cr_2O_3 are present in the unit cell. The hexagonal lattice constants are a=4.954 Å, c=13.584 Å (at 26°C) (Swanson et al., 1955). Average Cr–O distances are 1.97 and 2.02 Å (Newnham & De Haan, 1962; Poole & Itzel, 1963). Cr–Cr distances vary from 2.65 to 3.65 Å and O–O distances vary from 2.63 to 2.99 Å (Newnham & De Haan, 1962). Bonding is primarily ionic, with a covalent contribution of over 20% (Renneke & Lynch, 1965).

Calcining of the greenish oxide, with consequent increase in crystal size, causes its color to change from green to blue-green to green-brown, to brown, and then to black; when finely ground, the green color is restored (Wilde & Rees, 1943).

Modern commercial pigments usually contain over 98% of the compound (Robinson, 1974) with reported major impurities of iron (0.04%) and sulfur (0.1–0.2%).

Four samples from the E. W. Forbes Pigment Collection, Harvard University Art Museums (Fogg), were qualitatively analyzed by emission spectrography. Traces of nickel, vanadium, copper, and/or manganese were detected in some of the samples; there was >0.1% nickel in two of the four and .01% to >0.1% vanadium in all four. All of these elements may be impurities from the original source of the chromium metal (probably chromite) used in the manufacture of the pigment. Trace amounts of silicon, iron, aluminum, magnesium, and calcium were also detected. Boron was detected in two of the four samples at levels of about .001% to .01%, and is presumed to be an artifact of the manufacturing process.

4.1.2 ***Hydrated chromium oxide.*** A reasonably representative composition of the pigment is reported as $Cr_2O_3.2H_2O$ or, less commonly, in the equivalent form $Cr_2O(OH)_4$. Based on the ideal formula, the pigment would consist of 55.4% chromium, 42.5% oxygen, and 2.1% hydrogen by weight. An alternative formula is CrO(OH) (Patton, 1974).

Its structure has not been studied in any detail. Two modern samples examined by x-ray powder diffraction gave very poor patterns. The most common manufacturing method, patented by Guignet in 1859 and essentially the same as is used today, involves the fusion of potassium bichromate with boric acid. Eibner (1909) and Church (1915) noted that some boric acid is probably chemically combined in the pigment. The few lines present in the x-ray powder diffraction patterns of the two modern hydrated chromium oxides can mostly be attributed to Cr–B–O ("chromium borate"), a material of uncertain composition and structure.

An electron diffraction examination of one sample of hydrated chromium oxide showed the material to be crystalline, but on a very fine scale. Patterns collected from areas of about 0.2 to 0.3 μm^2 consisted of a series of arcs, indicating a large number of more or less randomly oriented crystals. Morphologies of some of the fibrous platelets visible in transmission electron micrographs (see section 5.1) suggest that the material may have a hexagonal symmetry, and the electron diffraction pattern can be catalogued fairly successfully on the basis of this assumption. The diffraction pattern, shown in figure 3, is given in table 1 for reference. The sample from which this pattern was taken contains boron, and gave a very weak x-ray powder diffraction pattern for "chromium borate," none of whose lines appear to be present in the electron diffraction pattern.

Seven samples of hydrated chromium oxides from the E. W. Forbes Pigment Collection, Harvard University Art Museums (Fogg), were qualitatively analyzed by emission spectrography. Trace elements similar to those found in the anhydrous chromium oxides were also identified in some of these samples. In all seven

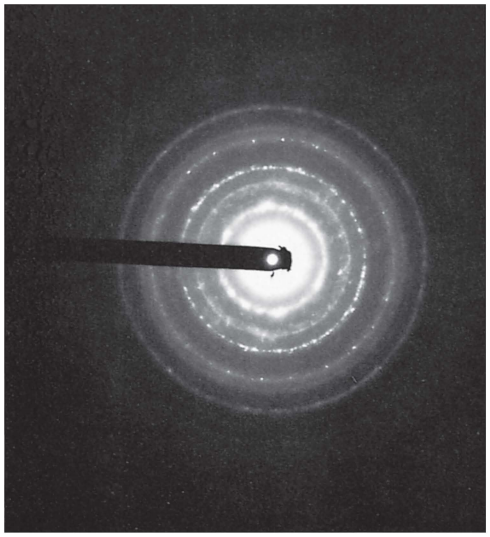


Fig. 3 Electron diffraction pattern (selected area) of hydrated chromium oxide pigment, George Rowney and Company, Forbes Pigment Collection, Harvard University Art Museums (HUAM/Fogg). See table 1. Taken from area (approximately 0.21 μm²) shown in fig. 9.

Table 1 **Electron Diffraction Pattern for Hydrated Chromium Oxide Pigment**[a]

d (Å)[b]
3.70
2.57
2.14
1.85
1.615
1.483
1.395
1.285
1.062
0.997
0.945
0.889

a. George Rowney and Company "viridian," E. W. Forbes Pigment Collection, Center for Conservation and Technical Studies, Harvard University Art Museums (Fogg).
b. Selected area pattern recorded at 175,000x magnification, covering an area of 0.21 μm². Camera constant checked with chromium(III) oxide.

boron was present at a level of >>0.1%, indicating that the Guignet process was probably used in its manufacture.

It is likely that hydrated chromium oxides are not always of one specific chemical composition, and in particular it appears that boron may not be present in all cases (see section 4.3).

4.2 **Sources**

Chromium oxide is currently widely available and hydrated chromium oxide is generally less readily available. Robinson (1974) listed three suppliers of hydrated chromium oxide.

4.3 **Preparation**

4.3.1 ***Chromium oxide.*** Vauquelin's 1809 *Mémoire* described the preparation of chromium oxide by decomposition of iron chromate. Vergnaud (1831) noted two methods of preparation: Thénard's technique of calcining mercury chromate and Laissaigne's method of calcining a mixture of potassium chromate and sulfur. Lefort (1855) also described several methods that produced chromium oxides with variable physical properties; he stated the best quality was produced by heating mercurous chromate, which, as Church (1915) later noted, is a "dry method" of manufacture. To replace the early expensive process, more economical procedures included calcining of three parts neutral potassium chromate with two parts ammonium chloride (sal ammoniac); the product was washed in hot water to remove soluble chlorides, dried, and again ignited. Another economical procedure involved calcining potassium chromate with sulfur, which reduced the chromate to the oxide; this procedure was first developed by Laissaigne (Vergnaud, 1831; Lefort, 1855; Eibner, 1909; Church, 1915). A fourth method involved combining four parts potassium bichromate with one part starch; this mixture was then calcined, washed, and recalcined.

Church (1915) also described "wet" methods that involved the reduction of solutions of alkaline chromate or dichromate, or precipitation of the sesquisalt of chromium by ammonia or a fixed alkali. The hydrated sesquioxide thus formed was washed and then calcined to produce the oxide.

Robinson (1974) noted that although many details of current manufacture remain proprietary, generally sodium, potassium, or ammonium dichromates are reduced with sulfur or carbonaceous material. Ammonium dichromate can be reduced by heating alone.

4.3.2 ***Hydrated chromium oxide.*** Guignet's 1859 method involved calcining a mixture of

boric acid and potassium bichromate; the material formed by this process was then thoroughly washed.

Bearn (1923) gave the ratios by weight of the starting components as about two parts boric acid to one part potassium dichromate, while Church (1915) gave a higher ratio of eight parts boric acid to three parts potassium dichromate. Bearn described the manufacture as involving two steps: an initial heating that produces $Cr_2(B_4O_7)_3$, a spongy mass of crude material, that is then hydrolyzed in cold water to yield the hydrated oxide and boric acid. Patton (1974) noted that current manufacture may involve other dichromate compounds such as sodium. Calcining is carried out for about six hours at dull red heat at approximately 500°C (932°F).

Eibner (1909) and Church (1915) noted that some boron is chemically combined in the final pigment, which the x-ray diffraction patterns confirm (see table 3 and section 5.2.1).

Church described another way of preparing the hydrated chromium oxide. Reduction of a solution of alkali chromate or dichromates with sulfur or other agents initially produced a hydrated oxide that upon calcining formed the anhydrous oxide. According to Church, air drying of the intermediate hydrated oxide created one form of the "transparent chromium oxide."

In their 1938 catalogue, Winsor and Newton noted viridian as the name they gave the pigment in watercolor and transparent oxide of chromium as the identical pigment in oil paint. It is possible, however, that these and other forms of hydrated chromium oxides may have occasionally varied in overall chemical composition as the manufacturing processes may also have varied. The process described by Church would have produced a boron-free material.

4.4 Adulteration and Sophistication

4.4.1 ***Chromium oxide.*** Occasionally, "chrome green" has been an interchangeable term for chromium oxide, as well as for a mixture of chrome yellow and Prussian blue; many authors, for example Moreau-Vauthier (1923), cautioned that the mixture was considerably less expensive and was sometimes sold as a chromium oxide counterfeit. Documents indicate the pure pigment was apparently rarely extended.

4.4.2 ***Hydrated chromium oxide.*** Perhaps primarily because otherwise it is difficult to disperse, hydrated chromium oxide has been sold in mixtures with the extender barium sulfate. Wehlte (1975) noted "permanent green, deep" (*vert permanent foncé; Permanentgrün dunkel*) as the name for such mixtures, which are less saturated and transparent than the pure pigment but can be dispersed more easily and are more stable in dispersions. Today the term permanent green more frequently applies to mixtures based on phthalocyanine green. Hydrated chromium oxide's high cost is undoubtedly another reason for the marketing of such mixtures (Eibner, 1909). Grades with various combinations of the two pigments are available. According to Wehlte "permanent green, light" is a mixture of permanent green dark and zinc yellow.

Although Hurst (1913) indicated the true chrome greens were usually adulterated with Brunswick green made from a mixture of lead chromate and Prussian blue—probably for economic reasons—this was not true of any of the seven dry pigment samples from the E. W. Forbes Pigment Collection that were analyzed.

5.0 Identification and Characterization

5.1 Optical and Chemical Microscopy

5.1.1 ***Chromium oxide.*** The particles are dull green when observed by reflected light. The refractive index is very high, 2.5 in lithium light (Merwin, 1917) causing it to be virtually opaque in the usual mounting media. Aggregates of individual particles are frequently present, with individual particles being comparatively small. At the typical upper limits of optical microscopes (1,000x), the particles appear fine and rounded (fig. 4).

Robinson (1974) gave a size distribution for a typical pigment, the average particle size being 3.8 µm. Scanning electron microscopic examination of one pigment from the E. W. Forbes Pigment Collection showed much finer size distribution as the smaller grains are 0.1–0.2 µm, and the largest are rarely over 1 µm (fig. 5). A transmission electron micrograph of the same pigment shows that the particles tend to be equant and often appear as hexagonal plates (fig. 6).

Kuovo and Vuorelainen (1958) noted that thin grain-edges are dark green and clearly anisotropic in large crystals of the mineral form of this compound, with pleochroism from emerald to olive green. Kuovo and Vuorelainen (1958) and Tennyson (1961) showed the most common forms for

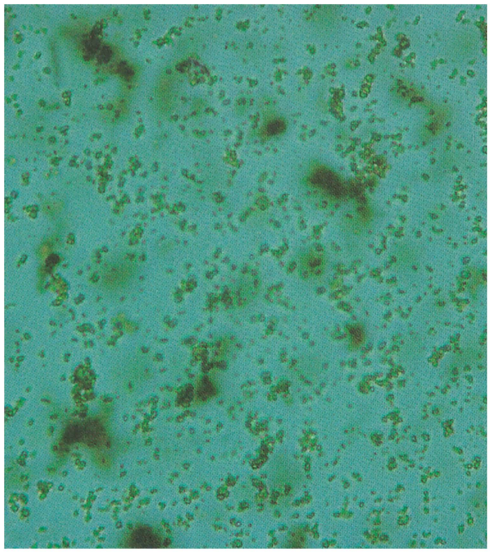


Fig. 4 Photomicrograph of chromium(III) oxide pigment in transmitted light. Reeves and Son, London, Forbes Collection (HUAM/Fogg). Mounted in Aroclor 5442, n=1.66. 500x.

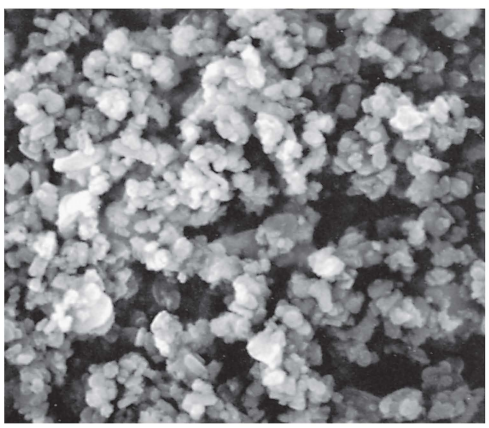


Fig. 5 Scanning electron micrograph of chromium(III) oxide pigment, Imperial Color, Forbes Collection (HUAM/Fogg). Secondary electron image of dispersed gold-coated sample. From Clive Hayzelden and Elizabeth Majewski, Harvard University. 6,500x.

the mineral to be hexagonal prisms and thick plates, characteristics that are apparently true also of the pigment.

Chromium oxide is virtually insoluble even in concentrated acids and bases; therefore, identification by microchemical means requires initial fusion. A sample may be fused with sodium carbonate and sodium peroxide on a platinum spoon

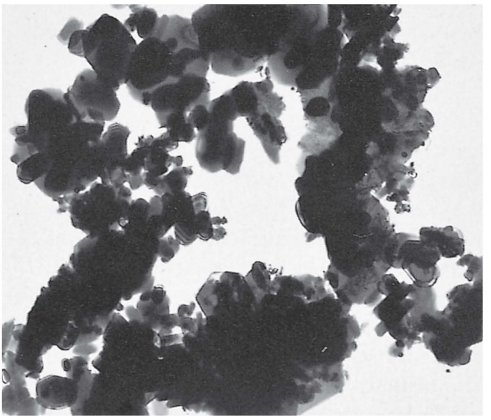


Fig. 6 Transmission electron micrograph of chromium(III) oxide pigment, Imperial Color, Forbes Collection (HUAM/Fogg). From Clive Hayzelden and Elizabeth Majewski, Harvard University. 19,000x.

and the melt is dissolved in two drops of concentrated sulfuric acid. Chromium is thus brought into solution as sodium chromate and can be tested for by any of several methods. Three methods noted by Plesters (1956) and Feigl (1958) are:

(a) Add one to two drops of a 1% solution of diphenylcarbazide in ethanol to a test drop on a spot plate. A violet color forms in the presence of chromate. This is the most sensitive of the three methods, with a limit of detection of 0.5 µg.

(b) Add a drop of silver nitrate to a drop of test solution on a spot plate or filter paper to form a dark red precipitate of silver chromate or dichromate. The limit of detection is 6 µg. Chamot and Mason (1960) noted that if only a very small amount of chromate is present, a yellow or orange solid solution of silver sulfate and chromate may form.

(c) Add a drop of lead acetate solution to a test drop to precipitate yellow lead chromate. The limit of detection is 6 µg.

5.1.2 ***Hydrated chromium oxide.*** By transmitted light, the particles are bright green, with a somewhat bluish hue (fig. 7A). The refractive index is moderate, Merwin (1917) reported α and β indices as 1.62 and γ as 2.12. The color between crossed polars is a mottled bluish green with a bright, nearly white appearance in some areas (fig. 7B). The particles usually show irregular undulose extinction, which Wagner and Renc (1936) attributed to strain in the particles caused by cooling during the manufacturing process. Individual particles are somewhat coarse, varying in size. They are typically irregular in shape and somewhat rounded. A count of 150 grains in the

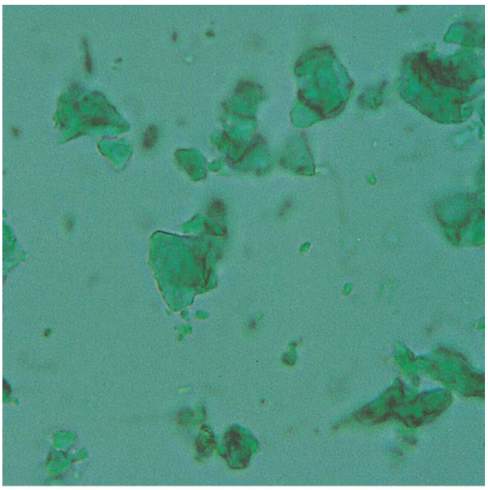
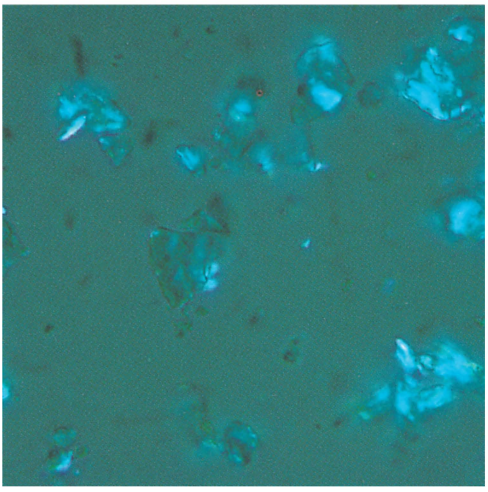


Fig. 7 Photomicrograph of hydrated chromium oxide pigment, F. Weber and Company, Forbes Collection, (HUAM/Fogg). Mounted in Aroclor 5442, n=1.66. 440x.
A. By transmitted light.



B. In crossed polars.

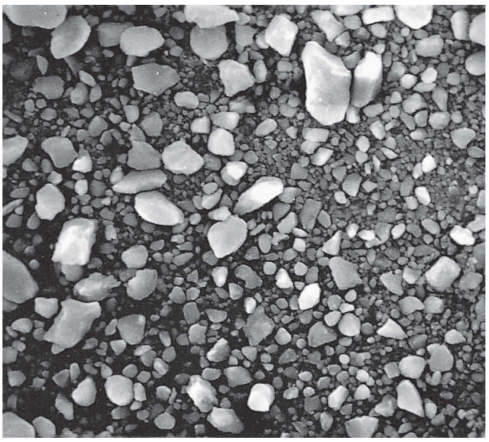


Fig. 8 Scanning electron micrograph of hydrated chromium oxide pigment, "viridian," George Rowney and Company, Forbes Collection, (HUAM/Fogg). Secondary electron image of dispersed gold-coated sample. From Clive Hayzelden and Elizabeth Majewski, Harvard University. 250x.

Fig. 9 Transmission electron micrograph of hydrated chromium oxide pigment, "viridian," George Rowney and Company, Forbes Collection, (HUAM/Fogg). From Clive Hayzelden and Elizabeth Majewski, Harvard University. 120,000x.

scanning electron micrograph shown in figure 8 indicated that 44% were less than 5 μm, 35% were 5 to 10 μm, 20% were 10 to 20 μm, and 1% was greater than 20 μm. The largest grain in the field is 45 μm in length. Although these appear to be individual particles, electron diffraction of the same pigment indicates that they are, in fact, aggregates of very much smaller individual crystals that are considerably smaller than can be observed by optical microscopy. In the transmission electron micrograph (fig. 9) the field of which is 0.53 μm wide, there are many small fibrous, tuft-like particles, about 0.07 to 0.12 μm long and 0.01 μm wide. Individual platelets are sometimes hexagonal or rhombohedral in shape, and are at other times irregular rounded polygonal shapes. The finely crystalline nature of the individual "particles" seen in the optical microscope is probably responsible for the undulose extinction.

Identification of hydrated chromium oxides by chemical microscopy is carried out by the same methods described for chromium oxide.

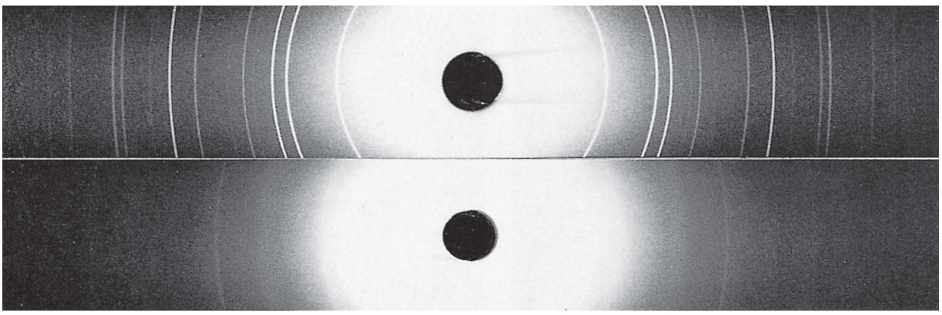


Fig. 10 X-ray diffraction powder patterns. From Glenn Gates, Scientific Research Department, National Gallery of Art, Washington. Photographs not to be used for measurement purposes.

A. Chromium(III) oxide pigment. Chromium oxide, opaque. Schmincke. Forbes Collection, Department of Conservation and Scientific Research, Arthur M. Sackler and Freer Gallery of Art (DCSR, Freer/Sackler), Smithsonian Institution, Washington.

B. Hydrated chromium oxide pigment. Viridian, hydrous chromium oxide, 231B, Paul Uhlich and Co., Inc., Forbes Collection (DCSR, Freer/Sackler).

5.2 Instrumental Methods of Analysis

5.2.1 ***X-ray diffraction.*** The current *JCPDS* (1988) x-ray diffraction data for chromium oxide are shown in table 2. This is the data from the National Institute of Science and Technology for the mineral eskolaite (Cr_2O_3). A Debye-Scherrer powder pattern for a representative pigment is given in figure 10A.

Hydrated chromium oxides analyzed for this monograph gave very poor x-ray powder diffraction patterns, the few lines of which can be assigned to "chromium borate," which is undoubtedly a minor component in the pigment. The standard data for chromium borate and the data for a viridian pigment are given in table 3. A Debye-Scherrer pattern is reproduced in figure 10B.

Table 2 **X-ray Diffraction Data for Chromium(III) Oxide**[a]

d (Å)	*I*
3.633	74
2.666	100
2.480	96
2.264	12
2.176	38
2.048	9
1.816	39
1.672	90
1.579	13
1.465	25
1.4314	40
1.2961	20
1.2398	17
1.2101	7
1.1731	14
1.1488	10
1.1239	10
1.0874	17
1.0422	16
plus nine additional lines to 0.7977	

a. *JCPDS Powder Diffraction File* 6-0504. From *JCPDS* (1988).

5.2.2 ***Infrared spectroscopy.*** Chromium oxide, like other anhydrous metallic oxides, absorbs infrared radiation only at the long wavelength end of the mid-infrared region, less than about 700 cm^{-1} or more than about 12 μm. Like other oxides with high refractive indices, it can produce a poor infrared spectrum unless carefully ground (Duyckaerts, 1959), although the particle sizes of most pigment samples are probably small enough to give a reasonably good spectrum without further preparation. Figure 11(A) shows a characteristic spectrum. Spectra have also been published by others, including McDevitt and Baun (1964), Afremow and Vandeberg (1966), and Nyquist and Kagel (1971). The sharp bands at 443 and 416 cm^{-1} correspond to two specific displacements of the O^{2-} sublattice with respect to the chromium(III) sublattice. The strongest bands in the spectrum, at 632 and 566 cm^{-1}, are probably due to various combinations of O^{2-} and chromium(III) displacements in the lattice (Farmer, 1974). Theoretical calculations indicate that there are two permitted vibrations parallel to

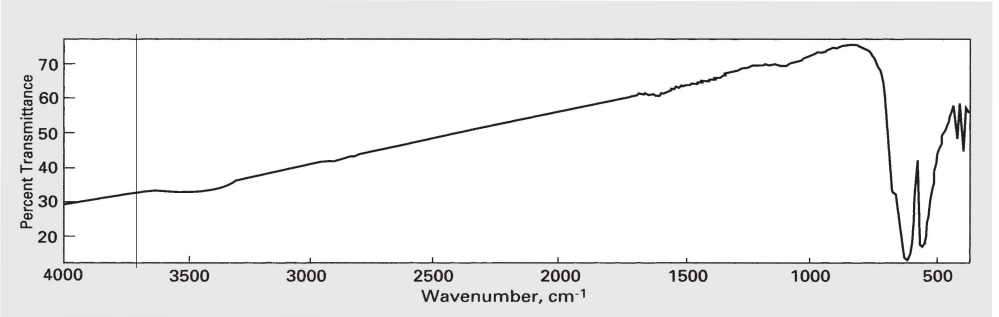
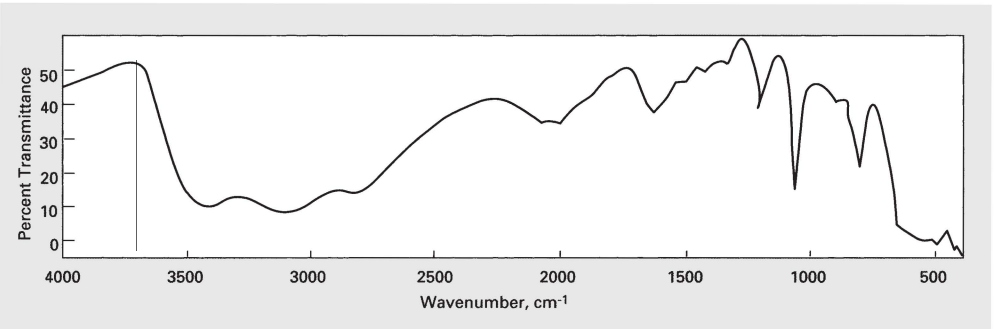


Fig. 11 Infrared spectra. From Barbara H. Berrie, Scientific Research Department, National Gallery of Art, Washington.

A. Chromium(III) oxide. Chromium oxide, opaque. Schmincke. Forbes Collection (DCSR, Freer/Sackler).



B. Hydrated chromium oxide. Viridian, hydrous chromium oxide, 231B, Paul Uhlich and Co., Inc., Forbes Collection (DCSR, Freer/Sackler).

Table 3 **X-ray Diffraction Data for Hydrated Chromium Oxide Pigment and "Chromium Borate"**

Rowney Viridian[a]		*Chromium Borate*[b]	
d (Å)	*I*[c]	*d* (Å)	*I*
9.0	m*	8.4	66*
3.3	w–m*	3.28	100*
2.70	vw	—	—
2.12	vw	—	—
1.95	vw	1.96	89
—	—	1.90	22
—	—	1.89	44
—	—	1.50	22
—	—	1.36	22
—	—	1.19	22

* Broad line

a. George Rowney and Company "viridian," E. W. Forbes Pigment Collection, Center for Conservation and Technical Studies, Harvard University Art Museums (Fogg).

b. *JCPDS Powder Diffraction File* 1-0691. From *JCPDS* (1988).

c. Intensities visually compared: m=Medium, w=Weak, vw=Very weak.

the c-axis and four modes perpendicular to the c-axis (Renneke & Lynch, 1965).

The spectrum of hydrated chromium oxide is similar to that of chromium oxide in the long wavelength end of the mid-infrared region, although the peaks are distinctly shifted to longer wavelengths, reflecting the influence of "water" on the crystal lattice. A characteristic spectrum is shown in figure 11(B). The strongest peaks occur at 555 and 481 cm^{-1}. Sharp, weaker peaks occur at 420 and 402 cm^{-1}. With water incorporated in the structure, this pigment also exhibits bands at shorter wavelengths.

5.2.3 ***Spectrochemical analysis.*** Chromium is the only element present above trace levels in pure pigment samples of chromium oxide and hydrated chromium oxide. The most sensitive arc lines for this element, given in order of increasing sensitivity, occur at 4289.721, 4274.803, and 4754.346 Å. Chromium can be detected above levels of about 0.0001% (Ahrens, 1951), and with large enough samples some trace elements may be

detected (see section 4.1). Hydrated chromium oxide manufactured by Guignet's process will contain boron, which can be detected if samples are large enough. The only two arc lines for boron occur at 2497.733 and 2496.778 Å. This element can be detected above levels of approximately 0.001% (Ahrens, 1951).

5.2.4 ***X-ray spectrometry (x-ray fluorescence).*** X-ray fluorescence techniques, whether in air-path or in electron beam instruments, will normally only detect chromium in samples of these pigments. Boron can also be detected (with difficulty) in hydrated chromium oxide by wavelength-dispersive x-ray fluorescence in electron beam microprobes. The two x-ray peaks for chromium are (with wavelengths given in parentheses): $K\alpha$, 5.411 keV (2.29092 Å); $K\beta_1$, 5.946 keV (2.08480 Å) (Goldstein et al., 1992).

5.3 Criteria for Identification

5.3.1 ***Chromium oxide*** is a very fine-grained pigment (many pigment particles are less than 1 μm) with a high refractive index that cannot be identified microscopically with certainty. Detection of chromium by emission spectrography, x-ray fluorescence, or other methods, coupled with an elimination of other possible sources for the chromium (for example chrome yellows in a mixed green pigment, hydrated chromium oxide, or chromium in one of the other very rare blue or blue-green chromium-containing pigments), would serve as a confirmation of a tentative microscopic identification. If a sufficiently pure sample is available, x-ray powder diffraction is definitive, as is an infrared spectrum. The distinctive absorption pattern of the pigment occurs in the region 700 to 400 cm^{-1} where there are few overlaps from other pigments or media.

5.3.2 ***Hydrated chromium oxide.*** The moderately sized particles of hydrated chromium oxide have a characteristic hue in transmitted light. When this color is coupled with the unusual interference colors and wavy extinction seen between crossed polars, the pigment can be identified with reasonable certainty microscopically. Microscopic examination should always be confirmed by detection of chromium and the elimination of other possible sources for this element, as discussed in section 5.3.1. If elemental analysis is carried out by emission spectrography, boron will probably also be detected if the pigment sample size is large enough. Hydrated chromium oxides have very poor x-ray powder diffraction patterns that are not useful for identification purposes, but their infrared spectra in the low wavenumber region (700–400 cm^{-1}) are quite distinctive.

6.0 Occurrences

Information about occurrences of the chromium oxide greens can be found in section 2.2, as well as in the occurrences lists. Additional reports of the use of these pigments by impressionist painters are included in Bomford et al. (1990), where there are cited numerous uses of viridian from 1869 and one use of opaque chromium oxide in 1872. Figure 12 shows an impressionist painting with extensive use of viridian.

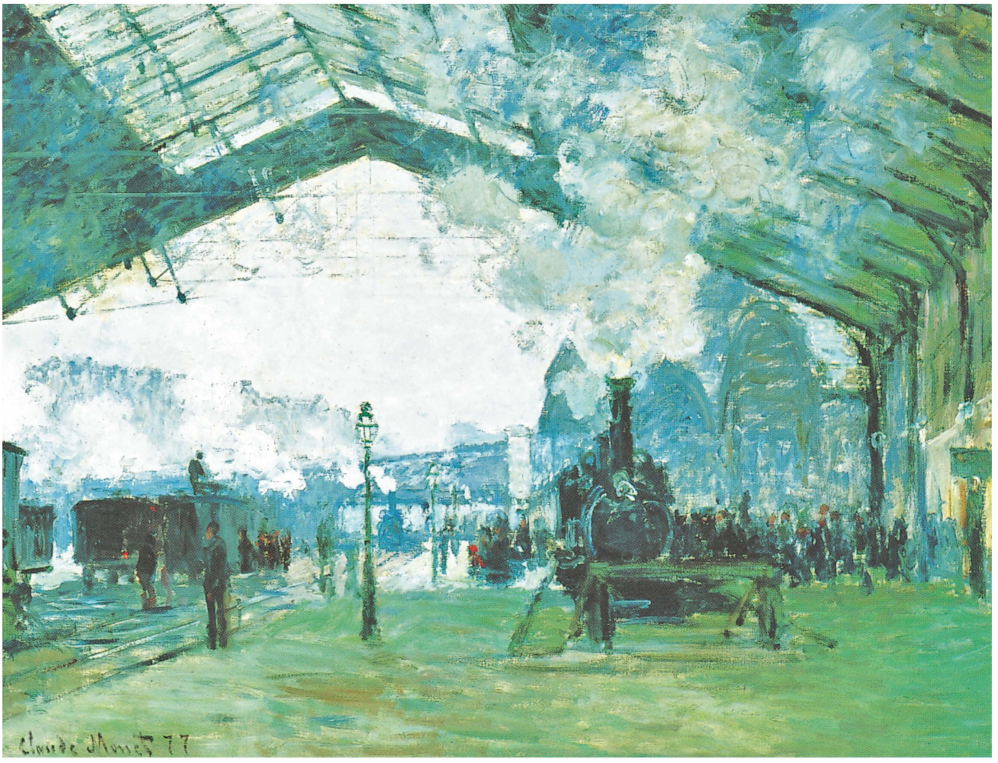


Fig. 12 Claude Monet, *Arrival of the Normandy Train, Gare Saint-Lazare*, 1877, oil on canvas. Mr. and Mrs. Martin A. Ryerson Collection, photograph © 1995, The Art Institute of Chicago. All rights reserved. 1933.1158. Viridian was found in the grassy area.

Occurrences of Chromium(III) Oxide Identified on Paintings in the Schack Galerie, Munich[a]

Date	*Artist and Title*
c.1845	Moritz von Schwind, *Rübezahl*
c.1846	Moritz von Schwind, *Mermaids at a Source in the Forest*
c.1849	Carl Rottmann, *Greek Seacoast with a Threatening Thunderstorm*
1850–1860	Moritz von Schwind, *King Krokus and the Dryad*
c.1855	Moritz von Schwind, *The Legend of the Bishop and the Devil*
c.1860	Arnold Böcklin, *Pan Frightening a Shepherd*
1863	Fritz Bamberger, *Afterglow in the Sierra Nevada*
1863	Albert Emil Kirchner, *View of the Piazetta and the Piazza of St. Mark in Venice*
1870–1871	Arnold Böcklin, *Ideal Landscape*
after 1875	Ludwig Neubert, *View of Olevano*

a. Analyses by Kühn (1969), using microscopy and emission spectroscopy.

Occurrences of Hydrated Chromium Oxide

Date	*Artist, Title, and Location*	*Analyst and Method of Identification*[a]
1863	Fritz Bamberger *Afterglow in the Sierra Nevada*	Kühn (1969)†
1863–1864	Anselm Feuerbach *Bathing Children*	Kühn (1969)†
1864	Anselm Feuerbach *Paolo and Francesca*	Kühn (1969)†
1864	Joseph von Führich *Christianization in the German Primeval Forests*	Kühn (1969)†
1864	Eugen Napoleon Neureuther *From Goethe's "Hermann und Dorothea"*	Kühn (1969)†
1865	Joseph von Führich *The Dead of St. Johann Nepomuk*	Kühn (1969)†
1868–1869	Edouard Manet *The Balcony* Musée de Louvre, Paris	Delbourgo and Rioux (1974) EBM
1869	Claude Monet *Bathers at La Grenouillère* National Gallery, London	Wilson et al. (1981) micr.
1874	Arnold Böcklin *Triton and Nereïde*	Kühn (1969)†
1875–1876	Pierre-Auguste Renior *Alfred Sisley* Art Institute of Chicago	Butler (1973) micr.
1876	Pierre-Auguste Renoir *Lady at the Piano* Art Institute of Chicago	Butler (1973) micr.
1876	Alfred Sisley *The Flood at Port-Marly* Musée de Louvre, Paris	Delbourgo and Rioux (1974) EBM
1877	Claude Monet *Arrival of the Normandy Train, Gare St. Lazare* Art Institute of Chicago 1933.1158 (see fig. 12)	I. Fiedler‡
1877	Claude Monet *Gare St. Lazare* National Gallery, London	Roy (1985) micr., LMA

*Identified on paintings in the Philadelphia Museum of Art, analyses by micr. and EBM
†Identified on paintings in the Schack Galerie, Munich, analyses by micr. and ES
‡Personal communication
a. Methods of analysis:
EBM=Electron beam microprobe
ES=Emission spectroscopy
LMA=Laser microprobe analysis
LSA=Laser emission spectroscopy
micr.=Light microscopy

Occurrences of Hydrated Chromium Oxide Continued

Date	*Artist, Title, and Location*	*Analyst and Method of Identification*[a]
1878	Edouard Manet *The Waitress* National Gallery, London	Bomford and Roy (1983) micr.
1878–1879	Edouard Manet *At the Café* Walters Art Gallery, Baltimore	Gifford (1984–1985) micr.
c.1879	Pierre-Auguste Renoir *The Seine of Asnières* National Gallery, London	Roy (1985) micr., LMA
1879–1882	Paul Cézanne *Landscape at Pontoise*	Butler (1984)*
1879–1883	Paul Cézanne *Bay of L'Estaque*	Butler (1984)*
1880	Paul Cézanne *Flowers in an Olive Jar*	Butler (1984)*
1882	Pierre-Auguste Renoir *Chrysanthemums* Art Institute of Chicago	Butler (1973) micr.
1883	Paul Cézanne *View of the Bay of Marseilles . . .*	Butler (1984)*
1883	Georges Seurat *Bathers* (Study) Art Institute of Chicago	Fiedler (1984) micr.
1883	August Wolf *Lovers in a Venetian Garden*	Kühn (1969)†
1884	Georges Seurat *Sunday on the Island of La Grande Jatte* (oil sketch) Art Institute of Chicago	Fiedler (1984) micr.
1884–1886	Georges Seurat *Sunday on the Island of La Grande Jatte* Art Institute of Chicago	Fiedler (1984) micr.
c.1886	Paul Cézanne *Mountains in Provence* National Gallery, London	Roy (1985) micr.
1886–1887	Paul Cézanne *Portrait of Madame Cézanne*	Butler (1984)*
1888	Vincent van Gogh *A Cornfield, with Cypresses* National Gallery, London	Leighton et al. (1987) micr., LSA
1888	Vincent van Gogh *Self-Portrait Dedicated to Gauguin* Harvard University Art Museums (Fogg)	Farrell and Newman (1984) micr., EBM
1888	Vincent van Gogh *Pear Tree in Blossom* Rijksmuseum Vincent van Gogh	Farrell and Newman (1984) micr.
1888	Vincent van Gogh *Gauguin's Armchair* Rijksmuseum Vincent van Gogh	Farrell and Newman (1984) micr.

Occurrences of Hydrated Chromium Oxide Continued

Date	*Artist, Title, and Location*	*Analyst and Method of Identification*[a]
1889	Vincent van Gogh *The One-Eyed Man* Rijksmuseum Vincent van Gogh	Farrell and Newman (1984) micr.
1898–1900	Paul Cézanne *Millstone in the Park . . .*	Butler (1984)*
1902–1904	Paul Cézanne *Mont Sainte-Victoire*	Butler (1984)*
1902–1906	Paul Cézanne *Mont Sainte-Victoire*	Butler (1984)*
1906	Paul Cézanne *The Large Bathers*	Butler (1984)*
1919	Pierre-Auguste Renoir *Seated Nude* Art Institute of Chicago	Butler (1973) micr.
1919	Pierre-Auguste Renoir *Flowers* Art Institute of Chicago	Butler (1973) micr.

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10
Titanium Dioxide Whites

MARILYN LAVER

1.0 Introduction

Titanium dioxide white pigments are products of twentieth-century industrial development. Because of their high hiding power, nontoxic nature, and reasonable cost, they have eclipsed other traditional white pigments in use worldwide.

Anatase (octahedrite), rutile, and brookite are the naturally occurring crystal forms of titanium dioxide (TiO_2). Brookite is a rare mineral that is not used for pigment manufacture. The anatase and rutile forms are synthesized as pigments; the history of their development for this purpose is marked by changes in formulation and manufacture designed to improve their properties in paints and other products. These changes can be employed to establish the chronology of their use.

Titanium dioxide whites can be found in a variety of artists' materials that include inks, pastels, and paints in media such as oil, lacquer, acrylic, and watercolor. Titanium dioxides have also been used in contemporary art objects as fillers and coatings for photographic, book, and fine papers, as colorants and opacifiers in ceramic glazes and glass, as delustrants in synthetic textile fibers, and as colorants in waxes, rubber, and plastic materials.

1.1 Pigment Definition

Titanium dioxide white pigments are synthetic products manufactured either as pure titanium dioxide or as a composite that typically consists of a base of barium or calcium sulfate onto which a coating of titanium dioxide has been precipitated. The pigments may be treated with thin inorganic or organic coatings to improve various properties (see section 2.2.3). The naturally occurring mineral rutile has also been used as a pigment although it is less satisfactory than the synthetic products in color and other properties (see section 2.2); the naturally occurring mineral anatase (octahedrite) is rare and there is no evidence it was ever used as a pigment.

1.2 Current Terminology

Pigment	*Variety*
English: titanium dioxide	anatase, rutile
French: oxyde de titane	anatase, rutile
German: Titandioxid	Anatas, Rutil
Italian: bianco di titanio	anatasio, rutilo
Spanish: dióxido de titanio	anatasa, rutilo
Russian: двуокись титана	анатаз, рутйл
Norwegian: titandioksid	anatas, rutil

The term titanium dioxide is preferred for both the anatase and rutile forms of the pigment and is an exact description of their composition, TiO_2. Titania is an accepted alternative but is used less frequently. Titanium dioxide white pigment is the term used here to include not only the two pure forms of the pigment but also early composites. This range of pigments is referred to in the *Colour Index* (1971) as CI Pigment White 6, no. 77891. The terms anatase and rutile are currently used to describe pigmentary materials as well as the natural minerals.

2.0 History

2.1 Archaic and Historical Names

Titanium white can refer to any white pigment containing a compound of titanium, such as barium titanate, zinc titanate, potassium titanate, titanium lithopone, titanium phthalate, or titanium silicate.

The name permanent white has been applied

to many pigments, including titanium dioxide whites. Winsor and Newton used permanent white as a synonym for titanium dioxide oil colors; however, they also used permanent white for their zinc white oil color. Gettens and Stout (1966) used the name permanent white for barium sulfate white. *Permanentwit* sold by Koninklijke Talens is a mixture of titanium dioxide and zinc white. Such descriptive but imprecise names can cause confusion and many are still in use today (see section 2.3.1). Occasionally, brand names such as Titanox have been used as generic names for composite and pure varieties of the pigment (see Gettens & Stout, 1966).

2.2 History of Development

Titanium dioxide white pigments are the products of twentieth-century technology. Although titanium is the ninth most abundant element in the earth's crust and there are more than sixty naturally occurring mineral species containing titanium (Giese et al., 1964), the element's existence was unsuspected until the end of the eighteenth century. Initial development of the synthetic white oxides took place slowly as they require careful purification and exact preparation to be satisfactory white pigments.

As noted in section 1.1, mineral anatase is not used in artists' materials. The mineral rutile, on the other hand, may have been used as a pigment; therefore, the presence of the rutile form of titanium dioxide in works of art or archaeological objects may not be restricted to the period of industrial manufacture. Colors made with ground mineral rutile are never the brilliant white or off-white of the synthetic titanium dioxides; because elements such as iron are present, their colors range from yellow through red-brown to almost black. The ground mineral form is less pure and the pigment particles are coarser and of different morphology than the modern precipitated pigments. References to ground titaniferous minerals, including the titanium dioxides, used as colored paint pigments can be found in patent literature of the nineteenth century. The industrial applications of paints using mineral rutile were limited, however, because it was difficult to grind.

The element titanium was independently discovered by William Gregor in 1791 and by M. H. Klaproth in 1795. Heinrich Rose was the first to study the intermediate product, hydrous titanic oxide (titanic acid) in 1821 (Woringer, 1916). The oxide was prepared for many years in laboratories in the course of analyzing for titanium, but its possibilities as a white pigment were not realized until the twentieth century. The milky precipitate of hydrous titanic oxide was an amorphous material that was not a reliable pigment unless it was calcined. The early preparations were yellow and when reduced in the presence of charcoal they became lavender blue; the use of this compound as a blue porcelain glaze was described in 1841 (see review by Lambrecht, 1939). Titanium compounds other than the dioxide were also proposed as pigments; a dark green titanium pigment made with potassium ferrocyanide by Elsner-Lampadius in 1832 was suggested as a substitute for the toxic emerald green, and Barnes (1899) described watercolor paintings containing red or yellow titanium tannate. In the late nineteenth century a synthetic titanium oxide product was used as an opacifier and to increase acid resistance in glazes and enamels (Leuchs & Leuchs, 1893; Wupperman, 1900; Woringer, 1916; Déribéré, 1936) and other titanium compounds including "artificial rutile" were being separated and prepared from various ores (Homan, 1901). A pigment based mainly on alumina and silica containing about 18% titanium dioxide and a high level of iron was made from a bauxite processing residue (Teisset, 1906). However, none of these early products had the appropriate combination of properties to be used as white pigments of any commercial or artistic significance.

2.2.1 *Development of the sulfate process.*

Research and development of white titanium dioxide pigment occurred simultaneously in Norway and the United States as large deposits of titaniferous ores in these countries were investigated as a potential source of iron.

In 1908 a Norwegian government commission was formed to seek uses for deposits of ilmenite ($FeTiO_3$). Reddish yellow pigments were developed based on crushed and roasted ilmenite in about 1909 (Farup, 1909, 1910b). About 1910 a method was devised to produce a purer, lighter-colored pigment by digestion of ilmenite with sulfuric acid and removal of iron, foreshadowing the modern sulfate process (Farup, 1910a; Jebsen, 1910). In 1913 a method was patented that yielded over 80% titanium dioxide using sulfation and calcination (Farup, 1916a) and in 1914 trials for producing white pigment on an industrial scale began (Heaton, 1922). The development of composite pigments formed by precipitating the titanium dioxide onto barium sulfate was

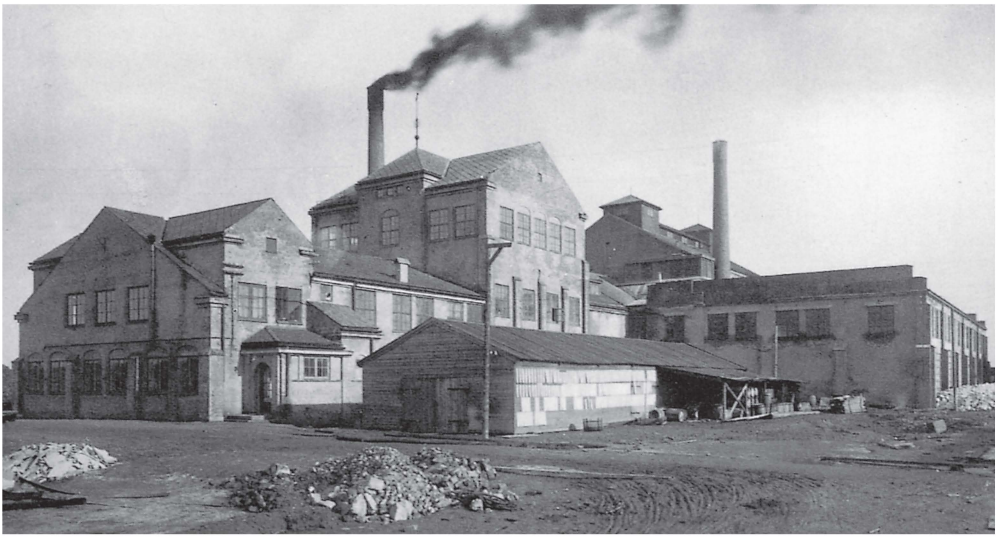


Fig. 1 The original titanium dioxide pigment plant in Fredrikstad, Norway, c. 1920. Photo from Kronos Titan A/S, Fredrikstad.

particularly successful. In 1916 the Titan Company A/S was founded, and construction of the factory at Fredrikstad, Norway (fig. 1) was completed by the summer of 1918. Regular production began in November 1918 (de Rohden, 1967). The initial Norwegian *Kronos Titanvitt* pigments were composites, with titanium dioxide precipitated onto barium sulfate; they "had the color of old India ivory" (Firing, 1935). Composite pigments were available commercially in Norway (fig. 2A) and elsewhere in Europe earlier than in America (*Oil, Paint*, 1920; Coffignier, 1922).

In the United States independent development also resulted in useful products from titanium-rich ores. The Titanium Alloy Manufacturing Company was incorporated in 1906 in Niagara Falls, New York, after Auguste Jacques Rossi succeeded in smelting the titaniferous ores to produce titanium alloys in an electric furnace. The possible development of a pigment was first realized in 1908 (Hallett, 1930; Rabaté, 1956). Patent applications for the manufacturing process were filed in 1912 (Rossi, 1911, 1912; Rossi & Barton, 1912a–c, 1913). By 1915 experiments with the pure pigments had not led to a commercially viable manufacturing process; pure pigments (over 99.5% anatase or rutile) were produced only in very small batches of a few pounds (W. Allsopp, personal communication, 1988). In 1914 a small test batch of composite pigment with calcium sulfate (Barton, 1914) was described as being "of a pronounced cream color" (Gardner, 1924), and the remarkable hiding power of this new pigment generated considerable interest. The Titanium Pigment Company, a subsidiary, was organized in 1916. Production of a composite pigment began in 1916 and by 1919 full-scale commercial production was underway. Until 1925 the sole product was 25% titanium dioxide on a barium sulfate base. Silicate composites (Ti-Sil, Ray-Sil) later had limited use mainly in the United States as exterior paint pigments (Bancelin & Crimail, 1939; Déribéré, 1943; Barksdale, 1949). A composite pigment using precipitated calcium carbonate was tried experimentally at an early date, but although technically feasible, it was not produced commercially because it was too expensive to manufacture (W. Allsopp, personal communication, 1988).

In 1920 the Titanium Pigment Company and the Norwegian Titan Company A.S.(1919) agreed to cross-license existing American and Norwegian patents and exchange technical information; the American company adopted the superior Norwegian sulfuric acid hydrolyzation method. These companies eventually formed the core of a large group controlled by the National Lead Company.

Development of anatase pigment production. The earliest commercially successful titanium dioxide white pigments were composites (see section 2.2). In the laboratory, anatase could be prepared by

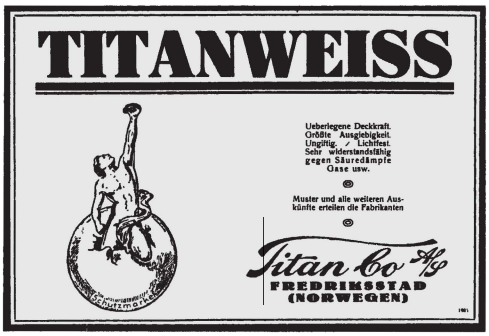
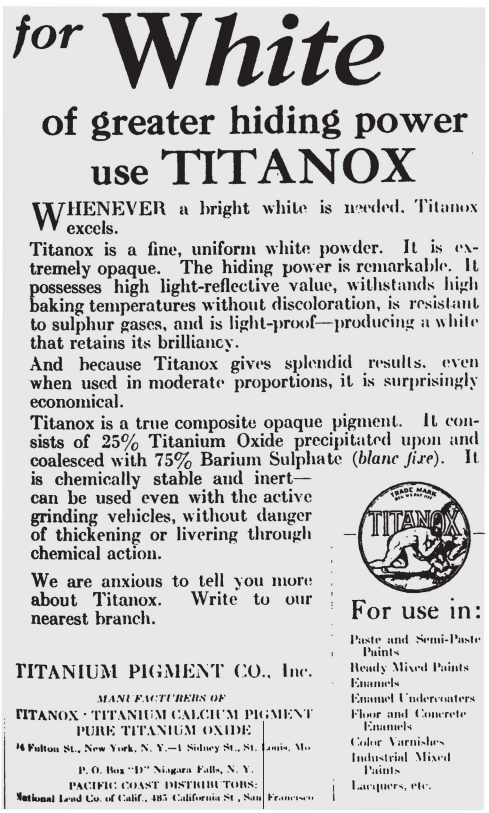


Fig. 2 Early advertisements for titanium dioxide pigments from Europe and North America.

A. From *Farben-Zeitung* 14 (2 January 1926), 819.



B. From *American Paint Journal* 21 (February 1927), 85.

calcination of synthesized titanic acid (the hydrous titanic oxide), a reasonably pure amorphous compound that was not in itself suitable as a paint pigment due to its poor technical properties (Heaton, 1922). However, calcination to raise the refractive index proved difficult and expensive on a production scale and resulted in anatase products that contained up to 20% coarse, gritty rutile. Composite pigments were somewhat easier to manufacture, and it was thought at the time that they had optical properties superior to pure anatase. The key process change, resulting in a commercially viable pure pigment, was developed about 1920 by the French firm Société de Produits Chimiques des Terres Rares, under the supervision of Joseph Blumenfeld. Initial patents covering the basic elements of the Blumenfeld process were applied for in 1922 (Weizmann & Blumenfeld, 1922a, b) and a few dozen kilograms of pure pigment were made (see section 4.3.1 for description of the process). The preparation method was based on the use of sulfuric acid, and the Société formed a partnership in 1922 with Fabriques de Produits Chimiques de Thann et de Mulhouse, a sulfuric acid producer, and granted them a license for the Blumenfeld process. Refinements to the method continued, and in 1923 production of a 96% to 99% titanium dioxide pigment began in France at Thann (Binder, 1924); it was marketed in pure form as well as in a mechanical mixture with blanc fixe (barium sulfate). Problems with pigment purity appear to have persisted; in 1927, the anatase produced at Thann was described as slightly yellow (Wait & Weber, 1934), probably due in part to a rutile component.

During the 1920s many plants were established worldwide; the types of pigments introduced during this decade are given in table 1. A plant using the Blumenfeld process was established in Czechoslovakia in 1923 and one in Italy began production in 1927. In August 1926 the Niagara Falls, New York, plant of the Titanium Pigment Company introduced the first pure anatase pigment produced in the United States (Hagar, 1927) (fig. 2B); their process was not licensed. In 1928 the Commercial Pigments Corporation, Baltimore, started production using the Blumenfeld process (Hixson & Plechner, 1929). National Titanium Pigments Limited operated a pilot plant in Barking, England, from 1927 to 1933; thereafter plants were opened in Luton under the name Laporte Industries (Klein & Rechmann, 1967).

In 1927 the National Lead Company in the United States bought control of the original Titan Company A/S, Fredrikstad, and also formed Titangesellschaft mbH as a joint venture with IG Farbenindustrie, Germany, and took over production from the Fredrikstad factory, which closed in 1928. Pure anatase pigments were made at

Table 1 **Typical Titanium Dioxide Pigment Compositions of the 1920s**

Product Name	*Approximate Composition*	*Comments*
Kronos Prima X	83% TiO_2	Fredrikstad, 1918–1919
Kronos Extra X	65%–69% TiO_2/25% $CaPO_4$/ 10% $BaSO_4$ (composite)	Fredrikstad, replaced Prima grade in 1919 (de Rohden, 1967)
Kronos Standard X	25%–30% TiO_2/5% $CaPO_4$/ 70% $BaSO_4$ (composite)	Fredrikstad
Kronos Special	15% TiO_2 (composite)	Fredrikstad (Coffignier, 1922; Robinson, 1922)
Kronos Standard A	25%–30% ZnO + 70% Standard X	Blended in Europe ("Titanium Oxide," 1933)
Kronos Extra A	30% ZnO + 70% Extra X	Blended in Europe
Kronos Standard T	25% TiO_2/75% $BaSO_4$ (composite)	After 1927
Kronos Extra T	50% TiO_2/50% $BaSO_4$ (composite)	After 1927
Blanc de Thann Or EB	98%–99% pure	Thann, from 1923 (extra white)
Blanc de Thann Or P	98% TiO_2	Thann, from 1923 (Heise, 1936)
Blanc de Thann *(Cachet argent, blanc, ou vert*)*	Mixtures with $BaSO_4$, ZnO	To meet market requirements
Titanox A	98% TiO_2	Niagara Falls, after 1926 (Hagar, 1941)
Titanox BX	16% TiO_2/84% $BaSO_4$ (composite)	Niagara Falls, soon discontinued
Titanox BXX	25% TiO_2/75% $BaSO_4$ (composite)	Niagara Falls, renamed Titanox B
Titanox C	28%–35% TiO_2/ 72%–65% $CaSO_4$ (composite)	Niagara Falls, after 1925
Other products	Titanated lithopones barytes and gypsum (about 15% TiO_2)	Available by 1926 (Stieg, 1985)

*Silver, white, or green seal

Leverkusen that same year (K. Meckenstock & R. Amberg, personal communication, 1986). By 1930 most companies were controlled either by the National Lead Company (whose process was not licensed for use outside the group), or by the Société de Produits Chimiques des Terres Rares, which had control of the licensing rights to the Blumenfeld process.

National Lead established many operations, including production for the British Empire, which began in 1934 in Billingham, England (British Titan Products). In Japan, production had been initiated by Sakai Kagaku Kogyo Company in January 1935, and three plants were operating by 1938 (K. Yamasaki, personal communication, 1985); in 1936 production began at Titan Kogyo Kabushi Kaisha. The massive ore deposits in the Ural Mountains had not been utilized (Dominion Bureau of Statistics, 1934) until Russia began producing anatase in the 1930s (Pamfilov et al.,

1939). About 1932, the Leningrad Institute had developed processing methods using sphene (chiefly $CaTiSiO_5$), a readily available ore ("Farbstoffe. Farben.," 1932). An experimental plant operated at Jaroslav, first using the seeded hydrolysis method of Mecklenburg (1928) and after several years the Blumenfeld method. In 1936, Glawkraska, a Russian concern involved in mineral pigments and lacquers was constructing a large factory to produce titanium dioxide white pigments in Chelyabinsk ("L'historique . . .," 1947). By 1948, a plant was under construction in India to make use of indigenous beach sand reserves of ilmenite (Johnstone, 1948). Although production of anatase near Melbourne began in 1933, Australia was relatively slow in developing its large ore reserves. In 1952 several hundred tons of high-grade titanium dioxide were produced annually in Tasmania, but most of Australia's pigment was imported (Bennett, 1952). Canada imported all its pigment until the first manufacturing facility was built in 1957.

The titanium dioxide pigment industry expanded dramatically from 1916 to 1946 to supplant the traditional white pigments, lead white, zinc oxide, leaded zinc oxide, and lithopone ("Titanium Pigments," 1948). Barksdale (1966) and Klein and Rechmann (1967) have outlined the complex growth of companies producing titanium pigments.

Development of rutile pigment production. A major development for the industry was the production on a commercial scale of rutile pigments, which were known to possess better hiding power and weathering characteristics than anatase. Anatase will convert to rutile if overcalcined, resulting in a coarse, sintered material not satisfactory as a pigment. Experimental pigments were patented and produced on a laboratory scale in 1931 in Czechoslovakia, Germany, and the United States (de Rohden, 1967). These small samples sparked a great deal of research, but it was not until 1937 that the two basic processes were refined to allow successful rutile production on an industrial scale (Tillman, 1937; Verein, 1937; Titan Co., 1938). In the first method, titanium dioxide was precipitated using seed crystals introduced during hydrolysis that allowed direct calcination to rutile. Pigment produced by this method was introduced commercially in 1938/1939 in Germany. Late in 1938, fine-particle rutile pigment also made by this method was undergoing testing in England (Tinsley & Bowman, 1949). Manufacture in both countries was interrupted by World War II. The second preparation method involved adding an agent that would control the conversion of anatase to rutile immediately prior to or during calcination. These agents included compounds of zinc, tin, magnesium, silicon, and lithium. In Great Britain, a grayish pigment (designated A.10) containing 10% antimony oxide was being tested in 1939 (Tinsley, 1943). A.10 had a larger particle size than pure anatase pigments (approximately 0.7 to 1.0 μm), as did a yellowish American rutile product, Titanox A-NC, which was also introduced in 1939. Titanox A-NC was manufactured until 1945 mainly to supply the United States Navy with a durable pigment (Stieg, 1985).

In the United States in 1940 National Lead produced commercial quantities of two new 30% rutile and calcium sulfate composites that used up to 1% zinc oxide to promote rutile formation during calcination. The first product, Titanox RC-HT, was an interior formulation with high hiding power, while the second, Titanox RC (January 1941), was more chalk resistant for exterior use (Anderson, 1941). The main difference between the two pigments was their particle size. In 1942, a pure fine-particle rutile that had a distinct yellow tone was produced (Tinsley, 1943; Kampfer, 1973). The range of products available in the United States in the 1940s containing titanium dioxide is given in table 2. During the early 1940s, anatase was blended with some of the rutile pigments to provide less expensive grades (W. Allsopp, personal communication, 1988). Up to 1947, American producers were the only manufacturers with a commercially viable product (Hibberd, 1947). It was not until after 1945 that rutile pigment became available in Europe (Coupry et al., 1987). In England it was first produced in 1948 (Taylor, 1955) and production in Germany resumed in 1952 (De Keijzer & Mosk, 1985). In 1952 a 50% rutile pigment precipitated on a calcium sulfate base was introduced in the United States (Stieg, 1960).

2.2.2 ***Development of the chloride process.*** The introduction of the chloride process for the manufacture of rutile pigment was a major change in production methods of titanium dioxide pigments. Preparation of pigment from titanium tetrachloride had been under investigation since the 1920s (Carteret & Devaux, 1921); in the late 1940s, manufacturers with access to large quantities of chlorine began to develop the

Table 2 **Typical Pigments Available in the United States in the 1940s. Products of the Titanium Pigments Corporation Are Given As Representative of the Range Available**[a]

Product Type	*Product Name*	*Description*
Anatase pigments (untreated except for milling)	Titanox A (regular)	Low and medium oil absorption
	Titanox A-WD and WDL	Water dispersible, contain small amount of alkaline phosphate
	Titanox A ceramic	Not a pigment grade
Anatase pigments (inorganic treatment, no organics)	Titanox A 168	1% Al_2O_3 coating (low and medium oil absorption)
	Titanox AA	Calcined with 1% Sb_2O_3; 1% Al_2O_3 coating
	Titanox A no. 24	About 1% Sb_2O_3, 1% Al_2O_3, and 0.05% Cr_2O_3
Composite pigments	Titanox C	30% anatase/$CaSO_4$
	Titanox B	25% anatase/$BaSO_4$
	Titanox B-30	30% anatase/$BaSO_4$
Rutile pigments	Titanox A-NC	Recalcined with 1% ZnO, coated with 1%–2% Al_2O_3 and SiO_2 (this was a 1939 pure rutile grade with larger aggregate size than anatase grades)
	Titanox RC-HT	30% rutile/$CaSO_4$ composite introduced in late 1940
	Titanox RC	30% rutile/$CaSO_4$ introduced January 1941
Adulterations	Titanox M	30% TiO_2 with magnesium silicate
	Titanated lithopones	15% TiO_2, 25% ZnS, 60% $BaSO_4$

a. Data from Robertson and Lutz (1940); Anderson (1941); Hagar (1941); Remington (1946); Weider (1952); Barksdale (1966); Stieg (1985).

process (Haber & Kubelka, 1931), succeeding on a pilot plant scale by 1948. However, even by 1952, the pilot plant pigments produced by E. I. du Pont de Nemours and Co., Delaware, were of poor quality, inferior to sulfate process pigments (Steig, 1985; Blakey & Hall, 1988). By 1957 high-quality chloride process pigments (Ti-Pure) were available in the United States in significant quantities. By the time of the 1959 opening in the United States of the first plant totally devoted to the chloride process by E. I. du Pont de Nemours and Co., Tennessee, these pigments had significantly higher purity, and smaller, more uniform particle size than pigments produced at that time by the conventional sulfate route. Within two years, the sulfate manufacturers had improved their processes to match the pigmentary properties. Chloride process pigments were first introduced in Europe in 1965 by British Titan Products (Whitehead, 1983), followed in 1967 by Titangesellschaft mbH, Germany. A chloride process anatase was briefly offered by E. I. du Pont de Nemours and Co. from 1975 to 1985; this pigment contained some rutile and its main commercial success was in the paper industry (W. McGinnis, 1976, and personal communication, 1988).

Currently, rutile pigment production worldwide

is three times that of anatase. In 1985, about one-third of the world's titanium dioxide pigment was manufactured by the chloride process and two-thirds by the sulfate process; all anatase is made by the latter method. Of the many patented methods, only the chloride and sulfate processes were commercially viable.

2.2.3 ***Additives and surface treatments.*** A significant area of industrial research was the development of additives and surface treatments for titanium dioxide pigments. Problems with the early anatase paints included yellowness, chalking on exterior exposure, and poor drying characteristics. As early as 1916, the addition of zinc oxide or lead white as a mechanical mixture to improve these properties was suggested (TAMCO, 1916). The benefits of adding calcium phosphate during processing were explored by Titan Co. A/S (1919); this soon became a commercially significant additive to reduce rutilization during calcination (de Rohden, 1967). Antimony oxide was used soon after its introduction in 1920 to aid in drying and was used in the 1930s to allow controlled formation of the rutile phase during calcination.

Surface treatments for anatase and rutile pigments, which are physically distinct from additives, are coatings that can change pigment properties for specific applications. Farup (1916b) patented a pigment coated with 2.5% aluminum hydroxide to improve chalk resistance. In the 1920s and 1930s many patents were issued for coatings including oxides and hydroxides, titanyl phthalates, insoluble fluorides, basic aluminum salts, silica, and antimony oxide (Barksdale, 1966). In the 1930s some of these coated pigments became commercially available. Surface-treated products were made in Baltimore in 1931 where sodium silicate was used as a dispersing agent absorbed on the pigment surface, followed by magnesium sulfate as a coagulant to form an insoluble silicate coating (Barnett, 1949; de Rohden, 1967). In Germany in 1935, Titangesellschaft mbH, Leverkusen, introduced their first surface-treated pigment, containing aluminum compounds. Titanium dioxides that were surface treated with inorganic coatings, including alumina, silica, and antimony hydrates, were marketed from 1935 to 1940 (Stieg, 1985). By about 1942 aluminum silicate coatings were patented. In modern pigment grades where the titanium dioxide content is as low as 75% to 80%, the remainder is made up of coatings. Secondary treatment with organic compounds was also used to alter surface properties (see section 4.4).

2.3 History of Use

2.3.1 ***Use in paint.*** Titanium dioxide white pigments were not used by the paint industry immediately following their development; this was partly due to their high price (despite their much superior hiding power). The industry was also influenced by the pigments' somewhat unreliable color, limited supplies in most countries, and a reluctance to change from traditional materials.

Before 1916, when pigments were being produced in small experimental batches, there was a limited amount of field testing by artists; in the United States, Auguste Jacques Rossi was said to have given a sample of anatase to an artist friend in New York state (W. Allsopp, personal communication, 1990). Use by artists at this time was rare and limited to those connected in some way with the researchers (Brachert, 1988). When composite titanium dioxide became available commercially, some limited application in industrial cellulose nitrate lacquers occurred as early as 1917 ("Development . . .," 1981). Once larger quantities became available after World War I, it was incorporated into ready-made paints and the paste paints popular at the time and was found to be suitable for spray painting, which requires a thinner paint consistency (Hellbusch, 1921). In Europe the first paint formulation using titanium dioxide was registered in 1919 by the Alf Bjerke Company, Norway (S. Halsør, personal communication, 1986); thus artists who used house paints might have been using composite titanium dioxide pigments as early as 1919. The paint industry remained skeptical into the 1920s of the claims made for titanium whites, and the general public was largely unaware of the new pigment (Heaton, 1922). F. Weber and Company, Philadelphia, introduced a composite called Permalba in 1920 (Mayer, 1969). The titanium dioxide and barium sulfate composite pigments were introduced in Britain in 1921 (Heaton, 1947). In France in 1922 the only titanium dioxide whites available on a commercial scale were imported from Norway (Coffignier, 1922).

In most countries progress was made in the early twentieth century in introducing a nontoxic alternative to lead white and by the early 1920s stringent laws restricting the use of lead white had been adopted in France, Austria, and Greece (Robinson, 1922). Artists' concern over the use of lead white is exemplified by the comments of an

Table 3 **Dates of Introduction of Titanium Dioxide White by Some Artists' Color Makers**

Year of Introduction	*Color Maker and Location*	*Comments*
1925	Société Bourgeois, France	Pure anatase; B. des Roseaux, 1991*
1927	Société Lefranc France	Pure anatase; B. des Roseaux, 1991*
1928–1934	Winsor and Newton, England	Titanium White Artists' Oil Colour, Designers Opaque Watercolour Permanent White; P. Staples, 1984*
Early 1930s	H. Schminke and Company Germany	P. Hesse and H. Müller 1984*
1937–1938	Koninklijke Talens BV Netherlands	Oil colors; J. Smeur 1984*
c.1938	Sadolin and Holmblad A/S Denmark	Oil colors; M. Christensen 1986*
After 1938	George Rowney and Co., England	A. French, 1984*
After 1938	Danacolors, Inc. United States	C. Dana, 1984*

*Personal communication

artist in England who expressed hope that titanium dioxide white would be an improvement over zinc white, which was being used as a replacement for the toxic lead white (Heaton, 1922).

Artists' color makers were slow to incorporate the new pigment in their production (table 3). In Norway, for example, where it was available very early, there was no demand for it as an artists' oil color; the Alf Bjerke Company, having introduced it in 1919, never added it to their line of artists' paints (S. Halsør, personal communication, 1986). Société Lefranc showed Moreau-Vauthier (1923) a new white oil-based artists' color (probably based on titanium dioxide) that was resistant to reaction with sulfur, which Lefranc planned to sell in France. Artists' manuals reflect gradual acceptance of titanium dioxide whites through the 1930s. Armfield (1930) mentions a "titanium white (potter's colour)" as having great covering power; however, it lacked the luster of lead white, giving a dead surface. Doerner (1934) suggested that the new pigment was useful for watercolor, tempera, and fresco secco, but qualified his remarks with criticism of its performance that included yellowing in oil (which, he noted, could be cured by adding zinc white), graying observed in a poster color, and fading of admixed coal-tar colors. Hiler (1935) described the new white (Permalba and Toxitan, among other names) as a potentially useful addition to the palette; he later (1942) recommended it as an inert, permanent white that had overcome its early disadvantages in oil.

The "titanium white" paints sold by artists' color makers vary considerably in composition. Due to their greater whiteness the early products based on anatase composites and mixtures were retained for many years after rutile pigments were introduced. More recently, however, rutile pigments have supplanted anatase in many product lines. Over the years, color makers subject to fluctuating supplies have purchased pigment from different manufacturers. Various grades of titanium dioxide, with or without surface treatments, are used to suit a variety of applications and vehicles. In oil media, the titanium dioxide pigment is usually diluted with barium sulfate, zinc oxide, or lithopone to improve its properties. All whites in acrylic emulsion media are based on titanium dioxide since lead white and zinc white are not stable in this medium (Gottsegen, 1987). Hebblewhite (1986) gave a list of artists' pigments containing titanium dioxide, which includes products called Chinese White, Flake White, Iridescent White, Isolating White, Permalba White, Permanent White, Super Hiding White, Superba White, Supra White, Texture White, Underpainting White, Utrecht White, and Zinc White, in various media including egg tempera, watercolor gums,

gouache, "poster," oil, acrylic, and alkyd. Due to its brilliant whiteness it is also an ideal choice for commercial ground preparations and for use in prepared canvases, generally mixed with zinc white or calcium carbonate, in diverse media (Fischer, 1930; Mayer, 1975).

In 1971 pigments used for artists' colors in the United States included zinc white at 400,000 lb./yr., anatase and rutile combined at 312,000 lb./yr., and lead white at 130,000 lb./yr. (Levison, 1973). The white pigments accounted for nearly half the total weight of all pigments used. Titanium dioxide used for artists' colors was approximately 0.02% of the total amount of that pigment used for all purposes in the United States.

2.3.2 ***Use in pastels.*** Anatase and rutile titanium dioxide pigments are currently used in pastels, particularly in the white, gray, and dilute colors (Schwartz et al., 1984). Ground mineral ilmenite ($FeTiO_3$), which is black, is also used as a dark colorant; ground mineral rutile is unlikely to be found as a pastel pigment since the ore is more difficult to grind than other pigments of the same color. Becher (1935) described titanium dioxide white used in school pastels. Two of nine European manufacturers surveyed used titanium dioxide white in their line of fine art pastels in 1940 (Bontinck, 1944). It was noted that these pastels, based on anatase, caused Prussian blue and alizarin to fade due to the photoactivity of the titanium dioxide (see section 3.4.2). Compared to lead white, titanium dioxide's handling properties in these early pastels were good, except for poor adherence to the paper when applied in thick layers.

2.3.3 ***Use in inks.*** As early as 1922 the new titanium dioxide pigments were described as ideal whites for use in illuminated manuscripts and for printing inks, where a thin layer with high hiding power was required (Heaton, 1922). They were used in inks as a colorant and opacifier during the 1920s (Kingsbury, 1934). Their resistance to discoloration when heated also made them suitable for decorating inks baked on metal. In modern inks, choice of the grade of titanium dioxide may depend on its optical properties, dispersibility in printing media, and abrasiveness (Dowling & Corless, 1969; Dowling, 1972). In gravure printing, for example, use of the less abrasive anatase pigment requires higher loading to achieve the same opacity as rutile pigment, which can result in greater cylinder wear, as well as decreased gloss. Among the grades of rutile available, sulfate-process pigments are preferred over chloride-process pigments because they are less abrasive (Blakey & Hall, 1988).

2.3.4 ***Use in paper.*** Titanium dioxide pigments are used as opacifiers, fillers, or coatings in many types of paper. Both anatase and rutile types have been used for various applications (Kampfer, 1973; McGinnis, 1984). There are early references to the use of titanium dioxide pigments in wallpaper, among other products (Thornton, 1927; Titanweiss, 1928; Hubert, 1931; Weber & Woodhall, 1935). Between 1931 and 1936 the composite and pure pigments were tried in most types of paper (Déribéré, 1934b; Kingsbury, 1934; Ravner, 1934; Willets, 1936a; Delhaye et al., 1984).

The incorporation of titanium dioxide into photographic paper to replace the traditional barium sulfate was described as early as 1934 (Déribéré, 1934a). From 1942 to 1954, Eastman Kodak produced an acetyl cellulose base material for color prints that incorporated titanium dioxide (Kolf, 1980). Paper bases for black and white photography used by professionals generally do not contain titanium dioxide; it is used more in paper for amateur photography and high-volume automatic printing. In the early 1960s, resin-coated (RC) black and white photographic paper was developed; rutile was used in some early products introduced by Eastman Kodak in the United States in 1961 (R. Ward, personal communication, 1987). The first resin-coated papers for color incorporating titanium dioxide were introduced by Eastman Kodak in 1967 in the United States, and in 1970 in Europe (Kolf, 1980; Heidke et al., 1985). These Kodak papers were initially made with rutile and later, beginning in 1984, with anatase (R. Ward, personal communication, 1987).

2.3.5 ***Use in enamels, ceramics, and glass.*** The earliest uses of synthetic titanium dioxide in the 1800s included the production of pottery glazes and vitreous enamels. Titanium dioxide can either be present as a chemical in solution or can retain its pigmentary properties as a chemically distinct compound. In the former case it is possible to use a material with poor pigmentary properties, such as ground mineral rutile (Barnes, 1896; Woringer, 1916; Youngman, 1930). Titanium dioxide is the most widely used pigment for white "glass colors" and in opal art glasses (Burgyan & Lowery, 1973).

2.3.6 ***Use with textiles and leather.*** In the late nineteenth century, the textile and leather industries exhibited considerable interest in titanium compounds of all kinds for use as mordants, colorants, and weighting and stripping agents (Barnes, 1896; Spence, 1904; Washburn & McGougan, 1921; Robinson, 1922; Wait & Weber, 1934). Binder (1923) described experiments using titanium dioxide in albumin, viscose, and acetyl cellulose media for printing on damask and cotton. By 1934, paints, dry pigments, and coatings such as shoe polishes and dressings containing titanium dioxide were widely applied to leather goods in the United States (Kingsbury, 1934). Titanium dioxide is often used to reduce the shiny luster of synthetic textiles; anatase rather than rutile is typically used as it is less abrasive to the processing equipment. About 1929, delustering methods were being developed for man-made fibers such as cellulose acetate and rayon (Déribéré, 1936); cuprammonium silk (rayon) delustered with titanium dioxide was introduced at the beginning of the 1930s, following collaboration between IG-Farbenindustrie and Titangesellschaft (*Kronos Guide*, 1968). By 1934 anatase was also replacing tin oxide in the silk-printing industry, as it did not yellow on aging (Kingsbury, 1934).

2.3.7 ***Use in rubber and plastics.*** Titanium dioxide as a replacement for zinc oxide in rubber products was an early success (Washburn & McGougan, 1921). In 1917 a patent was issued for its use in linoleum (Heise, 1936), and it was introduced as a filler and colorant in plastic items such as imitation marble, pearls, horn, ivory, and shell ("L'utilisation . . .," 1930; Strauss, 1937). It was also an additive to plastic materials such as celluloid, cellulose acetate, viscose, urea-based and artificial resins. Because of its high opacity, titanium dioxide was used as early as 1934 in plastic products based on casein hardened with formol (Déribéré, 1934b) and in materials made with hardened gelatin and albumin.

2.4 Dates of Use

Titanium dioxide pigment in a near-white crystalline form was first developed in 1908. Relatively pure anatase and rutile were produced by 1915 on a small scale, but they were not generally available.

Composite anatase pigments with barium sulfate became commercially available in Norway and the United States in 1916, although production was limited in both countries until late 1918. This composite is no longer made by the major producers. National Lead, for example, discontinued the anatase and calcium sulfate composite in 1944 (R. Ensminger, personal communication, 1988). The anatase and calcium sulfate composite, introduced in the United States in 1925, was phased out in the early 1940s after rutile and calcium sulfate composites with increased hiding power and chalk resistance were introduced in 1940 (Stieg, 1960). By 1950 the calcium sulfate composites had almost replaced the barium sulfate composite pigments in the United States; in Great Britain and other countries, however, extended or composite pigments were almost exclusively of the barium type (Coates, 1950). In Europe the production of composite anatase pigments ended in 1971, reflecting the transition to pure or near-pure titanium dioxide grades (de Rohden, 1967; Coupry et al., 1987). In the United States, National Lead made the rutile and calcium sulfate composite until 1972 (R. Ensminger, personal communication, 1988). The trends in production of different grades from 1935 to 1960 have been summarized by Stewart (1964).

Good quality pure anatase pigment was first commercially produced in France in 1923 and is still being made. Small quantities of expensive but inferior anatase pigment containing up to 20% gritty rutile were available earlier (Coffignier, 1922; Willets, 1936b). Anatase pigment made by the chloride method was introduced in 1975 and ceased production by 1985.

In late 1938 a pure rutile pigment was introduced in Germany and a rutile product was undergoing testing in England, but rutile products were not available in Europe until 1945. The early rutile-based pigments tended to have significantly larger particle size than their anatase counterparts. A pure fine-particle rutile pigment was introduced in the United States in 1942. The first rutile pigments made by the chloride method were developed in 1948 and became commercially available in 1954. By 1957 these pigments were purer and had finer and more uniform particle size than sulfate process products; to remain competitive, sulfate process manufacturers improved the rutile pigment significantly during the early 1960s. Pure rutile products currently comprise about 75% of the world's titanium dioxide pigment production (Blakey & Hall, 1988). Rutile pigment continues to be manufactured by both the chloride and sulfate process.

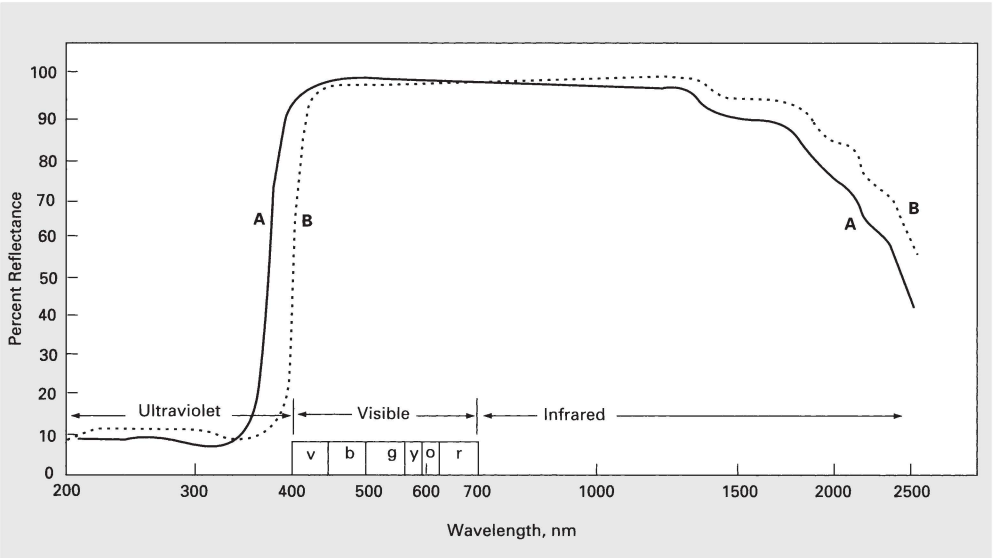


Fig. 3 Spectral reflectance of anatase and rutile titanium dioxide in the near ultraviolet, visible, and infrared range. (A) rutile, (B) anatase.

Titanium dioxide pigments coated with alumina were first patented in 1916, but not introduced commercially until the 1930s. A silicate-coated anatase was manufactured in the United States in 1931; other coatings were introduced between 1935 and 1940. Pigments with various inorganic and organic coatings continue to be manufactured (see section 4.4).

Colored titanium dioxide pigments were patented in the 1920s and introduced mostly during the 1930s. Lead titanate, for example, was introduced in 1935. Iridescent and metallic pigments with titanium dioxide precipitated on a base such as mica, were introduced in the 1960s (Greenstein, 1973). Polymeric pigments containing titanium dioxide have been in production since the mid-1970s.

3.0 General Pigment Properties

3.1 Color and Spectral Reflectance

3.1.1 ***Visible.*** Anatase and rutile white pigments both absorb some light in the 400 to 500 nm region (fig. 3). The rutile form absorbs more strongly and consequently has a yellower tone while anatase is a bluer white. The surface coatings applied to many modern titanium dioxide pigments are largely transparent and have little effect on the optical properties of the base pigment. Figure 4 illustrates a slight elevation of reflectance in the violet and blue region observed for some coated rutile pigments. The yellowness of rutile titanium dioxide is sometimes overcome by adding blue or violet tinters or fluorescent brighteners. In modern paint formulations, the most commonly used colorants are phthalocyanine blue and carbazole violet; carbon black and other pigments have also been used (J. Hall, personal communication, 1987). The yellowish color noted in some early anatase preparations can be partly attributed to contamination with rutile formed during poorly controlled calcination.

The whiteness of the pigments is reduced by the presence of even trace quantities of impurities. Some of the early anatase pigments had a reddish cast, mainly due to the presence of up to 1% of unremoved iron compounds (Heaton, 1947). The presence of iron was blamed for the poor color of the early products, but other elements such as vanadium, chromium, manganese, cerium, cobalt, and copper can also affect the color and must be removed (Ourisson, 1934; Weyl & Förland, 1950; Torlaschi et al., 1970). Methods of manufacture that produce high-purity pigments of brilliant whiteness have become standard since the late 1950s. The relative brightness of titanium dioxide artists' pigments available in 1939 was demonstrated spectrophotometrically (Barnes, 1939). In a medium of parchment size, pure anatase titanium dioxide and a mixture of titanium dioxide

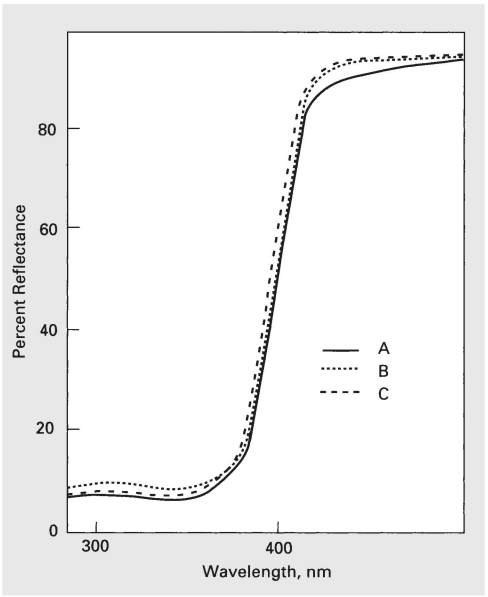


Fig. 4 Spectral reflectance in the ultraviolet range of uncoated and coated rutile pigments. (A) 99% rutile, uncoated, (B) 92.5% rutile coated with oxides of aluminum, silicon, zirconium and having an organic surface treatment, (C) 82% rutile coated with oxides of aluminum and silicon.

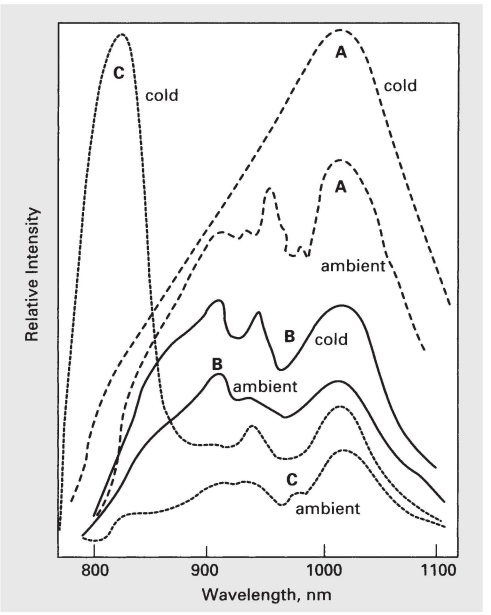


Fig. 5 Luminescence spectra of titanium dioxide pigments produced by the sulfate and chloride processes showing the effects of cooling. (A) anatase (sulfate process), (B) rutile (chloride process), (C) rutile (sulfate process). From Allen et al. (1978), with permission.

with 75% barium sulfate were rated at a relative brightness of 95.8% and 95.7% respectively, compared to 94.9% for zinc white and 87.3% for lead white.

Some contemporary artists may be using commercial pigments that consist predominantly of titanium dioxide deliberately colored through the addition of inorganic impurities. Tinted pigments in a wide range of colors can also be made by partial reduction of the titanium dioxide or absorption of an organic colorant (see section 4.4). These pigments consist of particles with uniform color (as distinct from those of a mixture), and their titanium dioxide content may be as high as 98%.

3.1.2 ***Infrared.*** Both pigments are highly reflectant to infrared radiation over a wide spectral range; rutile titanium dioxide is more reflectant than the anatase form, particularly toward the far infrared. In the examination of paintings using an image converter in the near infrared region, titanium dioxide white was ranked sixth out of twenty-six pigments in reflectance to radiation in the 800 to 1,200 nm range. The ability of a hiding layer of titanium dioxide pigment in oil to obscure a tempera underdrawing was slightly less than but comparable to that of lithopone or lead white (Heiber, 1968). In powdered samples, the reflectance that could be photographically recorded from Titanox A pigment did not differ considerably from that of whiting (calcium carbonate), barium sulfate, lead white, lithopone, or zinc white (Farnsworth, 1938).

Infrared luminescence is emitted by some pigments on illumination with visible light in the blue-green region. In a photographic study of artists' oil pigments, lead white was found to give a slightly brighter emission than zinc white or titanium dioxide white, although all three gave a very faint response (Bridgman & Gibson, 1963). Allen et al. (1978) showed that an intensified infrared luminescence that is highly temperature-dependent is observed in some titanium dioxide pigments illuminated with ultraviolet light at low temperatures. They differentiated between rutile pigments made by the chloride process and the sulfate process using spectrofluorimetry at liquid nitrogen temperatures (fig. 5). A range of uncoated and coated sulfate-process rutile pigments showed the same low-temperature spectral features, but had a varying emission intensity; this

appears linked to the amount of coating material and the photoactivity of the various grades (Allen et al., 1979; Allen & McKellar, 1980). Anatase pigment gives its strongest emission when irradiated with ultraviolet light of wavelength 340 nm, the emitted light having a strong spectral peak in the green region at 540 nm. Rutile pigment is most efficiently excited at 375 nm, but gives only a relatively weak infrared emission with its peak at 815 nm. A photographic method based on this principle did not uniquely identify sulfate-process rutiles among fifty-five samples from different manufacturers.

3.1.3 ***Ultraviolet.*** The reflectance characteristics of anatase and rutile into the ultraviolet region, below about four hundred nanometers, are illustrated in figures 3 and 4. Ultraviolet radiation is strongly absorbed by both; rutile absorbs further than anatase into the violet region. The ultraviolet absorption characteristics are affected very little by the surface treatments used to improve durability of rutile pigments.

The absorption of actinic radiation has practical consequences for many materials of concern to artists and conservators. For example, the ultraviolet/violet component of light sources can be reduced by painting the walls and ceiling of a room with rutile titanium dioxide (Feller, 1964). The ultraviolet screening characteristics of glass or plastic are greatly improved by the addition of a small amount of titanium dioxide, which is often used in food containers (Beals & Strimple, 1963) and as a coating on optical glass. The greatest adverse effects of ultraviolet absorption by titanium dioxide result when the eventual dissipation of energy occurs through chemical reactions that degrade associated materials such as media or other colorants (see section 3.4.2).

The appearance in ultraviolet light of objects containing titanium dioxide depends on factors such as the illumination system, presence of admixed pigments, and medium. Murley (1962) observed that both rutile and anatase were nonfluorescent when illuminated by ultraviolet sources with no visible light present. However, under the conditions typically used to examine paintings, a weakly visible emission in the violet region is likely to be observed (see, for example, Beutel & Kutzelnigg, 1931; Déribéré, 1942; Crown, 1968; Kodak, 1972). This is due in part to reflection by the pigment particles of visible components of the lamp light not totally removed by the filter system. Consequently, when the illumination contains violet light, anatase (which is more reflective than rutile in the violet region of the spectrum) gives a slightly brighter response. Any change in the visible emission from commercial pigments due to inorganic coatings is minimal when either short- or long-wave ultraviolet illumination with intensity maxima at 254 or 360 nm, respectively, is used. Laboratory mixtures of pigments, which approximate the content of the early composites containing barium sulfate and calcium sulfate, were found to give the same dark violet appearance as pure anatase. In contrast, mixtures containing zinc white, which itself fluoresces, gave a yellow-green fluorescence related in intensity to the amount of zinc oxide present. In paintings, where a high medium-to-pigment ratio is often present, it is common for the fluorescence of pigments to be changed to such an extent through quenching or addition by the medium that identification using gross ultraviolet examination is impossible. The development of fluorescence of oil paint on aging is not inhibited or changed by the presence of titanium dioxide pigment (De la Rie, 1986). Brandon (1981) noted that paper containing titanium dioxide appears dark under ultraviolet illumination.

3.2 Hiding Power and Tinting Strength

Light scattering is the main mechanism by which white paints opacify paint films. This factor is determined primarily by the refractive index of the pigment particles. Rutile has an average refractive index of 2.72, the highest of any of the white pigments; anatase has an average index of 2.54. Figure 6 illustrates the relationship between hiding power and refractive index for a series of pigments, when parameters that would otherwise affect the hiding power (including particle size and pigment-volume concentration) are kept constant.

The early literature, despite its nonstandard test methods, gives an idea of the improvement in hiding power afforded by the titanium dioxide pigments. Table 4 shows the order in which Heaton (1922) ranked the new pigments using the Pfund cryptometer method.

Pure anatase pigments have significantly better hiding power than the composite grades. Hagar (1927) rated the improvement at two and one-half times over the barium sulfate composite pigment. Of the anatase composite pigments, the anatase and calcium sulfate pigment gave better hiding characteristics than its barium sulfate counterpart

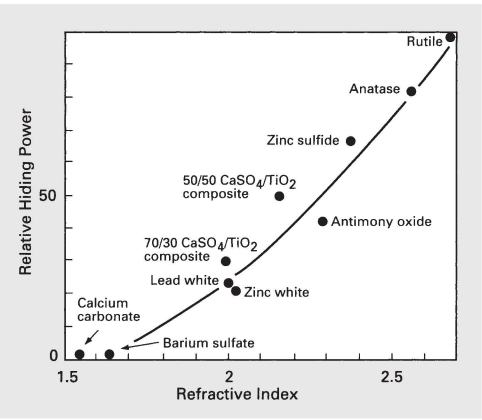


Fig. 6 Relationship of hiding power to refractive index for white pigments. From *Kronos Guide* (1968), with permission, and Mitton (1973).

Table 4 **Hiding Power of White Pigments**[a]

Pigment	*Relative Weight for Equal Hiding*
Extra titanium white	130
Standard titanium white	100
Zinc white	77
Lithopone	65
Lead white	46
Basic lead sulfate	35

a. From Heaton (1922).

(Ryan, 1930). The 30% rutile and calcium sulfate composite introduced by the National Lead Company in the 1940s had hiding power increased again by about one-fifth over the comparable anatase composite (Stieg, 1985), still considerably less than that of pure anatase. The subsequent introduction of pure rutile resulted in greater hiding by 20% to 25% over pure anatase (Mitton, 1973).

Although the titanium dioxide pigments were more expensive than traditional whites, their greater hiding power made their use economical (table 5).

By 1940 Titanox C (see table 2) had become the least expensive of all white pigments in terms of hiding power cost (Hagar, 1940). The closest competition was from lithopones (co-precipitated zinc sulfide and barium sulfate) of the high-strength or titanated variety, and Titanox A and B.

Tinting strength—the ability of a pigment to lighten or obscure a colorant—is also determined primarily by the refractive index of the pigment,

Table 5 **Cost of White Pigments per 100 sq. ft. of Paint Surface at Complete Hiding**[a]

Pigment Type	*Cost in U.S. Dollars*
Lithopone	$0.22
Titanox (25% titanium dioxide)	0.24
Zinc oxide (American)	0.29
Lead white (basic carbonate)	0.43
Lead white (basic sulfate)	0.53

a. From Hixson and Plechner (1929).

although the medium and other factors play an important role. Rutile has a great advantage over anatase in tinting strength when the medium has a high refractive index. Conversely, in water-emulsion paints or papers its hiding power and tinting strength are only slightly greater than those of anatase (Tinsley & Bowman, 1949). The tinting strength of these pigments has been constantly improved since their introduction. The pure anatase grades have three times the tinting strength of Titanox B, and about two and one-half times that of Titanox C (Hallett, 1930). Rutile pigment initially had a relative tinting strength (measured by the Reynolds constant volume method) of 1,000, while today rutiles can be manufactured with a tinting strength from 1,650 to 1,900 (Kampfer, 1973). The tinting strength of anatase typically is between 1,200 and 1,300. For comparison, the tinting strength of lead white has been measured at approximately 140, zinc white at 170, lithopone at 280, titanated lithopone at 430, and zinc sulfide at 859 (O'Brien, 1948).

3.3 Permanence

Both rutile and anatase white pigments in general are lightfast (*Colour Index*, 1971; Levison, 1976). However, exposure to light can cause a phototropic color change under certain circumstances. The slightly reduced form, $TiO_{1.995}$, is blue. A reversible blue-gray discoloration can be produced on the pigment surface due to the formation of titanium of a lower valence, Ti^{3+}, either during irradiation under reducing conditions in the laboratory (Renz, 1921) or in the presence of reducing media such as urea formaldehyde or melamine resins used in the manufacture of paper laminates (Willets, 1970). Even in alkyd enamel paints, titanium dioxide has been observed to acquire a blue tone on exposure to direct sunlight over a period of hours; rutile undergoes this reversible color change to a lesser extent than does anatase (Dawson, 1942). Surface treatment of the

pigment with silica or alumina reduces this phototropic effect (Barksdale, 1966).

The presence of trace impurities in pigment particles can also cause changes of color on exposure to light. Photoreactions in the titanium dioxide lattice can in turn cause impurities to form colored species. This type of light sensitivity was noted in some of the less highly refined early pigments. Problems with the reversible darkening of ceramic glazes or powdered pigment exposed to daylight over a period of hours were attributed to trace metal contaminants such as iron (Williamson, 1937, 1939; Weyl & Förland, 1950). Chromium, copper, and manganese at concentrations as low as ten parts per million cause color changes on exposure to light with a high content of ultraviolet; high sensitivity to light in titanium dioxide pigments containing antimony, niobium, and nickel has also been observed (Torlaschi et al., 1970; Ritter, 1973). Improved processing was found to eliminate the tendency of early pigments to "blush" or redden in bright light, either when dry or mixed with oils (Tinsley, 1943). Modern titanium dioxide pigments are manufactured to high standards of purity to ensure the removal of trace impurities, which would adversely affect the permanence of their color.

The color of the pigments is affected by temperature. Reversible yellowing occurs at temperatures above 200°C in rutile pigment and above 300°C in anatase pigment.

In tests to determine the color stability of pigments during neutron autoradiography, excessive doses of reactor neutrons and their accompanying radiations produced no change in titanium dioxide (Sayre & Lechtman, 1968).

3.4 Compatibility

3.4.1 ***Chemical compatibility.*** The anatase and rutile pigment forms are both chemically inert, as distinct from their photochemical reactivity (see section 3.4.2), and do not react directly with airborne pollutants, organic solvents, media during drying, or other pigments. Heaton (1922) suggested that the resistance of titanium dioxide pigments to acids and alkalies was an advantage for their use in true fresco.

Nonreactivity with paint media was noted as a disadvantage for industrial paints in tests of anatase pigments in the early 1920s since it resulted in soft films that were slow to dry, particularly in oil media. Heaton (1922) suggested that this increased drying time was an advantage for use in artists' colors. Anatase pigments dry faster than rutile grades (*Kronos Guide*, 1968). Drying characteristics of both anatase and rutile pigments can be improved by adding pigments such as zinc oxide, resin, or driers (manganese, cobalt, or lead compounds). Pigment coatings can affect drier efficiency (Wilska & Salminen, 1982).

Yellowing of the medium that occurs on aging of titanium dioxide paints can be studied separately from light-induced yellowing. In the absence of light, artists' paints containing pure anatase pigment or a slightly more chalk-resistant modification in linseed or poppy-seed oil media, turned straw-yellow in a short period of time. The addition of zinc white or lead white was found to almost completely eliminate this yellowing (Asmuss, 1941). Adding zinc oxide to titanium dioxide in safflower oil was also found to reduce yellowing (Levison, 1976). Paints comprised of anatase, rutile, or coated rutile pigment in oil-modified alkyds yellow at the same rate under low-light conditions at ambient temperatures, although under dark conditions at 60°C the pigment grade makes a difference and anatase exhibits the poorest performance. Addition of zinc oxide or organic yellowing inhibitors decreases yellowing (Simpson, 1981). In scorching tests up to 220°C for safflower oil paint films, a titanium dioxide and barium sulfate paint darkened less than zinc oxide or lead white paints; of the three, it recovered its color most completely under bleaching irradiation with visible light containing negligible ultraviolet (Tahk, 1980).

The effects of dry titanium dioxide pigment on the yellowing of paper fibers differ from its interactions in a medium that totally coats the pigment particles. Studies by the British Standards Institute determined that in paper containing titanium dioxide the pigment had no undesirable side effects (J. Grant, personal communication, 1986). Raw photographic paper stock containing the pigment showed only the normal tendency to yellow in accelerated reversion tests (R. Ward, personal communication, 1987). Paper manufacturers have noted that yellowing in paper is inhibited by the presence of titanium dioxide because its high hiding power masks the early accumulation of yellow degradation products (Willets, 1937). In tests on sulfite-soda paper and rag paper, titanium dioxide fillers (either pure or as a composite with 70% barium sulfate) gave paper very nearly the same stability to heat aging as did clay fillers (Shaw & O'Leary, 1938). The rag papers used in these experiments were retested after thirty-six

years of natural aging; they showed extremely high zero-span breaking lengths, which were attributed to titanium dioxide's role in preventing aluminum attachment to carboxyls by preferential absorption (Wilson & Parks, 1980). However, increasing the titanium dioxide content from 5% to 15% in these papers caused a slight decrease in permanence rating.

In some works of art, the strains caused by swelling of the paint film on exposure to solvents can result in physical damage and the presence of some pigments can affect the rate and extent of swelling. Mechanically, titanium dioxide is nonreactive to relative humidity. The lack of hysteresis in the weight change of pigmented linseed oil films as relative humidity is cycled from zero to 90% is at least partly attributed to the fact that reaction products such as soaps are not formed (Nelson & Rundle, 1923). A paint film of titanium dioxide in linseed oil shows the same relative change of elasticity (stiffness) between zero and 70% RH as those containing zinc white or lead white and shows the least softening at high relative humidity (S. Michalski, personal communication, 1989). When the relative humidity is raised above 90%, swelling occurs in linseed oil-based films containing anatase (Browne, 1955a); in latex and alkyd media, titanium dioxide forms the least absorptive films of the three pigments (Browne, 1956a, b). Anatase and rutile pigments in linseed oil initially absorb water faster than zinc white or lead white when paints are totally immersed in water (Long, 1949), but at equilibrium the paint films are only slightly more absorptive than those containing lead white and much less so than those incorporating the highly absorptive zinc white (Browne, 1955b; Eissler & Princen, 1968). Composite pigments, for example with calcium sulfate, can have very different water absorption characteristics (Long, 1949). The effect of titanium dioxide, relative to other whites, on the swelling during application of organic solvents to linseed oil paints varies depending on the solvent (Browne, 1956c).

3.4.2 ***Photochemical compatibility.***

Photoreactions of titanium dioxide. Anatase and rutile pigments are strong absorbers of ultraviolet light (see fig. 3); rutile absorption extends into the violet. Both are photochemically active, that is, the absorption of light can lead to chemical reactions (Sullivan, 1972; Solomon & Hawthorne, 1983). Deterioration can occur via various photogenerated oxy-species or by direct electron transfer between irradiated titanium dioxide and an adsorbed organic species. Typically, the presence of water and oxygen allows formation of reactive hydroxyl and hydroperoxyl radicals (see fig. 9), which can cause breakdown of the associated organic or inorganic materials, including binders or colorants. Hydrogen peroxide is generally only formed in aqueous media. Volatile degradation products such as carbon dioxide, water, carbon monoxide, and formaldehyde migrate out of the film (Rosa & Elm, 1959).

Almost all of the ultraviolet radiation absorbed by a pigment-medium mixture containing titanium dioxide is absorbed by the pigment (Hughes, 1970). The greater part of this energy is dissipated as heat (Murley, 1962), although some may be transferred to neighboring molecules. The effects of titanium dioxide on associated materials can be protective (particularly where the medium would photodegrade readily in the absence of pigment); however, degradation reactions such as chalking, fading of colorants, yellowing or cracking of media, and weakening of fibers can also occur. Pigmented paint films may become thinner due to degradative penetration of ultraviolet to some depth beneath the film surface (Colling & Dunderdale, 1981). Whether the material is damaged or protected by the ultraviolet/violet absorption depends on whether the rate of the degradative reactions due to the photoactivity of the pigment is greater or less than the rate of breakdown of the medium alone. Grades of rutile titanium dioxide have been developed in which the photoactivity has been greatly reduced; these are the pigments of choice for artists and conservators.

In any medium, the potential for photodegradation is greater with anatase grades of pigment than with rutile grades; the reasons for this are still the subject of debate. Two main methods are presently in use that reduce as much as possible the activity of rutile, which has the higher opacifying power. One method is to introduce stabilizing elements such as zinc or aluminum into the rutile lattice. The other method is to use coatings, including hydrous oxides of silicon, aluminum, and zirconium, which act as a physical barrier, limit the diffusion of the oxidizing species out from the pigment surface, and may also aid in their destruction (Wiseman, 1976; Blakey & Hall, 1988). Many types of deterioration including cracking of exterior alkyd paints can be linked to pigment grade (Valpola, 1978). Measurements on

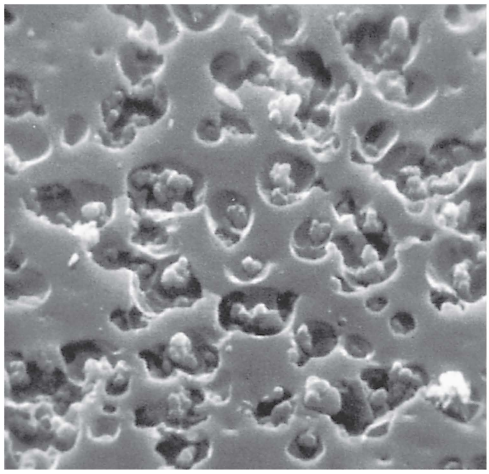
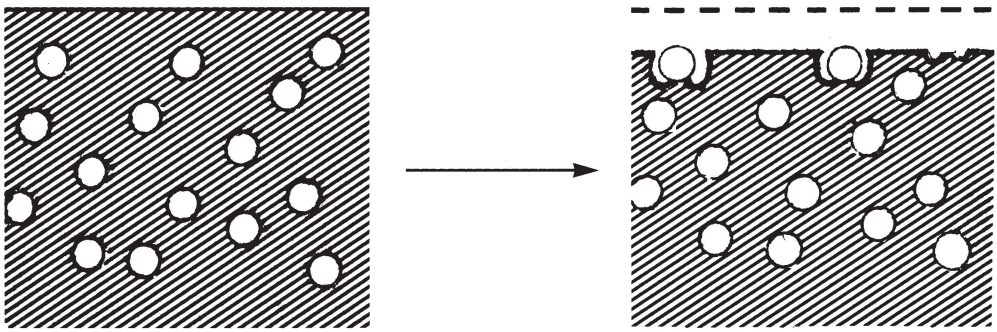


Fig. 7 A. Scanning electron micrograph of a degraded alkyd paint film containing anatase titanium dioxide pigment (5% pigment volume concentration). 7,300x.

B. Schematic diagram illustrating the enhanced deterioration of the medium in the vicinity of the photoactive pigment particles as seen in A. From Völz et al. (1981), with permission.



commercial pigments showed a hundredfold variation in photoactivity (Irick et al., 1981). Zinc oxide is often added to control degradation, as it is a strong ultraviolet absorber and is less photoactive than pure titanium dioxide. By comparison, barium sulfate and lead white, although not particularly photoactive, transmit more ultraviolet and consequently can allow more deterioration to occur in sensitive vehicles than do zinc oxide or titanium dioxide pigments (Stutz, 1926; Feller, 1967).

The effects of light intensity on titanium dioxide pigmented systems have been investigated (Egerton & King, 1979). In a rutile paint with a medium that is easily oxidized directly by ultraviolet light, relatively greater deterioration will occur at high light intensities than in a system where the binder is more stable. All wavelengths tested that were below the optical absorption edge had an equal effect on rutile-catalyzed reaction rate. Wavelength does, however, affect the rate of direct breakdown of the unpigmented medium (Simpson, 1986).

Scanning electron microscopy (figs. 7A and 8A) has been used to compare the breakdown of paint pigment-media systems in which the pigment aggravates the deterioration to those in which it affords protection (Kämpf et al., 1973; Völz et al., 1981). The processes are particularly well illustrated in a film made by Völz and his co-workers from a series of photomicrographs of artificially aged paints (available from Bayer AG, D-4150, Krefeld-Uerdingen, Germany). In an anatase-alkyd paint, the medium is attacked and eroded immediately surrounding the very photoactive pigment, leaving pigment particles in hollows in the paint film (fig. 7B). In a comparable alkyd paint based on less photoactive rutile pigment, direct ultraviolet degradation of the medium predominates, and pigment particles are left supported on pillars of medium, which are protected from irradiation as seen in figure 8B. Directional protective effects such as these pillars would be less likely to occur during natural aging with variable illumination direction and more diffuse light sources. Where less durable media are

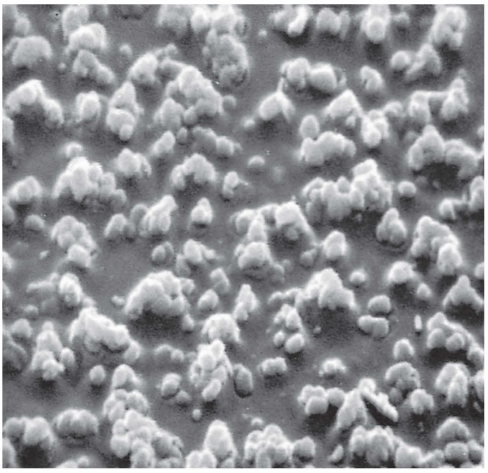
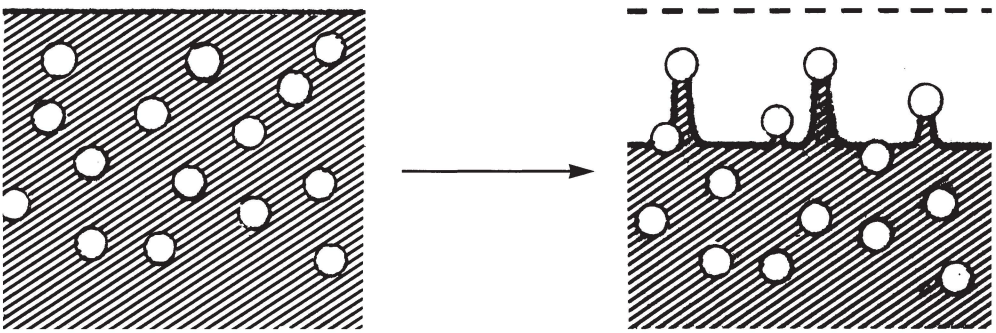


Fig. 8 A. Scanning electron micrograph of a degraded alkyd paint film containing a coated rutile titanium dioxide pigment (5% pigment volume concentration). 7,300x.

B. Schematic diagram illustrating the deterioration of the medium that occurs when a less photoactive pigment protects the medium from the effects of light as seen in A. From Völz et al. (1981), with permission.



used, the breakdown of the medium directly by ultraviolet predominates, making even moderately durable titanium dioxide pigments effective for reducing deterioration. For example, rutile pigment has been shown to protect an alkyd medium, an acrylic resin, and a polyvinyl acetate dispersion, while accelerating the breakdown of polyurethanes (Rosa & Elm, 1959; Kämpf et al., 1973; Blakey & Hall, 1988). Linseed oil has even less resistance than alkyds to photochemical breakdown (Ray, 1953; Barksdale, 1966). Oxidation reactions have been observed in gum arabic solutions (Clay, 1957) and in cellulose (Schurz & Kienzl, 1958). Polymers that can be oxidized, such as polypropylene and cellulose esters, are more adversely affected by the presence of photoactive pigments than are oxidation-resistant types (Irick et al., 1980). Anatase pigment in Paraloid B-72 (a methyl acrylate ethyl methylacrylate copolymer frequently used in conservation) was found to accelerate its deterioration on exposure to ultraviolet (Lyall, 1981; B. Koivisto, personal communication, 1988). Adding ultraviolet stabilizers to many types of media can improve durability.

Photoreactions in artists' materials. Exterior murals will exhibit chalking if one of the more photoactive grades of titanium dioxide has been used. Chalking is caused by deterioration of the paint medium. Loss of gloss and mass results as the medium is physically removed, leaving the pigment as a loose powder on the surface. Admixed colors appear to fade, although chalking can be distinguished from fading spectrophotometrically (Johnston & Feller, 1963). Where the medium is resistant to oxidation, whitening may occur without loss of pigment, resulting in a blanching effect (Feller, 1967). "Self-cleaning" white exterior paint takes advantage of chalking, because of the continuous loss of material (including dirt) washed from the surface. A free-chalking grade of pigment, such as untreated anatase, used in a work of art could cause eventual aesthetic problems on exposure to ultraviolet light, oxygen, and water. A few instances of this

problem in art works have been reported in color field paintings where anatase pigment in an acrylic medium was exposed to moisture (A. Roy, personal communication, 1986). Titanium dioxide in dammar resin used as a conservation retouch paint may cause intermediate layer chalking similar to that seen with zinc oxide in dammar (Feller, 1966). Organic layers (for example, varnish films or sheet polypropylene) in close contact with paint containing photoactive grades of titanium dioxide have been found in some cases to show enhanced deterioration due to the migration of oxidative species from the paint layer (Murley, 1962; Lyall, 1981).

To avoid these photoactivity problems, artists' color makers generally supply the less active rutile grades for oil colors, some with added coatings or stabilizing elements. Anatase can still be found in artists' pigments, however. Artists using house paint or powdered pigment should confirm with the manufacturer that they are using a nonchalking grade of titanium dioxide. Chalking and most other photoreactions can be eliminated by using filters on display lights that remove the actinic ultraviolet/violet light or by using light reflected off a white wall painted with rutile titanium dioxide (see section 3.1.3). Lowering the relative humidity can dramatically reduce chalking rates of paint in latex media (Hoffmann & Saracz, 1969).

The photoactivity of titanium dioxide pigments also may affect the color of sensitive materials with which it is mixed. Dyes that are stable to light when adsorbed on lead white or lithopone can rapidly fade in the presence of titanium dioxide (Keidel, 1929). Accelerated fading has been reported on azo dyes and basic dyestuffs such as madder lake; the addition of zinc oxide in some cases can reduce this effect (Wagner & Zipfel, 1932). Discoloration of inks has been observed, particularly in formulations with sensitive binders such as polyamides (Dowling & Corless, 1969). Wehlte (1975) noted that Prussian blue faded reversibly in experiments when it was diluted with titanium dioxide and exposed to strong light in the presence of moisture, although he commented that in fifty years of experience, he had not observed this phenomenon in a work of art. This effect can be diminished by the addition of zinc oxide (Barksdale, 1966). Sensitive dyes such as alizarin lake can be protected from fading by admixture of a nonphotoactive grade of rutile titanium dioxide (Johnston-Feller, 1986). Reduced fading of artists' oil paint containing madder lake and rutile titanium dioxide mixed with barium sulfate is achieved by adding zinc oxide; color fading is reduced by half when 15% to 20% zinc oxide is added. Paint made with zinc oxide performs better under fluorescent lights, and worse in sunlight than the mixture of titanium dioxide pigment and zinc oxide (Levison, 1976).

In pastels containing titanium dioxide, the color change of whites and grays on exposure to ultraviolet light is minimal, although a considerable change in luminosity was observed in tests on an anatase-based pastel (Schwartz et al., 1984). Fixative layers of Klucel and Elvamide resins did not discolor significantly, but underwent some luminosity changes. In general, there is so little medium relative to the amount of pigment in a pastel that yellowing is not likely to be a serious effect.

The instability of photographs on resin-coated paper containing titanium dioxide in a polyethylene layer (see, for example, Severson, 1987) can be attributed at least partly to the photoactivity of the pigment. Image fading, embrittlement, and cracking during display and storage can be ameliorated by protection from ultraviolet/violet light, or by the addition of stabilizing compounds, including antioxidants and peroxide scavengers, to the polyethylene and to the fiber base (Parsons et al., 1979; Kolf, 1980).

Cellulosic textile fibers delustered with titanium dioxide (typically 0.3%–2%) undergo accelerated breakdown and show a decrease in the average degree of polymerization, due to incorporation of the pigment (Lang et al., 1955). Rayon, nylon, and cotton are readily degraded, whereas wool is not (Allen & McKellar, 1980). The areas of damage in internally delustered viscose have been described as spherical shells around the pigment particles, inside the fiber (Treiber, 1955). As with paints, rutile causes less damage than anatase, and high concentrations of pigment may have a protective screening effect.

Both cellulosic papers and those containing lignin undergo ultraviolet-induced chemical changes even in the absence of pigment (Brandon, 1981; Feller et al., 1982). A coating layer of pigment protects the paper beneath by absorbing ultraviolet light, although the binder in the coating may be at risk, depending on its own photostability. Pigment present as a filler, where the particles are attached mainly through heteroflocculation to the outer surface of the fibers, would not cause damage to the same extent as in an

internally delustered cellulosic textile. In fact, the higher concentrations (usually up to about 7%) may have an advantageous screening effect, particularly with the rutile grades.

3.5 Chemical Properties

Both anatase and rutile white pigments are very resistant to chemical attack. Titanium dioxide is relatively unaffected by aqueous alkalies and is insoluble in organic solvents. The reactivity of titanium dioxide to acids depends on the temperature to which it has been heated during preparation (Whitehead, 1983). Titanium dioxide precipitated from solution and gently heated to remove water is soluble in concentrated hydrochloric acid. However, if it is heated to approximately 900°C, as in calcination during pigment production, its solubility in acids is considerably reduced. Titanium dioxide pigment dissolves slowly in hot concentrated sulfuric acid. The presence of an alkali metal or ammonium sulfate, which raises the boiling point of the acid, can aid dissolution. In solubility tests, a commercial anatase pigment was about 90% dissolved in concentrated sulfuric acid at 150°C after one hour; under the same conditions, only about 10% of a rutile pigment dissolved (Rechmann, 1967). Hydrofluoric acid can also be used to dissolve the pigment. Ores containing a high concentration of titanium dioxide are more refractory than the pigments and may require fusion, which is accomplished with molten sodium and potassium hydroxides, carbonates, and borates.

Titanium dioxide is amphoteric, although acid properties predominate over basic (Blakey & Hall, 1988).

Rutile is the more thermally stable form of titanium dioxide. Anatase, if heated, will not melt but rather transforms to rutile with the evolution of approximately 12.6 kJ/mol (3.01 kcal/mol). The minimum temperature at which this proceeds at a significant rate is approximately 700°C, and the change is not reversible (Whitehead, 1983). In pigments, transformation can occur from 400°C to 1,200°C (see section 5.3.9). Rutile melts at 1,825°C. The specific heat of both forms is 0.17 calories per degree Celsius pe gram (Blakey & Hall, 1988).

3.6 Oil Absorption and Grinding Properties

The higher oil absorption of the early pure anatase grades relative to traditional white pigments was a source of complaint until about 1928 among some of the customers of Thann and Mulhouse; the pigment was modified to reduce oil absorption by adding peptized titanium dioxide (15% to 20%) to the hydrolysis product prior to calcination (de Rohden, 1967). In 1922, mixing the Norwegian pigment in oil using a mixer and crushing rolls was a long and difficult procedure, but it was possible to improve oil absorption through preliminary use of a grinding mill (Coffignier, 1922). The oil absorption could be decreased from 25% to 17% (lb. oil per 100 lb. pigment) if grinding was done in a pebble mill, an American practice (Clark, 1975), rather than on a triple roller mill (Remington, 1935).

Table 6 **Absorption of Oil and Water Media[a] (Pounds of Medium Per 100 Pounds of Pigment) in Percent**

Pigment	*Oil*	*Water*
Anatase titanium dioxide	20–24	25–30
Rutile titanium dioxide	15–20	20–35
Zinc oxide	13–22	16–24
Lithopone 30%	10–23	12–26
Antimony oxide	11	13
Zinc sulfide	10	12
Lead white	8–12	10–15

a. From Tioxide Canada Inc. (1971).

Oil absorption of some early anatase pigments was: titanium dioxide, 24% to 26%; Titanox C, 21% to 23%; Titanox B, 16% to 17% (Ryan, 1930). Pigments of the same composition prepared by different manufacturers were compared by Gardner (1937) who showed the wide range of oil absorption that could be achieved through control of grinding or surface treatment at that time. The absorption of oil and water by some modern white pigments is given in table 6.

The grinding qualities, or dispersibility, of titanium dioxide pigments depend on particle characteristics such as size, size distribution, and shape, and on surface properties relative to the medium. Artists should be aware that there are pigment grades specifically designed for different media such as plastic, lacquer, resin, aqueous, or oil. For example, pigment treated with 0.5% silicone oil, although easily dispersed in plastic media, will have a greater tendency to agglomerate in linseed oil than will an untreated pigment (Tioxide Canada, Inc., 1971).

Under normal conditions, the surface of untreated titanium dioxide is dominated by oxy-

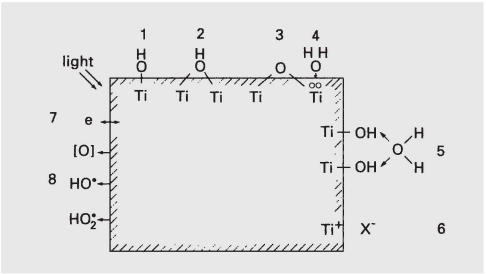


Fig. 9 Diagram showing the principal surface features of a titanium dioxide particle. From Solomon and Hawthorne (1983), John Wiley and Sons, Publisher, with permission. *Key:* (1) basic terminal hydroxyl groups (2) acidic bridge hydroxyl groups (3) labile Ti–O–Ti bonds (4) water molecules adsorbed at Lewis acid sites (5) water molecules bound to surface hydroxyls (6) adsorbed anions such as processing residues (7) potential electron donor and acceptor sites (8) adsorbed oxidants generated through photoreactions.

gen atoms and adsorbed hydroxyl groups (fig. 9), giving it a polar surface that allows easy dispersion in polar media such as water (Wiseman, 1976). Lengthy grinding can cause increased hydrophobicity, mainly due to the relative loss of surface hydroxyl groups (Kawashima & Meguro, 1976). Surface treatment can change the dispersibility by causing adsorption or chemical bonding of different ions or molecules on the surface. Adsorbed ions, which provide mutual repulsion between pigment particles (such as silicic or phosphoric acid), or organic groups such as trimethylsilane bonded to the surface will make the pigment appear nonpolar and allow wetting in nonpolar media. Titanium dioxide pigment can also be given a more positive or negative surface charge, depending on the surface treatment. Alumina coatings can give positively charged characteristics, which give good wetting and stability in nonaqueous systems (alkyds and solvent industrial paints). Silica coatings give more negative characteristics and thus are suited for aqueous emulsion systems. Dispersibility of the pigment can also be affected by the addition of an appropriate surfactant to improve wetting of the particles or a deflocculant to overcome the adhesive forces between particles.

Some early users observed that the handling qualities of titanium dioxides in oil were not as good as those of other pigments (Wait & Weber, 1934). Some of these paints also settled out to form a hard, indestructible cake during shelf storage (Barnett, 1949). Occasional problems with thickening of paints made with barium sulfate composite pigment in a varnish medium (such as copal or tung oil varnishes) were solved by grinding the pigment in a special medium and then thinning the mixture with the final mixing varnish (Hagar, 1927). Later tests of titanium dioxide pigment in poppy-seed, dammar, or linseed oil showed satisfactory grinding and handling properties (Urban, 1941); introduction of surface treatments also helped to overcome these handling problems. Levison (1973) reported that products that may tend to be too flowing or stringy when ground alone can be improved by dilution of up to 60% with extenders such as barium sulfate.

3.7 **Toxicity**

An important advantage of the titanium dioxide whites is that they are nontoxic. When purified to certain specifications they can be used in pharmaceuticals, foods, and other products. Uncoated anatase pigments are generally used for these purposes. Some suppliers reprocess coated pigments to remove the silica or alumina coating or specific trace elements, generally by washing in acid (J. Kohnstamm, personal communication, 1986).

Titanium dioxide is not toxic to mildew and fungal growth (see for example, Gardner et al., 1933; "Disinfectant Paints," 1936; Meier & Schmidt, 1952). Zinc oxide or a fungicide may be added to the pigment if fungistatic qualities are desired (Wiseman, 1976).

Titanium dioxide in powder form is similar to any dust in that it will provoke some cellular response in the lungs and can cause irritation of the eyes or mucous membranes. The extent of any toxic effects of inhalation due to the presence of trace element contaminants or of coating materials is not known (Wilska, 1976). Skin contact with the powdered pigments can cause dryness because they absorb water and natural oils due to their fine particle size; prolonged exposure should therefore be avoided (Whitehead, 1983).

4.0 **Composition**

4.1 **Chemical Composition**

Titanium dioxide white pigments are made in the anatase or rutile crystal form. The earliest pigments, called composites, consisted mainly of anatase titanium dioxide usually precipitated onto barium sulfate or calcium sulfate. A silicate composite was developed but had limited use and a composite based on calcium carbonate

was tried experimentally but was not produced commercially.

Pure titanium dioxide (over 99.5% anatase or rutile) could be produced in the laboratory in very small batches (for example, by Auguste Jacques Rossi between 1906 and 1915); however, difficulties were encountered in manufacture on an industrial scale (W. Allsopp, personal communication, 1989; see section 4.3.1). The pure anatase pigment first marketed in 1923, containing 96% to 99% titanium dioxide, probably contained at least some rutile; some early products may have contained up to 20%. According to an American producer, during the late 1920s and 1930s the rutile content could be controlled to under 0.5%. Anatase produced by the chloride method during 1975 to 1985 contained a significant proportion of rutile. Mechanically mixed rutile and anatase pigments were also marketed in North America during the late 1930s and later to obtain less expensive grades and, in house paints, to promote free chalking.

Typical pigment compositions of the 1920s are given in table 1. An analysis of an early composite produced in Norway showed the major components to be 66.44% titanic acid, 12.48% barium sulfate, 0.37% silica, 10.54% phosphoric acid, 8.06% chalk, and 0.72% iron oxide (Coffignier, 1921).

The trace elements present are residues from the ore source or are introduced during manufacture. Identification of a particular manufacturer through trace element analysis of titanium dioxide artists' pigment is practically impossible, as companies have shared ore sources and also changed suppliers as necessary. A considerable international trade in finished pigments complicates such identification. Chronology can be established in some cases by distinguishing between the sulfate and chloride production methods (see sections 4.3.1 and 4.3.2) based on trace elements. Determination of chlorine or sulfur in titanium dioxide is often impossible due to the presence of medium or of a pigment such as barium sulfate; the distinction is based on other elements. Chloride process pigments are generally more highly purified and are made from rutile ore, which has a different trace element composition than the ilmenite used in the sulfate process. The high purity of chloride process pigments is illustrated in table 7.

Table 7 **High Purity of Chloride Process Pigments. Trace Elements in Parts Per Billion[a] (Typical Production Control Figures)**

Element Present	*Typical*	*Maximum*
Antimony	5	11
Arsenic	10	250
Barium	600	6,000
Cadmium	50	400
Chromium	1,000	1,250
Copper	400	1,080
Lead	1,000	7,900
Mercury	15	160
Selenium	5	50
Tellurium	500	8,000
Tin	3,000	5,300

a. B. Whitney, personal communication, 1989.

Trace elements such as niobium (Nb) remain after sulfate-based processing but are removed in the chloride preparation method. For example, in sulfate process pigment made from Norwegian ilmenite (0.007% Nb) or Australian ilmenite (0.10% Nb), the finished pigments contained 0.012% and 0.220% niobium, respectively. The chloride process, on the other hand, reduced the niobium content from 0.24% in a rutile ore to a level below the detection limit of 0.003% (Rechmann, 1978). Other trace elements that may be useful in distinguishing manufacturing methods are zirconium, hafnium, and tantalum. Antimony is sometimes added to sulfate process pigments during manufacture, and levels above about twelve parts per million (ppm) were observed in neutron activation analysis of fourteen out of twenty-seven pigments of this type (R. Hancock, personal communication, 1988). Twenty chloride process pigments were analyzed and all were below 12 ppm. Low concentrations of antimony can occur in pigments made by either method. Similarly, elevated trace levels of lead indicate use of the sulfate process, as the pigments can take on 90 to 100 ppm lead from pipes and tanks during manufacture (J. Kohnstamm, personal communication, 1986). Even in 1950, the maximum lead content of a good brand of titanium dioxide pigment was 150 to 250 ppm (Coates, 1950). Lead or antimony are not always good indicator elements, however, because they may be present as contaminants in artists' materials.

The distribution of trace elements within the pigment particles is determined during manufacture. During precipitation, some of the elements in the solution (copper, chromium, iron, magnesium, niobium, and antimony) are incorporated

Table 8 **Typical Composition of Rutile-Based Titanium Dioxide Products**

Element	*Rutile Ore*[a]	*Synthetic Rutile*[b]	*Typical Sulfate Process Rutile*[c]	*Typical Chloride Process Rutile*[d]	*Maximum Level in Pigment*[e]
Titanium dioxide, percent	95–96	92–96	80–97	80–97	—
Silicon, percent	0.33–0.82	0.07–0.47	0.014–3.83	0.04–3.0	3.8
Aluminum, percent	0.084–0.36	0.26–0.78	1.2–3.1	0.09–2.6	3.4
Iron, ppm	5,000–6,000	12,000–18,000	31–60	10–100	200
Niobium, ppm	1,000–3,000	1,800–3,600	38–2,200	<30–200	3,000
Vanadium, ppm	3,000–4,000	60–1,100	4–9.8	<3	20
Chromium, ppm	700–2,000	500–3,400	1–5.1	1	10
Manganese, ppm	<80–1,500	200–8,000	0.21–2.1	0.28–3.7	2,000
Magnesium, ppm	<60–200	100–540	30–125	10–100	300
Phosphorus, ppm	87–170	134–740	<90–790	<2,000	2,200
Zirconium, ppm	4,000–7,000	1,100–5,000	<30–3,400	10–80	500
Calcium, ppm	72–350	71–430	200–300	40–300	1,000

a. Beach sands (eastern Australia, South Africa) and alluvial deposit (Sierra Leone); Whitehead (1983).
b. Beneficiated ilmenites such as Hitox, Benelite, and Rupaque. From Hitox technical data sheet, Benelite Corporation of America; Whitehead (1983).
c. Rechmann (1978); Tioxide technical data sheets. Zirconium can be present as an additive in some grades.
d. Rechmann (1978); Irick et al. (1981).
e. Rechmann (1967). Pigment additives are included in the analytical results.

evenly throughout the pigment, while others (phosphorous, potassium, sulfur, and vanadium) precipitate later and concentrate on the surface (Rechmann, 1967).

Ground mineral rutile, which could have been used to a minor extent by artists, can be easily distinguished on the basis of its trace elements from any of the synthetic sulfate or chloride process rutile pigments. Mineral rutiles contain varying levels of iron, vanadium, chromium, tin, manganese, nickel, zirconium, and silicon ranging up to one thousand times those of rutile pigments (Rechmann, 1978). Occasionally, impurities such as niobium can be as high as 26% and tantalum up to 36% (Rose, 1969; Taylor, 1987). Table 8 shows the composition of products based on rutile.

4.2 Sources

There are three main starting materials for the production of titanium dioxide pigments; manufacturers may import ore from several geographical sources. The traditional sulfate process generally uses ilmenite ore (a black ore of approximate composition $FeO.TiO_2$ with 35% to 80% TiO_2 content). The more recent chloride process requires a richer ore with reduced iron content, such as mineral rutile (95% TiO_2), or alternatively, a treated feedstock such as slag (70%–85% TiO_2), or beneficiated ilmenite ("synthetic rutile," 90%–97% TiO_2).

Ilmenite is variable in composition and widely distributed in nature, with world production being about ten times that of rutile ore (Barksdale, 1966; *Geology and Resources*, 1976; Blakey & Hall, 1988). The two principal commercial sources are rock deposits and secondary deposits in beach and river sands. Significant rock deposits occur in Norway, Canada, the United States, Russia (notably the Ural mountains), South Africa, Finland, and Sweden. Titaniferous sand is found in Travancore in southern India, in the United States in western Florida, and in Australia, New Zealand, South Africa, Brazil, and Sri Lanka; Malaysia also produces significant quantities of ilmenite as a byproduct of tin mining. In the 1920s, world production was concentrated in Norway and the United States.

Mineral rutile, which typically contains 95% titanium dioxide, is found in all types of rocks (Robinson, 1922; Taylor, 1987) although natural deposits of commercial magnitude are rare. Australia is currently the chief exporter of rutile that is mined mainly from beach sand. Africa has large mineral rutile deposits, particularly in Sierra Leone and South Africa. Productive reserves of this mineral are also found in the United States, India, Norway, Sri Lanka, and Brazil.

To supplement supplies of mineral rutile, low-grade ilmenite is purified to remove iron, usually

by leaching with sulfuric or hydrochloric acid; the end product is "synthetic rutile," containing over 90% titanium dioxide. As an alternative, titanium slag, consisting of 70% to 85% titanium dioxide, can be produced as a byproduct of iron manufacture from ilmenite-hematite deposits, as in Richards Bay, South Africa (since 1978) and Quebec, Canada (since just after World War II). This slag can be used by both sulfate and chloride process plants.

An unusual and extensive mineral anatase deposit, which contains about 10% titanium dioxide, recently discovered near Araxá in Minas Gerais, Brazil, is being used to produce titanium concentrate. Potential problems in pigment manufacture may result from its relatively high phosphate content (Blakey & Hall, 1988).

4.3 **Preparation**

Coarse, colored titanium dioxide pigments based on the mineral rutile and mentioned in nineteenth-century literature were made by grinding the mineral and mixing it with a suitable medium. A 1917 patent drawing (fig. 10) illustrates the differences between ground rutile and precipitated titanium dioxide pigment. Jet mills were introduced about 1946 that were capable of reducing the particle size of ground material from over 1 μm to less than 0.5 μm (R. Ensminger, personal communication, 1988).

At present white titanium dioxide pigments are commercially produced by either the sulfate or chloride processes in numerous variations. Both processes can be tailored to produce either the anatase or rutile crystal form. The processes have been described as being "covered by a maze of patents which would require a second King Solomon to unravel" (Firing, 1935), and involve thousands of minor changes. At the core of each variation, however, remains the basic chemistry described below. Other methods have been developed, including the fluoride, bromide, nitrate, sulfide, and chloroacetate processes (Barksdale, 1966), but none has been used successfully on a commercial scale.

4.3.1 ***Sulfate process.*** The sulfate process is a complex industrial operation with extremely exacting conditions; it is based on the following simple chemical reactions:

$FeOTiO_2 + 2H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + 2H_2O$ (digestion)

$TiOSO_4 + 2H_2O \rightarrow TiO(OH)_2 + H_2SO_4$ (hydrolysis)

$TiO(OH)_2 \rightarrow TiO_2 + H_2O$ (calcination)

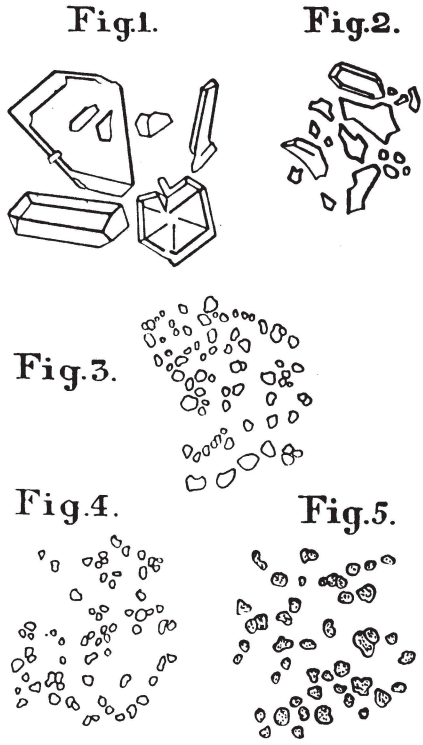


Fig. 10 Copy of a patent drawing from Goldschmidt (1917d). 1,000x. Printed at 440x. (1) Mineral rutile crystals (2) ground mineral rutile (3) "amorphous titanic hydroxide particles" on completion of hydrolysis (4) "amorphous titanium dioxide particles" following calcination of the material shown in (3), at 700°C (5) crystalline titanium dioxide particles produced during the controlled calcination of the material shown in (3), at 950°C.

The titanium-bearing ore (ilmenite or titaniferous slag) is ground and reacted with sulfuric acid. Removal of iron sulfates is effected by reduction to ferrous ions (usually by the addition of scrap iron) followed by cooling and removal of crystalline hydrated ferrous sulfate. The remaining titanyl sulfate in the solution is thermally hydrolyzed, precipitating as a hydrated oxide. The oxide is washed and calcined to produce either anatase or rutile pigment. The transition from the jet black ilmenite starting material to the brilliant white product is visible in the dust on the outside of some sulfate process plants (fig. 11).

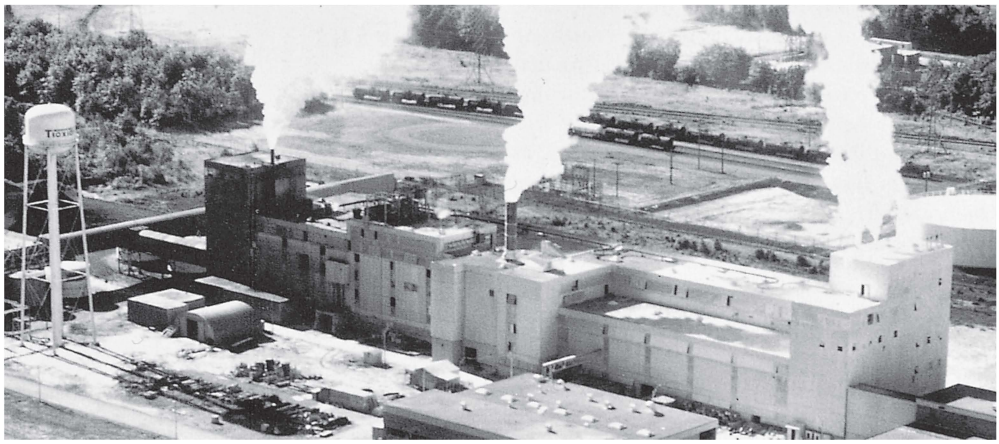


Fig. 11 The sulfate process plant of Tioxide Canada Inc., Sorel, Quebec. Black ilmenite ore is fed into the factory (left) and travels through the plant (right) during processing into white titanium dioxide for shipping. Photo from Tioxide Canada Inc.

The properties of the final pigment can be adjusted by careful control during the hydrolysis step. The flocculent precipitate formed during hydrolysis consists of micelles made up of colloidal crystallites of approximately 0.02 µm (Blakey & Hall, 1988). The agent that is added to promote nucleation can be varied to ultimately produce either the rutile or the anatase crystal structure. In the process modification introduced by Blumenfeld, which was the first to allow production of pure anatase, the "seed" was colloidal material produced by introducing a titanyl sulfate solution into hot water. Externally prepared seeds can also be used. Current commercial production of the rutile pigments is ensured by the addition of nuclei such as titanium orthohydrate. Addition or precipitation in the solution of barium or calcium sulfate prior to hydrolysis of the titanium dioxide was found to be the best method of producing composite pigments and the titanium dioxide is typically present as a particulate coating in the product. Following hydrolysis, the white hydrated oxide (titanic acid) or composite is purified by washing and filtration. In some early anatase pigments, compounds including phosphates, carbonates, borates, alkali metal salts, or halides were added for various purposes, such as neutralization or peptization (Wait & Weber, 1934). Compounds used to modify the properties of the final product can also be added (for example, antimony trioxide to reduce photoactivity). The precipitated titanium dioxide at this stage consists of aggregates of particles too small and loosely associated to be used as pigment. Formation of a usable pigment requires calcination, usually in a rotary oven at a temperature of 900°C.

The critical pigment properties begin to develop during calcination as the particles recrystallize and grow. Particle size and crystal structure (anatase or rutile) are adjustable at this point, and thus careful control is required. Early composite and "pure" anatase pigments contained minor amounts of rutile. The quantity of rutile that could be tolerated in the final product was limited, as uncontrolled rutilization results in the "welding" of micellar units into oversized aggregates, giving a coarse, sintered product, which is difficult to grind and not suitable as a pigment (fig. 12). Addition of particular seed nuclei during hydrolysis is one way to promote controlled formation of rutile; an alternate procedure is to add finely divided rutile (produced for example, by independent hydrolysis of $TiCl_4$ solutions) or other promoters just prior to calcination (Coates, 1950). The hydrous titanium oxide can also be doped with zinc or aluminum ions to allow rutilization at lower temperatures.

The final calcined products are ground to reduce the number of crystallites in the sintered particle aggregates. The ultimate crystal size is not controlled by grinding, but is determined during the precipitation and calcination stages (Work & Tuwiner, 1934). Manufacturers aim for a particle size of approximately 0.2 µm, but the range can be from 0.14 to 0.4 µm, depending on the application. The average particle size of early Titanox pigment was determined to be approximately 0.4 µm (Green, 1924). Particle size distri-

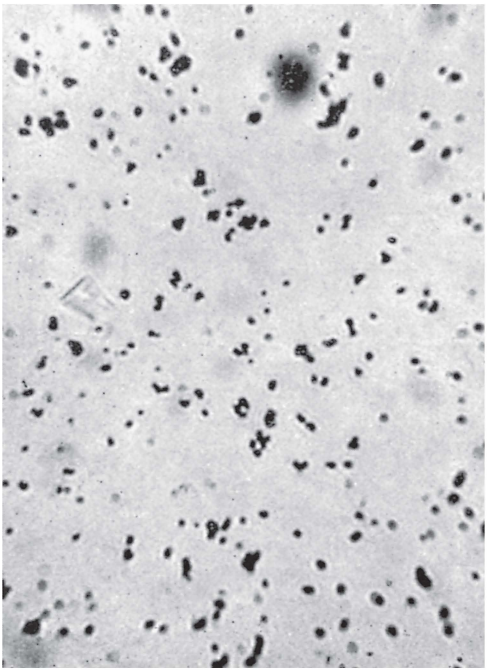


Fig. 12 Photomicrographs of rutile pigments by transmitted light. From Tinsley (1943), with permission. c. 440x.

A. Product of a properly controlled conversion to rutile pigment by calcination.

B. Uncontrolled rutilization during calcination results in a coarse, sintered rutile unsuitable for most pigmentary uses.

bution varies according to pigment grade, with composites generally having a wider size range. Hansen (1938) determined the particle size distribution of some early Kronos pigments by sedimentation methods. In 1941, the mean surface diameter of the newly introduced American-made NC rutile was given as 0.6 μm, larger than an anatase pigment having a diameter of 0.28 μm (Martin, 1941). Measurements given by Hughes (1952) suggest a trend for rutile pigments to have a slightly larger particle size than anatase pigment (0.20–0.23 μm as opposed to 0.17–0.19 μm), and for the composites to be larger yet (0.5–0.8 μm [Willets, 1936a, 1970; Willets & Bingham, 1948; Weider, 1952]). Grinding is typically done by micronizing, milling in a ring roller mill, ball mill, or sand mill, or in water containing silicate or phosphate dispersants. After they are filtered, washed, and dried, the uncoated anatase or rutile pigments may be given further surface treatment.

4.3.2 ***Chloride process.*** The more recent chloride process has the advantages of being a more compact, continuous operation, with fewer waste disposal problems, and a potentially purer distilled product. It is, however, a more difficult technology that requires more energy (Darby, 1980), higher-cost starting materials (which themselves have effluent disposal problems), equipment resistant to high temperature and corrosion, and high safety standards due to the toxicity of many of the chlorinated byproducts. The basic reactions of the chloride process are:

$$TiO_2 + C + 2Cl_2 \rightarrow TiCl_4 + CO_2$$
$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$$

In the current commercial process, an ore with high titanium dioxide content is reacted with gaseous chlorine in the presence of coke in a fluidized bed at approximately 900°C. This ore is usually mineral or synthetic rutile, although some variations in the process allow lower-grade ore such as ilmenite and leucoxene to be used. The titanium tetrachloride gas produced is scrubbed, condensed to a liquid, and purified by distillation. A rutilization catalyst such as aluminum chloride or other additives can be introduced if desired. Vapor phase oxidation of the tetrachloride at about 1,200°C is the final reaction. Crystallization

takes place in milliseconds rather than the hours of calcination required in the final step of the sulfate process. This gives rise to problems in the production of the less thermally stable anatase form, and it is not now made using this method. Chloride process anatase contained a significant amount of rutile (du Pont, c. 1975).

4.4 Pigment Grades, Adulteration, and Sophistication

Most of the titanium dioxide-containing paints and pigments designed over the years for various applications have contained additions of other compounds. The two principal reasons for these additions were the perceived higher cost of titanium dioxide compared to traditional pigments, and the desired improvement of properties (notably drying speed in oil, chalk resistance, and dispersion). As of 1985, more than 580 individual grades of pigment were produced worldwide (Blakey & Hall, 1988).

Various international groups have developed standards of manufacture for titanium dioxide white pigments, describing titanium dioxide content, volatile and soluble matter, sieve residues, and other characteristics. These include ISO 591-1977, reapproved 1985, ASTM D476-73, reapproved 1984 for the United States, and JIS K5116-1973, reapproved 1979 for Japan.

One of the main methods used to tailor pigment properties to specific end uses is the application of surface coatings. The many varieties currently manufactured can be categorized on the basis of their after-treatment (Dowling, 1972):

Uncoated dry-milled anatase and rutile (with less than about 2.5% of modifying elements such as zinc and aluminum)

Coated and refined anatase and rutile (typically over 93% to 97.5% titanium dioxide and with a coating of 1% to 3% alumina or silica and possibly organic treatment)

Coated and super-refined pigments (generally rutiles of 93% to 97.5% purity, with final milling carefully controlled)

Heavily coated and refined pigments (anatase or rutile, usually less than 93% titanium dioxide, up to 20% of coating material, such as silica or alumina)

Inorganic coatings of two or more colorless hydrous oxides may be applied either simultaneously or sequentially. The coating materials are typically added to a pigment slurry where the hydrated oxides are precipitated onto the pigment surface by variation of pH under very carefully controlled conditions. The most common materials are alumina and silica, but others such as zirconia are used for certain applications. Coatings have also included phosphorous, boron, barium, magnesium, zinc, and tin compounds, and small amounts of cerium, chromium, manganese, or cobalt compounds. Inorganic coatings of alumina and silica are not necessarily continuous (Wiseman, 1976), and analysis has shown that silica tends to deposit out first, resulting in a surface rich in alumina (Toussaint, 1978). The unevenness of pigment coatings has been illustrated in electron micrographs (Kämpf & Völz, 1968); see also section 5.3.4.

Secondary organic surface treatments are applied more often to rutile pigments than anatase grades, typically at a level of up to 1%. The most commonly employed compounds are polyols, long-chain alcoholic amines, and silicone-based materials, for example, pentaerythritol, triethanolamine, and dimethyl siloxane (Whitehead, 1983).

Materials added prior to crystallization may form mixed phases with the titanium dioxide. For example, addition of antimony oxide can produce an antimony–titanium–oxygen compound during calcination, and zinc oxide can transform to zinc titanate (Barksdale, 1966). Chalk-resistant phthalate coatings were found to consist of a semivitreous shell of titanium phthalate.

Tinted titanium dioxide pigments in a range of colors have been produced by several methods: the absorption of organic pigments on the white base, partial reduction to a lower oxide (Goldschmidt, 1917b, c), incorporation of trace metals (McKinney & Smith, 1935), or calcination to form titanate compounds such as lead titanate, which was introduced in 1935 (Goldschmidt, 1917a). The colors include red, yellow, blue, green, gray, and buff (Strauss, 1937). Some of these tinted pigments have a titanium dioxide content of approximately 98% and retain the advantages of the pure pigment.

Color in the pigment is not always a desirable characteristic. In the early years of development of anatase- and rutile-based pigments, production difficulties often resulted in inferior yellow products that were impure, coarse, or a mixture of both forms (see section 2.2 and 4.1). This yellowness was sometimes masked through the addition of blue or violet tinters or optical brightening agents.

Pearlescent pigments, introduced in the 1960s, are made by depositing anatase or rutile on a large particle substrate (5-150 μm) with a low refractive index, such as mica (Greenstein, 1973). The

thickness of the titanium dioxide layer can be adjusted to produce different interference colors; a coating of colored metal oxide, including iron and chromium oxides, can be added (Goebel & Stoecklein, 1987). Artists using automotive spray paint for special effects may well be using products containing these pigments.

A type of pigment introduced in the mid-1970s following several years of development consists of large-size polymeric beads (typically over 10 μm) containing titanium dioxide, combined in some products with air-filled microvoids (Whitehead, 1983; Stieg, 1985). Pigments of this type have found limited use in paper products as well as in flat latex paints.

5.0 Identification and Characterization

Analytical methods typically used on objects of artistic and historical interest are optical microscopy, chemical analysis, and instrumental methods. Optical microscopy can give information about the morphology and identity of various components of many pigments. However, in the case of titanium dioxide pigments, practical difficulties intervene in obtaining optical measurements because of the extremely small particle size. Supplementary analysis is often required to distinguish some formulations.

Titanium is a frequent impurity in mineral-based pigments, and if not removed during the manufacturing processes it can remain in paints as well as in art objects, including those of glass and ceramics. As a common impurity in clays and mineral pigments, it can appear in natural earth colors such as ochers (Feller, 1971), green earth (A. Roy, personal communication, 1986), and Egyptian blue (Matson, 1957). In oil paintings by Jan Vermeer, titanium was detected in 106 out of 151 analyses of white, red, blue, yellow, green, brown, gray, and black paints in which titanium dioxide white pigment was not present (Kühn, 1969). Small amounts of titanium were found in plaster in wall paintings at Ajanta and Ellora in India (Paramasivan, 1975), argillite carvings from Slatechuck Creek in Canada (rutile); (Adair, 1979), a wall painting at Dunhuang, China (J. Sirois, personal communication, 1988), and drawing crayons in the caves at Alta Mira, Spain (Garrido, 1978). Titanium may be detected in clay-filled papers, as most filler clays contain 1% to 3% titanium (Brandon, 1981). Low levels of titanium have been detected in European and American papers made from 1770 to 1900 (Hanson, 1981), in black ink areas of paper from a Gutenberg Bible of the 1450s (Cahill et al., 1984), and in twelfth- to fifteenth-century parchments (Cahill et al., 1987). Titanium-containing artists' pigments other than titanium dioxide are available: for example, light yellow lead titanate, $PbTiO_3$; sun yellow, $Sb_2O_3/Sb_2O_4.NiO.TiO_2$; titanium green, Co_2TiO_4; and black iron titanate, $FeTiO_3$. Potassium titanate, which appears opaque white but has enhanced ultraviolet reflectivity at lower wavelengths than titanium dioxide, is used in some papers containing fluorescent dyes (Willets, 1970). Several identification techniques are often necessary to correctly interpret the composition of a titanium-containing pigment.

Even the confirmation of rutile or anatase using other methods may be subject to interpretation, as is illustrated by the evaluation of the fifteenth-century Vinland map (McCrone, 1976). Pigmentary anatase was found in microscopic samples, although the small amount present has introduced doubt as to whether its presence indicates forgery (Cahill et al., 1987). As with any analysis of historical or artistic material, the interpretation of the analysis can differ depending on the sampling strategy and analytical technique used.

5.1 Optical Microscopy

Both anatase and rutile are tetragonal in crystal form but they are not isomorphous. Both are birefringent. Average values for properties such as refractive index are often quoted for the precipitated pigments, based on the randomly oriented crystallographic direction of large numbers of very small particles. Some physical properties are given in tables 9 and 10. The outstanding optical characteristic of synthetic rutile and anatase, when observed microscopically, is very high relief that results from the extremely high refractive indices. In routine microscopy, the refractive indices of the pigment can rarely be determined because of technical difficulties. When mounted in a medium such as Aroclor 5442 (n=1.66), pigment particles appear black in transmitted light, and for this reason it is essential that observation be augmented by examination in reflected light, in which the particles appear white. The fine particle size can give the preparation the appearance of a foggy cloud that shows low-level birefringence under crossed polars. The birefringence does not disappear when the sample is treated with dilute

Table 9 **Physical Properties of Anatase and Rutile Pigment**[a]

Property	*Anatase*	*Rutile*
Crystal structure	Tetragonal	Tetragonal
Optic sign	Uniaxial, negative	Uniaxial, positive
Refractive index (mineral data)	2.54–2.55 n_ω 2.5612; n_ϵ 2.4880	2.71–2.72 n_ω 2.605–2.616 n_ϵ 2.899–2.903
Birefringence	High, (–) 0.073	Very high, (+) 0.29
Density (g/cm^3)	3.7 (coated) to 3.9	3.75 (coated) to 4.2
Hardness (Mohs scale)	5–6	6–7

a. Data from Slepetys (1972); Shelley (1975); Solomon and Hawthorne (1983); Whitehead (1983); Blakey and Hall (1988).

Table 10 **Refractive Index and Specific Gravity of Various Titanium Dioxide Pigments**[a]

Pigment Type	*Average Refractive Index*	*Specific Gravity*
Titanium dioxide (amorphous)	1.8–2.23	—
"Pure" anatase (example: Titanox A)	2.3–2.65	3.88–3.94
Anatase composite 25%TiO_2/75% $BaSO_4$ (example: Titanox B)	1.89–2.3	4.1–4.3
Anatase composite 30% anatase/75% $CaSO_4$ (example: Titanox C)	1.87	3.13
Rutile composite 30% rutile/75% $CaSO_4$	1.98	3.25

a. Data from Coffignier (1922); Heaton (1922); Hagar (1927); Hixson and Plechner (1929); Déribéré (1936).

nitric acid, as it does in the case of lead white or zinc white. Typical pigment photomicrographs are shown in figure 13.

Rutile particles are colorless tetragonal crystals that are usually prismatic, often acicular, and likely to have vertical striations (McCrone & Delly, 1973). In the size range of 1 μm, the particles appear to be evenly rounded or oval, with frequent twinning; cleavage may be either distinct or poor; fracture is conchoidal to uneven. In the larger particles, low-to-moderate first-order interference colors may be observed. Currently produced pigmentary rutile is generally of uniform size in the range of 0.2 to 0.5 μm, too small for crystal faces to be discerned. Frequently, agglom-

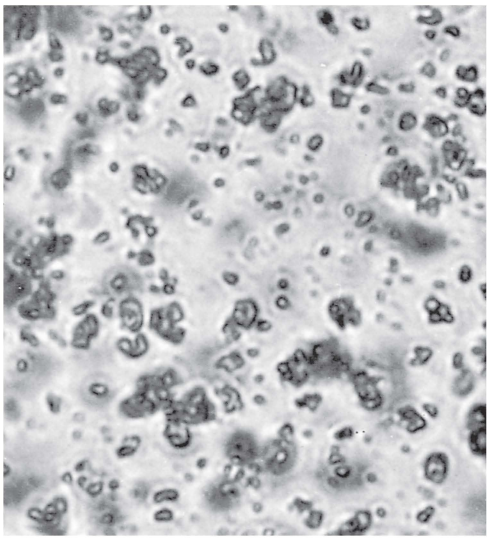
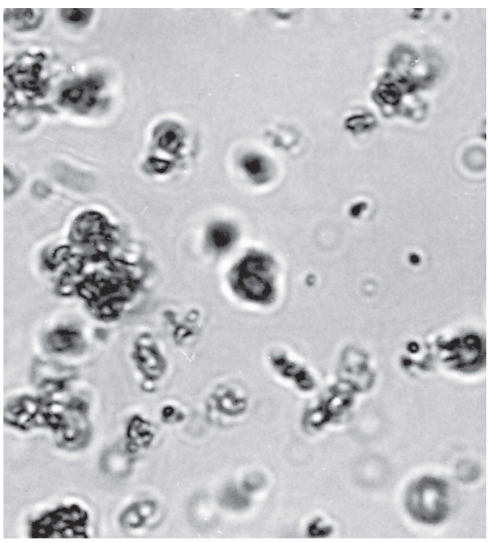
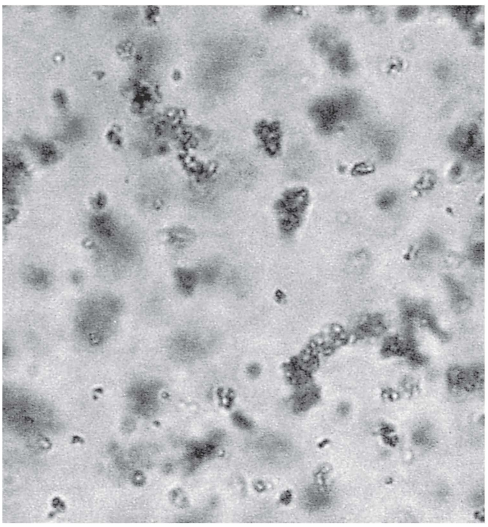


Fig. 13 Photomicrographs of titanium dioxide white pigments by transmitted light, mounted in Aroclor 5442, n=1.66. 100x oil immersion objective. 1,250x.

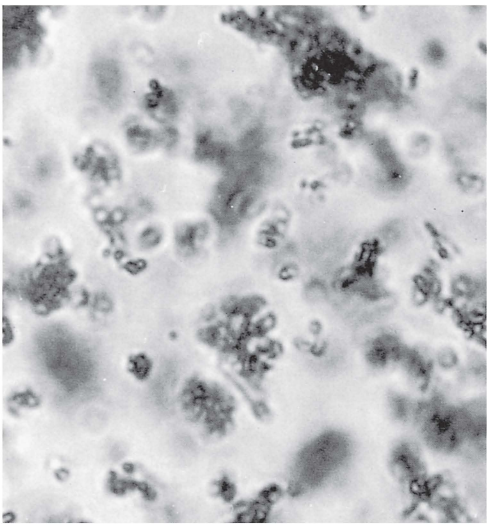
A. Anatase pigment, Titanox A, Titanium Pigment Company. Samples A–C from Forbes Pigment Collection, Freer Gallery of Art, Smithsonian Institution, Washington.



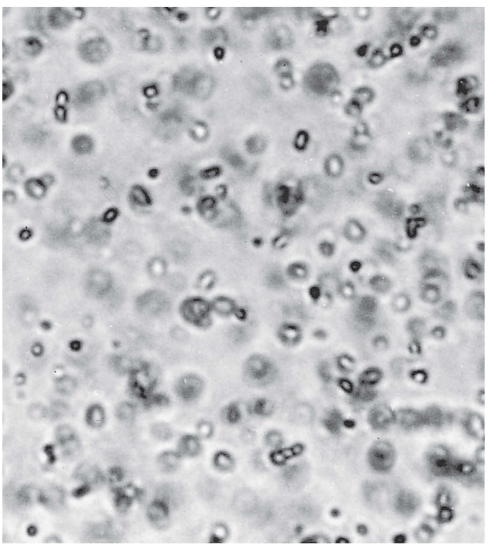
B. Anatase and barium sulfate composite pigment, Titanox B, Titanium Pigment Company; Fezandie, May 1936.



C. Anatase and calcium sulfate pigment, Titanox C, Titanium Pigment Company.



E. Rutile and calcium sulfate composite pigment, Titanox RC-HT. Sample from NL Chemicals, Inc.



D. Rutile pigment, New Jersey Zinc Company, R-745-15, collected June 1969. Sample from Freer Gallery of Art.

erates are observed that may appear tan to gray-brown due to light scatter or opaque due to the high indices.

Anatase particles are comprised of colorless, tetragonal crystals that are usually pyramidal, and have perfect basal and {011} cleavages; dispersion is strong (McCrone et al., 1979). Some anatase pigments may have acicular particles. Most particles appear white between crossed polars due to light scattering, while a few may show genuine low first-order polarization colors and extinction. Pigment particles are typically from 0.2 to 0.5 μm in size, often equant. Agglomerates of up to several micrometers in diameter may form.

The optical characteristics of mineral anatase and rutile were described by Palache et al. (1944) and Shelley (1975). When ground, these do not have the uniform fine particle size and generally rounded shape of the modern precipitated products (see fig. 10). Rutile, when produced under conditions of poor control of the calcination process, also has a coarse particle size and differs in morphology from the finer material in most pure rutile pigments (see fig. 12).

The distinction between anatase and rutile can be made microscopically using polarized light and a mounting medium consisting of a melted mixture of sulfur and selenium, 14:86 by weight (McCrone, 1990). The glassy, deep red medium has a refractive index of 2.59, close to the omega index of both anatase and rutile; the particles of both compounds will therefore nearly disappear twice during a complete rotation of the microscope stage. Both indices of rutile are higher than 2.59, while those of anatase are both lower. If the microscope is focused just above best focus, rotating the stage will show rutile particles as having bright centers and anatase particles as having dark centers. This test, using the phenomenon of the Becke line, should be done in close comparison to similarly mounted reference standards.

In a sample from a work of art, the distinction

between a true composite and a pigment that is a simple mixture with barium sulfate can be difficult to observe in the light microscope. Average particle size of composites is generally greater than that of pure grades, with a wider distribution of particle sizes and a higher proportion of large particles (see section 4.3.1). Under polarized light, an experimental composite pigment dating to 1914 was seen to consist of luminous calcium sulfate particles coated with smaller particles of opaque titanium dioxide (Barton, 1914). Comparative micrographs of some early pigments are discussed by Ragg (1927) (see also fig. 13). In some cases, a differentiation can be made by testing with methyl violet, which colors titanium dioxide preferentially; micrographs of this test show that mechanical mixtures contain small violet particles of titanium dioxide and large white particles of barium sulfate, whereas composites appear as gray particles of reasonably uniform size (Bancelin & Crimail, 1939). In calcium sulfate composites, moderately birefringent anhydrite ($CaSO_4$) particles can often be discerned. Anatase may be distinguished from calcium sulfate and barium sulfate in mixed pigments using ultraviolet microscopy (Haslam & Hall, 1934).

Colored titanium dioxide pigments, made either by absorbing an organic colorant onto titanium dioxide, or by chemical alteration, can be distinguished microscopically from mixtures of pigment and colorant, as all particles have a uniform color and morphology. Paper filled with titanium dioxide can be examined using cross-section methods (Quackenbush, 1979).

5.2 Chemical Identification

Although both forms of titanium dioxide are resistant to chemical attack, they can be brought into solution for microchemical identification. The insolubility of titanium dioxide in alkalies and all but the most aggressive acids can be used to advantage for its separation from other materials with which it may be mixed. Other pigments insoluble in mineral acids include barium sulfate, silica, and china clay.

5.2.1 ***Hydrogen peroxide test for titanium.*** Titanium dioxide can be dissolved with hot sulfuric acid. This causes no problems when powdered pigment is available for testing, but in samples containing admixed medium, such as paint or paper, the presence of black, charred organic material makes the color reaction difficult to see. The following method, developed by Flaschka (1951) to accelerate pigment analysis time, circumvents this problem and can be used on paint and pigment samples:

> In the flame of a Bunsen burner melt a bead of potassium hydrogen sulfate ($KHSO_4$) in a tiny platinum wire loop. Touch the drop to the sample, picking it up, and melt the bead repeatedly until the organic material chars and disappears in the bead, leaving the bead milky in appearance. This procedure may take several passes through the flame. Dissolve the bead in one or two drops of dilute sulfuric acid (concentrated acid diluted 1 in 10 by volume) in a test tube, with the assistance of heat from the burner. Place a drop of this solution on a spot plate or in a test tube and add a drop of 3% hydrogen peroxide (H_2O_2); if titanium is present, the drop will turn a yellow or orange color.

This test has been used to detect approximately 1 µg of titanium in powdered pigment; titanium in oil paint samples as small as 20 µg can be detected by this method. A sample on paper, which contains considerably less pigment than paint, requires a larger sample for the color reaction to be visible. No interferences were found from any other white pigments or from colored pigments containing elements that have been suggested as causing interferences, such as chromium (chrome green, orange, or yellow), molybdenum (in molybdenum orange), or iron (in hematite). Potential interferences from media, acetate-based in particular, are removed by the fusion-ashing step.

5.2.2 ***Other chemical tests.*** A test using mercury to reduce titanium can be performed on pigment samples (McCrone, 1982):

$$2Hg^0 + Ti^{4+} \rightarrow Ti^0 + 2Hg^{2+}$$

A stain for titanium in dried paint layers, using phenazone (antipyrine) and potassium iodide in hydrochloric acid was described by Whitehead (1939).

Determination of titanium, as well as silicon and aluminum coating materials, by wet-chemical methods is discussed in such publications as ASTM Standard D-1394-76, reapproved 1987. It should be noted that silicon was present as an impurity in early pigments (see section 4.1), and it may also be found infrequently in the silica base of some composites. Most wet-chemical methods are based on reduction of titanium to Ti^{3+} in a sulfuric acid solution and titration with an indicator. A quantitative procedure based on hydrogen peroxide for the determination of titanium dioxide in paper is given in TAPPI T439 (Brandon, 1981) and ASTM Standard D-686-76, reapproved 1982.

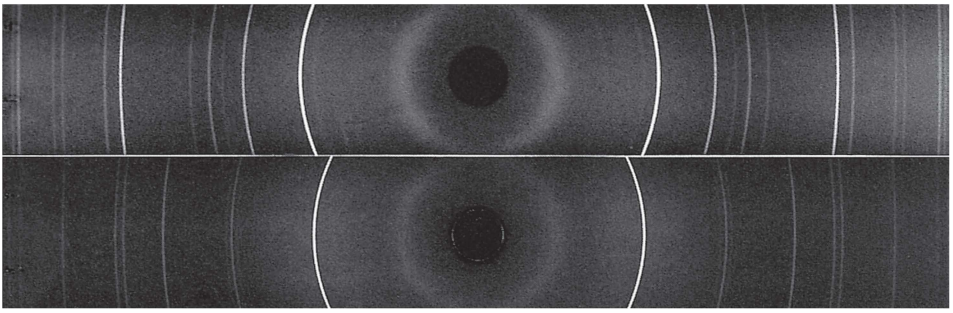


Fig. 14 Typical x-ray diffraction powder patterns of titanium dioxide pigments (CuKα radiation).

A. Anatase 99.9%. Aldrich Chemical Co., Inc.
B. Rutile R-HD6X. Tioxide Canada Inc.

5.3 Instrumental Methods of Analysis

5.3.1 ***X-ray diffraction.*** The anatase and rutile forms of titanium dioxide can be distinguished from each other and from co-precipitated or admixed pigments such as barium white or zinc white by x-ray diffraction. Data for anatase and rutile are given in table 11. Typical patterns for the two more common forms are shown in figure 14. Interferences from other artists' pigments can be overcome with the high resolution of diffractometry. Aragonite ($CaCO_3$) and lead sulfate ($PbSO_4$) have lines close to the principal line of rutile at 3.25 Å, these occur at 3.27 and 3.22 Å, respectively. The principal line of zinc white at 2.476 Å overlaps slightly with one of the stronger rutile lines at 2.487 Å. Anhydrite ($CaSO_4$) has its major line at 3.50 Å, close to the strongest line of anatase at 3.52 Å. The diffractometry method given by ASTM D-3720-84 reports interference from $CaSO_4$ in the quantification of anatase and rutile mixtures, with extreme particle size differences having an effect on the results. Diffraction patterns of commercial pigments can illustrate some of these spectral overlaps (König, 1956). The amorphous alumina and silica coatings cannot be detected in samples of surface-treated pigments by x-ray diffraction, using either cameras or diffractometry.

Both rutile and anatase belong to the tetragonal system (ditetragonal-bipyramidal); their structure is illustrated in figure 15. Rutile has lattice constants a=0.459, c=0.296 (in nanometers), and space group D_{4h}^{14} with Z=2 and point group $P4_2/mnm$, while the values for anatase are a=0.379, c=0.951, and the space group is D_{4h}^{19} with Z=4 and point group $I4_1/amd$ (Cromer & Herrington, 1955; König, 1956; Swanson et al.,

Table 11 **X-ray Diffraction Data for Anatase and Rutile**
$CuK\alpha_1$ λ=1.54056 Å; 25°C

Anatase[a]		*Rutile*[b]	
d (Å)	*I*	*d* (Å)	*I*
3.52	100	3.25	100
2.431	10	2.487	50
2.378	20	2.297	8
2.332	10	2.188	25
1.892	35	2.054	10
1.6999	20	1.6874	60
1.6665	20	1.6237	20
1.4930	4	1.4797	10
1.4808	14	1.4528	10
1.3641	6	1.4243	2
1.3378	6	1.3598	20
1.2795	<2	1.3465	12
1.2649	10	1.3041	2
1.2509	4	1.2441	4
1.1894	<2	1.2006	2
1.1725	2	1.1702	6
1.1664	6	1.1483	4
1.1608	4	1.1143	2
1.0600	2	1.0936	8
1.0517	4	1.0827	4
1.0436	4	1.0425	6
1.0182	2	1.0364	6
1.0070	2	1.0271	4
0.9967	2	0.9703	2
0.9555	4	0.9644	2
0.9464	4	0.9438	2
0.9246	<2	0.9072	4
0.9192	2	0.9009	4
0.9138	2		
+additional lines below *I*=4		+ additional lines below *I*=12	

a. *JCPDS Powder Diffraction File* 21-1272 (*JCPDS*, 1988).
b. *JCPDS Powder Diffraction File* 21-1276 (*JCPDS*, 1988).

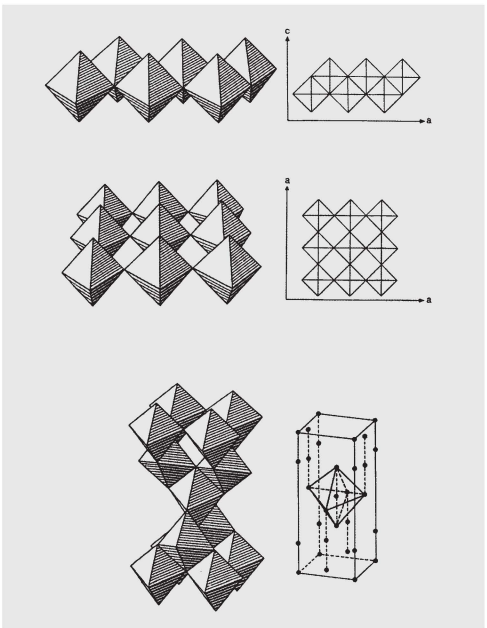
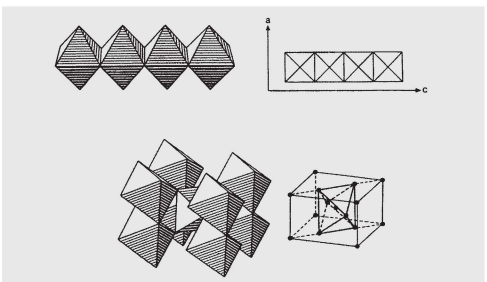


Fig. 15 Crystal structure of anatase and rutile. From *Kronos Guide* (1968), with permission.
A. Octahedral layers and chains in anatase, lattice arrangement, unit cell.



B. Octahedral chains in rutile, lattice arrangement, unit cell.

1969). In both forms, the titanium atom is surrounded by octahedra of six oxygen atoms; each oxygen is bonded to three titanium atoms. The octahedra are joined in such a way that in rutile each octahedron has sides in common with two other octahedra, and in anatase with four other octahedra. The existence of shared edges in a structure decreases its stability; consequently rutile is the more stable modification (Tinsley & Bowman, 1949).

X-ray diffraction investigations in 1924 on the early pure pigment produced in France showed that the anatase structure was already formed in the "amorphous" hydrolysis product (de Rohden, 1967). X-ray diffraction is now commonly used in production control to monitor the ratio of anatase to rutile. Most commercial preparations of anatase or rutile contain a trace of the alternate form. If a sufficient sample is available for x-ray diffractometry, quantification of the two forms is easily made to levels of about 1% (Jenkins & De Vries, 1970). Alternatively, by using a Gandolfi or Debye-Scherrer camera, the most intense lines of the minor component can be detected without difficulty at a concentration of 5% (see fig. 14).

Direct diffractometry has also been applied for the identification and quantification of fillers and pigments on paper (see for example, Breunig & Weninger, 1974; Bluhm et al., 1984).

5.3.2 ***Infrared and Raman spectroscopy.*** Pure anatase and rutile can be differentiated from each other and from other white pigments on the basis of their infrared spectra (fig. 16). The pigments are characterized by broad absorptions in the 700 to 400 cm^{-1} range. Rutile has a strong absorption at 675 cm^{-1}, with a shoulder at 550 cm^{-1} and a weaker peak at 420 cm^{-1}. Anatase has broad major absorptions at 690 and 540 cm^{-1}. The rutile spectrum was discussed in detail by Farmer (1974). Quantification of anatase-rutile mixtures was carried out by Afremow and Vandeberg (1966). Spectral features due to hydroxyl ions on the surface of anatase and rutile were described by Solomon and Hawthorne (1983). Processing residues such as chloride have a minor effect on the infrared spectrum (Jackson & Parfitt, 1971; Morterra et al., 1979). Slight differences between spectra of natural anatase and the commercial pigment noted by Tarte (1963) may be due to particle size and shape or to a noncrystalline component in the pigment. During analysis of dry pigment samples in the diamond-cell microsampling device, the high refractive index of titanium dioxide can cause problems of scattering and band distortion (Laver & Williams, 1978). Mixtures of some pigments such as titanium dioxide and zinc white can be problematic due to an overlap of peaks. Coatings of silica and alumina can be detected in infrared spectra (fig. 17) (see also Feller et al., 1971).

Titanium dioxide cannot be identified in paper coatings using attenuated total reflectance with a KRS-5 crystal since the refractive indices of anatase (2.55) and rutile (2.71) are higher than that of the crystal (2.4). The crystals having higher refractive indices than titanium dioxide, such as germanium, do not transmit frequencies in

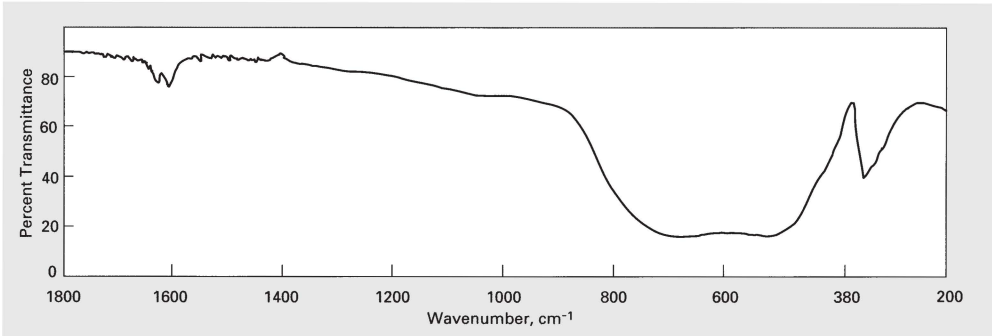
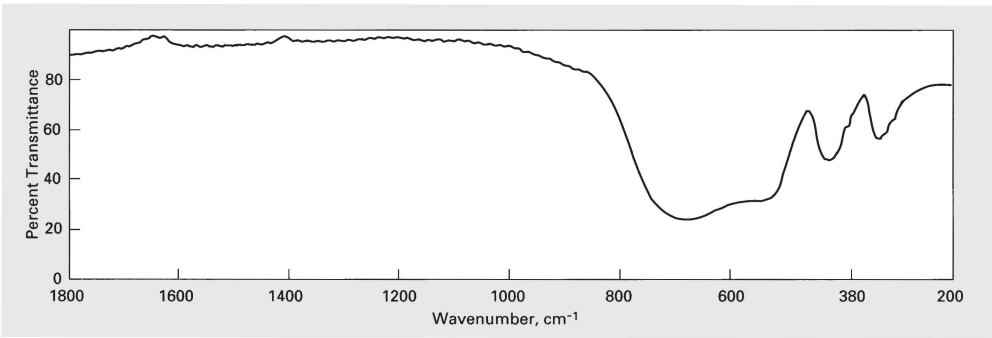
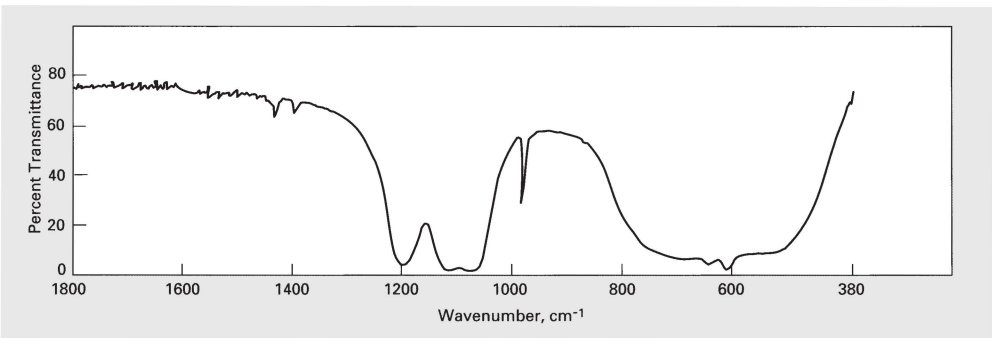


Fig. 16 Infrared spectra of titanium dioxide (samples run as KBr pellets).

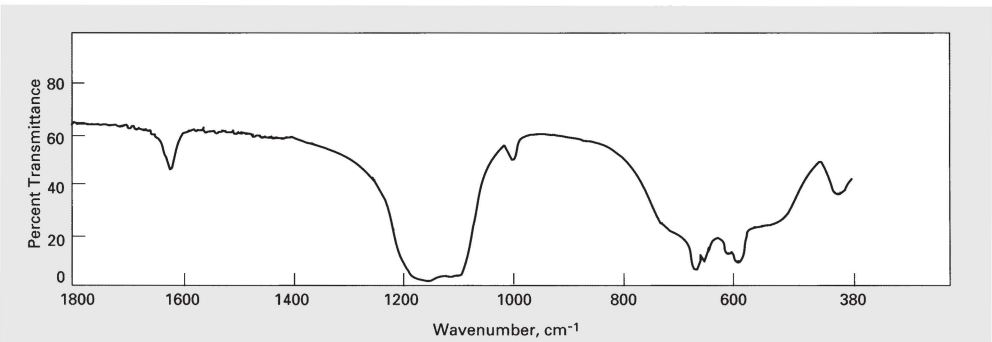
A. Anatase.
B. Rutile.





C. 25% anatase, 75% $BaSO_4$ (composition similar to early composite pigment).

D. 30% rutile, 70% $CaSO_4$ (composition similar to early composite pigment).



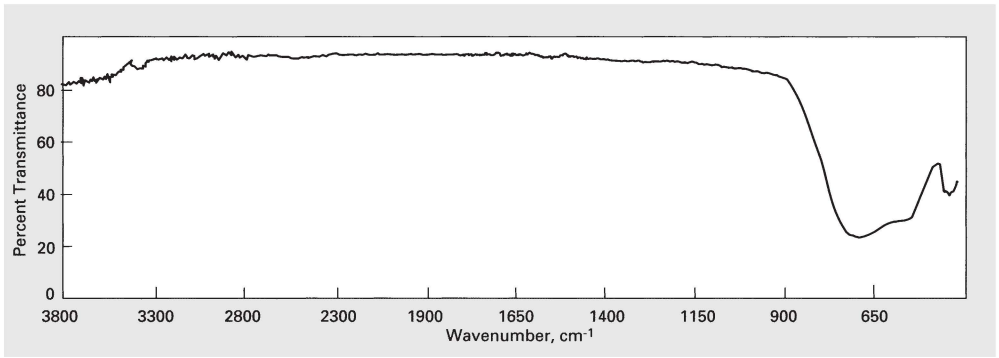
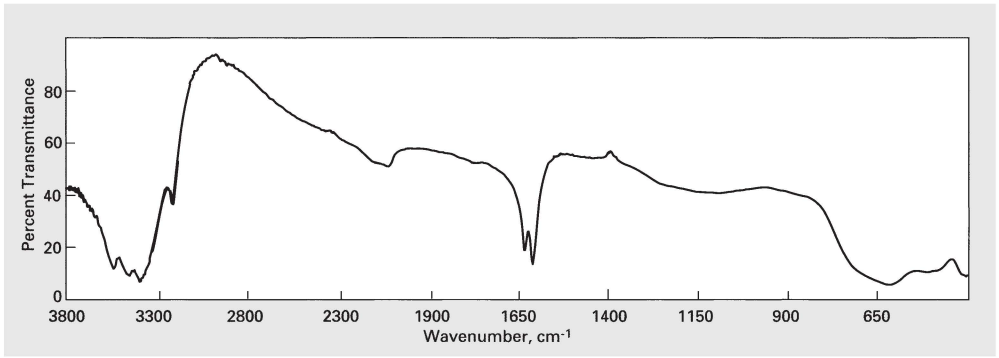
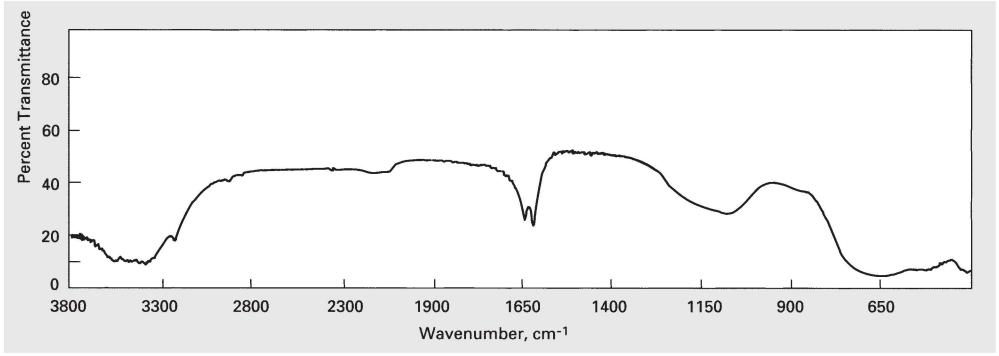


Fig. 17 Infrared spectra of coated titanium dioxide pigments. A. Rutile, no coating.



B. 93% rutile coated with Al_2O_3 and SiO_2.



C. 82% rutile coated with Al_2O_3 and SiO_2.

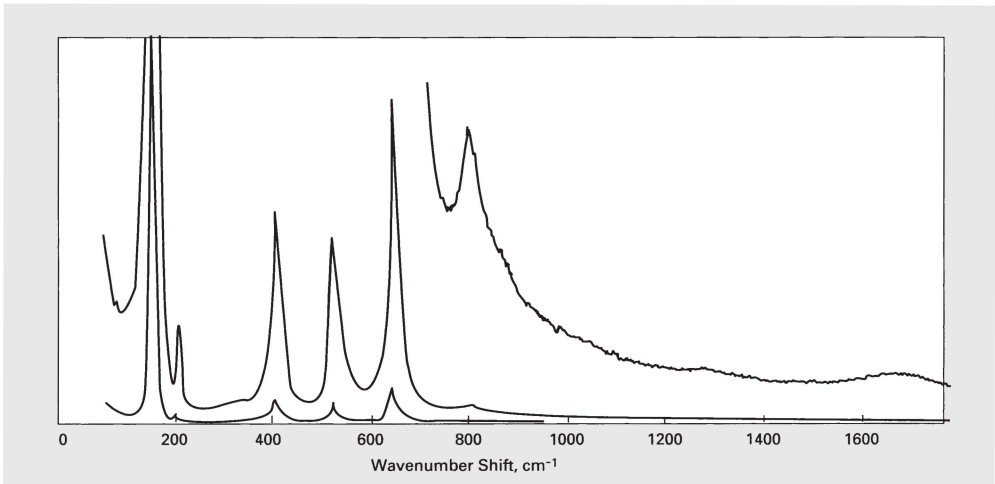
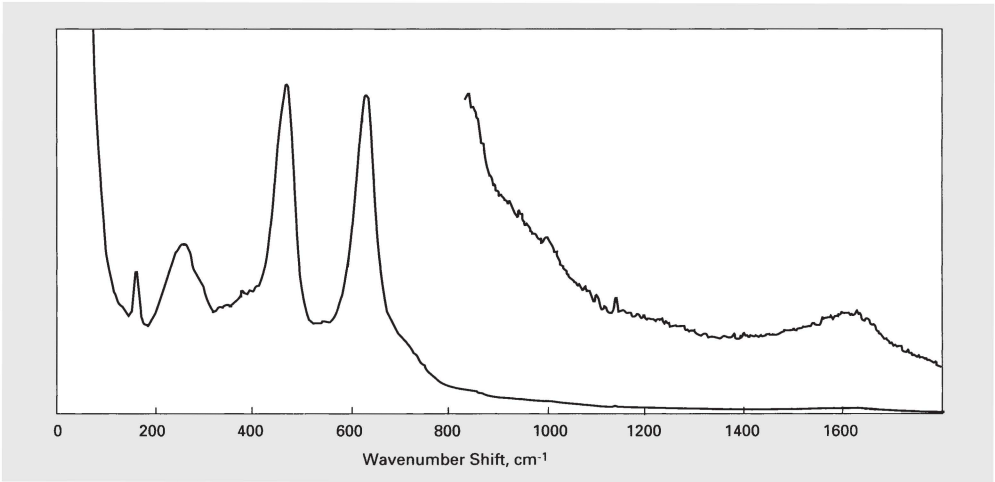


Fig. 18 A. Raman spectrum of pigment grade anatase (Kronos AD) with expanded scale (at right) to show small peaks over 850 cm^{-1} and reduced scale below to show the relative size of the major peak at 143 cm^{-1}. Raman spectra by Doug Moffatt, National Research Council of Canada.



B. Raman spectrum of pigment grade rutile (Kronos RLK) with expanded scale (at right) to show peaks over 700 cm^{-1}.

the region of the major absorption bands of these pigments (Michell, 1972).

Fourier transform infrared-photoacoustic spectroscopy has been used to study the effects of weathering in the surface layers of samples from paint films containing titanium dioxide (Hodson & Lander, 1987).

Raman spectroscopy is effective in distinguishing anatase from rutile (Capwell et al., 1972). Anatase shows its most intense line at 143 cm^{-1}, with lesser lines at 194, 326, 393, 512, 635, and 794 cm^{-1}, while rutile has two major lines at 442 and 607 cm^{-1} and others at 143, 236, and 825 cm^{-1}. The major vibrations were classified by Beattie and Gilson (1968). Figure 18 illustrates these differences. Figure 19 shows the spectrum of a sample from the blue paint containing rutile from *Animal Environment* (c. 1980s) by Canadian artist Norval Morrisseau. Rutile was also identified from infrared spectra in areas of blue in *Poppy Tree* (c. 1980s), another painting by Morrisseau (fig. 20). The Raman method is particularly sensitive to anatase, and gives a very intense band at 143 cm^{-1}; rutile shows a weak band at this

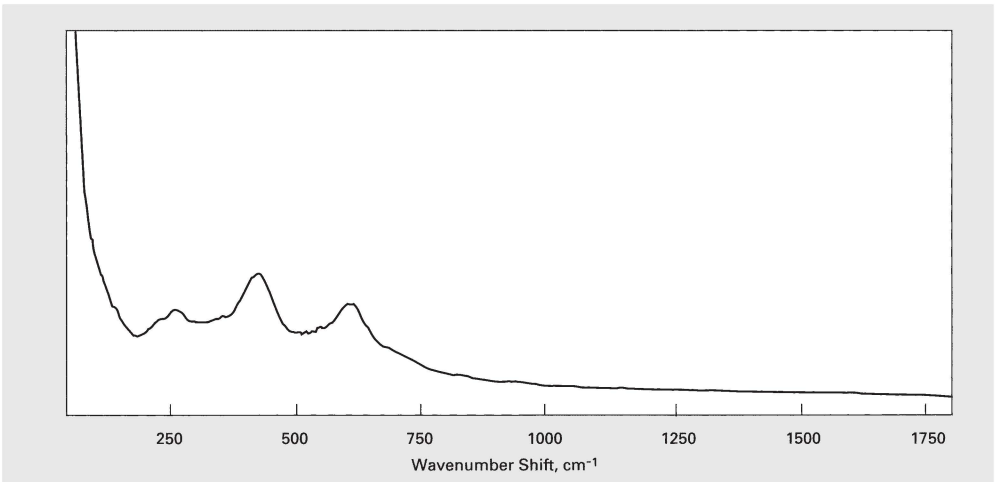


Fig. 19 Raman spectrum of a paint sample containing rutile, from *Animal Environment* c. 1980s, a painting by Norval Morrisseau. Wavelength 514.5 nm, argon ion laser, 20mW at sample, 90° scattering.

frequency. In a 1:1 mixture of anatase and rutile by weight, the peak height at this wavelength is approximately thirty times more intense than the highest peaks due to rutile (Capwell et al., 1972). Raman spectroscopy can be used to determine semiquantitatively the anatase content of mixtures with rutile (Beattie & Gilson, 1968).

Raman microspectrophotometry can also be used on pigment in situ on artifacts or on small samples (Braga et al., 1992); despite the decrease of signal to noise ratio, identification of major components is often possible. Coupry et al. (1987) reported some difficulty in identifying zinc oxide in a mixture with rutile (Raman peak for zinc oxide at 436 cm^{-1}). Further, for some rutile and anatase pigment samples in which zinc or barium were indicated by x-ray spectrometry, there were no Raman peaks detected that could be attributed to zinc or barium compounds. However, a band at 983 cm^{-1} appearing in spectra of samples from two paintings by Pablo Picasso was attributed to admixed barium sulfate. During microspectrometric analysis of samples from paintings and test mixtures made by Lefranc et Bourgeois, no interfering fluorescence from pigments, oil medium, or driers was observed. Some fluorescence, attributed to the presence of gelatin, has been noted in analyses of anatase in watercolor paper (Delhaye et al., 1984). The low-temperature spectrofluorimetric method referred to in section 3.1.2 allows distinction between some sulfate and chloride process pigments.

5.3.3 ***Spectrochemical analysis.*** Titanium dioxide is relatively involatile in the arc compared to other oxides, such as zinc oxide (Ahrens & Taylor, 1961). Spectral emission lines between 2000 and 9000 Å excited in an arc source, in order of decreasing sensitivity, are 3653.5, 4981.7, 3349.9, 3341.9, and 3372.8 Å; visible lines emitted in an electric arc are at 4982, 4999, 5007, and 5014 Å (Epstein, 1977). Arc and spark analysis lines are described in more detail by Török et al. (1978) and in the *M.I.T. Wavelength Tables* (1969).

The absolute limits of detection of titanium using different excitation sources have been compared by Zil'bershtein (1977). The extensively used dc carbon arc is one of the most sensitive sources, allowing detection of as little as 0.2 ng of the element. For analysis of paint samples, Crown (1968) gave a general detection limit for the method as 1 to 10 ppm.

A method for quantitative spectrochemical analysis of eighteen impurity elements in titanium dioxide was given by Wells and Carpenter (1962); working concentration ranges are generally 10 to 1,000 ppm. The elements that are potentially useful to distinguish chloride-process and sulfate-process pigments are present at levels near or below the detection limits for emission spectroscopy with a spark or dc arc source, and consequently a more sensitive method is required (*Kronos Guide*, 1968). Using an inductively coupled plasma (ICP) source, analysis of coating and trace

Fig. 20 Norval Morrisseau, *Poppy Tree*, c. 1980s, acrylic on canvas, Glenbow Museum, Calgary, Alberta 986.226.5. Areas of blue contain rutile, determined by FTIR analysis.

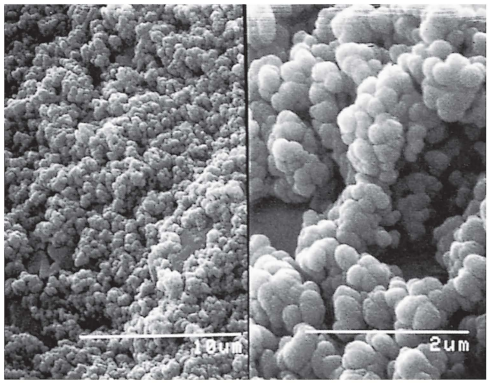
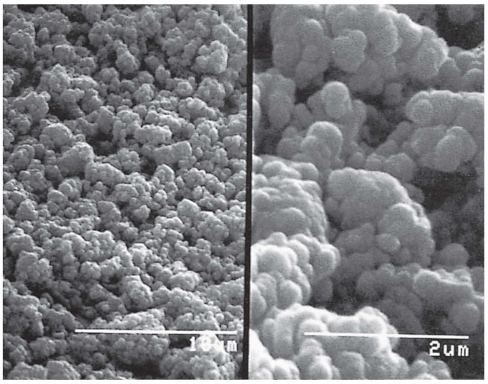
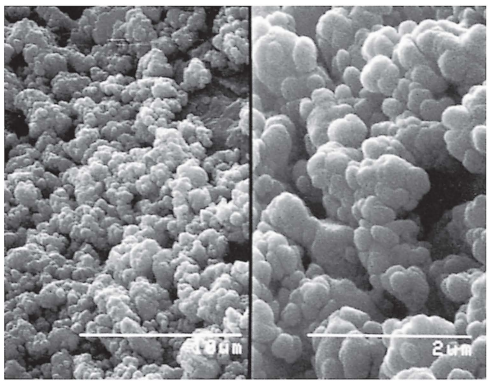


Fig. 21 Scanning electron micrographs of samples shown in figure 13A–E. *Left:* 2,300x. *Right:* 11,000x.

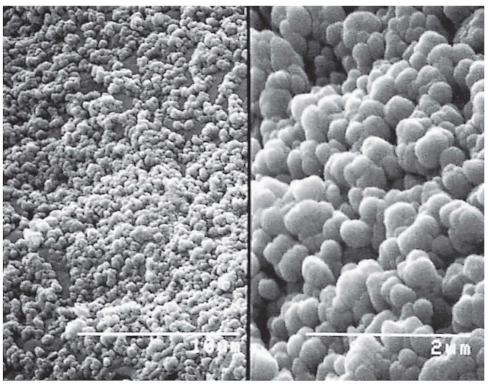
A. Anatase pigment, Titanox A, Titanium Pigment Company. Samples A–C from Forbes Pigment Collection, Freer Gallery of Art, Smithsonian Institution, Washington.



C. Anatase and calcium sulfate composite pigment, Titanox C, Titanium Pigment Company.

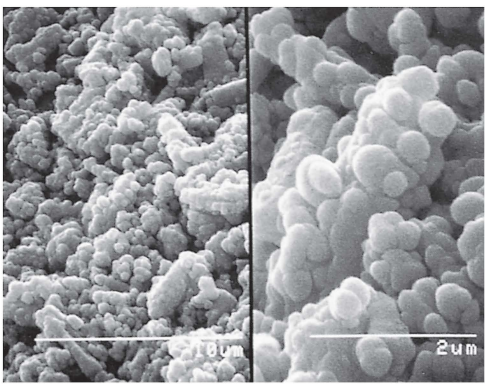


B. Anatase and barium sulfate composite pigment, Titanox B, Titanium Pigment Company; Fezandie, May 1936.



D. Rutile, New Jersey Zinc Company, R-745-15, sample from Freer Gallery of Art, Smithsonian Institution, Washington, collected June 1969.

elements can be done with as little as 5 to 10 mg of paint (Hutton, 1984). In commercial operations where relatively large amounts of powdered sample are available, slurries and emulsions have been used very successfully for analysis with an ICP and also by atomic absorption spectrophotometry in a flame or in an electrothermal atomizer (Fuller et al., 1981). Extraction methods have been used to concentrate some trace elements (Dornemann & Kleist, 1984). A method for analysis of titanium content by atomic absorption spectrophotometry is given in ASTM Standard D-4563-86, using a nitrous oxide flame.



E. Rutile and calcium sulfate composite pigment, Titanox RC-HT, sample from NL Chemicals, Inc.

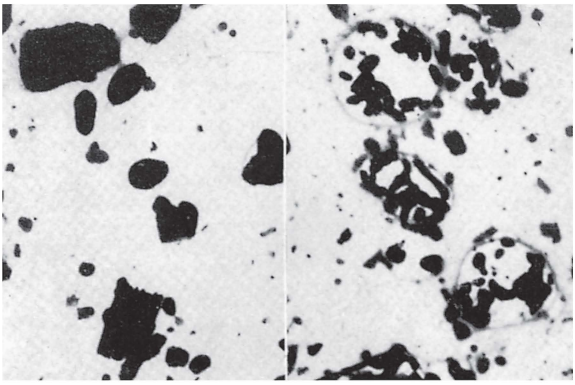
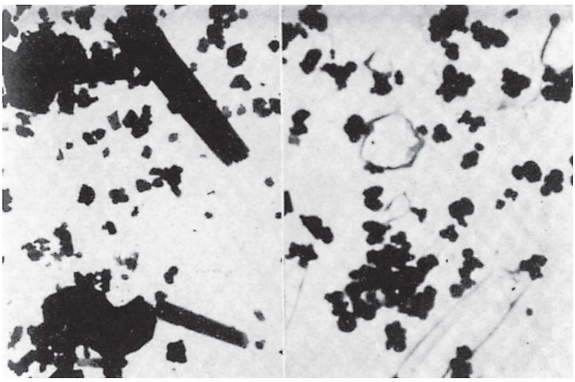


Fig. 22 Transmission electron micrographs of rutile composites and blends. From Alessandroni (1949), with permission. 4,600x.

A. Composite rutile and calcium sulfate pigment.

B. Composite rutile and calcium sulfate pigment with the anhydrite leached out, leaving rutile particles gathered around the voids.



C. Blend type rutile and calcium sulfate pigment, mechanical mixture.

D. Blend type rutile and calcium sulfate pigment with the anhydrite leached out, showing no particular association of the rutile with the calcium sulfate (anhydrite) particles.

5.3.4 ***Scanning electron microscopy and transmission electron microscopy.*** Imaging of titanium dioxide pigments in a scanning electron microscope can be used to determine average particle size and some features of particle morphology in powdered pigment (fig. 21). Examination of paints using this method is more difficult than examination of powdered pigment. The coatings on the more recent pigment grades are not distinguishable using either secondary-electron or backscattered-electron imaging; they can, however, be detected by elemental analysis if an x-ray spectrometer is incorporated in the system. The inorganic coatings are extremely thin, and the corresponding peaks are present only as traces in the spectra. The overlap of titanium K series lines with the L series of barium is discussed in section 5.3.5.

Examination of composite or coated pigments by transmission electron microscopy can provide a great deal of information regarding structure. The distinction between a rutile and calcium sulfate composite pigment typical of the 1940s, in which rutile is precipitated onto anhydrite (calcium sulfate) particles, and a mechanical mixture of the two components is shown in figure 22. The titanium dioxide does not evenly coat the base particle in the composite, but adheres to it as finely divided particles.

The appearance of recently produced rutile pigments, coated with silica and alumina, is shown in figure 23. These coatings are not always uniform, and in some cases the "coating" material may exist as a separate entity alongside the titanium dioxide pigment particles. Electron microscopy has been used to show that in some pigments the silica forms spherical aggregates of approximately twenty nanometers in diameter, while alumina has a threadlike or veil form (Kämpf & Völz, 1968). Coated rutile was examined by transmission electron microscopy of ultrathin sections (pigment mounted in resin); the coating of aluminum, silicon, zirconium, and organic compounds, whose thickness was estimated at five to eight nanometers, could not be discerned even at high magnifications (Coupry et al., 1987). How-

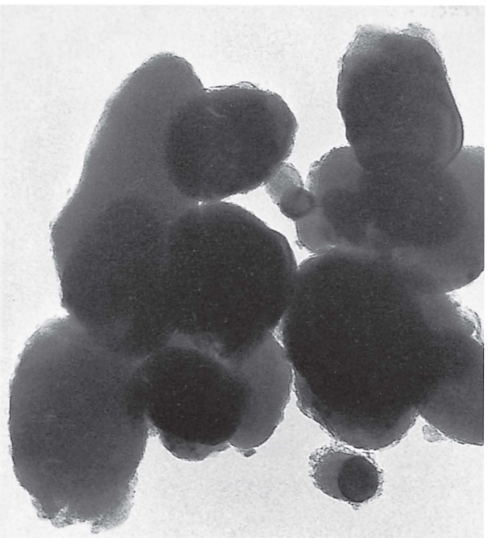


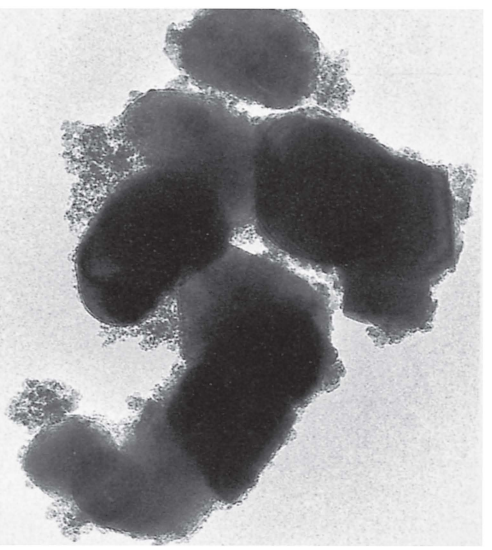
Fig. 23 Transmission electron micrographs. Samples and micrographs from Tioxide Canada Inc. 66,000x.

A. Uncoated rutile pigment.

B. Rutile with a normal coating of silica and alumina.

ever, the elements in the coating were confirmed by both wavelength-dispersive and energy-dispersive x-ray spectrometry. Some nylon transmission electron microscopy grids have been noted to contain approximately 1% titanium (Chandler, 1977).

5.3.5 ***X-ray spectrometry (x-ray fluorescence).*** Titanium may be detected in situ on paintings, paper, and other artifacts by x-ray secondary emission (fluorescence) spectrometry using either radioisotope or tube excitation and lithium-drifted silicon or germanium detectors. The main lines for titanium are $K\alpha_1$ at 4.510 keV (I=100), $K\alpha_2$ at 4.504 keV (I=50), and $K\beta_{1,3}$ at 4.931 keV (I=15). Lines due to barium that overlap some of these can cause confusion; they include $L\alpha_{1,2}$ at 4.467 keV (I=100) and $L\beta_{1,3,4}$ at 4.828 keV (I=75). Two nearby barium lines, weak but without interference from titanium, are the $L\beta_2$ at 5.156 keV (I=30) and $L\gamma_1$ at 5.531 keV (I=10) (Johnson & White, 1970; Goldstein et al., 1992). Using computerized multiple least squares fitting to standard spectra, as little as 1% by weight of titanium dioxide can be detected in a mixture of titanium dioxide and barium sulfate. The actual level of TiO_2 in composites and mixtures is usually much higher than this—for example, an early pigment of relatively low TiO_2 content would generally contain at least 15% barium sulfate.



C. Rutile heavily coated with silica and alumina.

The x-rays emitted by a radioisotope or tube easily penetrate through paper artifacts and the pigmented layers of a typical painting and can provide analytical data on layers underneath the surface of such objects. Radioisotope excitation can be used to quantify filler concentrations in different thicknesses of paper (see for example, Buchnea et al., 1982). Tube excited x-ray energy

spectrometry can detect trace elements in titanium dioxide down to the parts per million level for some elements (Ortec, Inc., 1975).

In wavelength-dispersive spectrometry, the titanium/barium overlap is easily resolved. Trace elements can be determined in the titanium dioxide with detection limits between about thirty and one thousand parts per million, if sufficient sample material is available (see for example, *Kronos Guide*, 1968). In tests in an electron beam microprobe on samples in the milligram range, however, trace elements such as niobium, zirconium, hafnium, lead, and arsenic could not be detected with wavelength spectrometry (S. Ercit, personal communication, 1988).

5.3.6 ***Neutron activation.*** There are five naturally occurring stable isotopes of titanium; with their abundances these are ^{46}Ti (8.25%), ^{47}Ti (7.45%), ^{48}Ti (73.7%), ^{49}Ti (5.4%), and ^{50}Ti (5.2%) (Walker et al., 1977). Three of these are activated by bombardment with neutrons to produce analytically useful radioisotopes: ^{47}Ti(n, p)^{47}Sc, ^{48}Ti(n, p)^{48}Sc, ^{50}Ti(n, γ)^{51}Ti (Kocher, 1981). It should be noted that ^{48}Sc can also be produced through a nuclear reaction with vanadium (^{51}V-(n, α)^{48}Sc) and ^{47}Sc can be produced from calcium (^{46}Ca(n, γ, β^-)^{47}Sc). Although the former reaction is not likely to cause a serious problem in the analysis of artists' materials, the presence of calcium in a ground or paint layer may interfere with quantification using this radionuclide, as it does in archaeological ceramic analysis (Hancock, 1985). In ceramic analysis, Ti in the presence of Ca can best be determined using the radionuclide ^{51}Ti, which in most "real" samples is produced only from a titanium isotope. Detection limits for this analysis using ^{51}Ti are quoted as 0.05% to 0.3%; ^{51}Ti is also produced from ^{51}V(n, p)^{51}Ti and ^{54}Cr(n, α)^{51}Ti, but the low abundances of these V and Cr isotopes in ceramics, relative to ^{50}Ti, combined with the much lower (n, p) and (n, α) activation cross sections make their interferences insignificant. In analyses of paint samples containing a high concentration of chrome-based pigments, this potential interference should be considered. Another type of interference may occur, caused by short-lived radioisotopes with peaks overlapping those of ^{51}Ti in the gamma ray spectrum, such as gadolinium (^{161}Gd) and tantalum (^{182}Ta^m) (Leclerc & Cornu, 1974). As the elements involved are rarely found in artists' materials, this is not a serious problem for most analyses.

Table 12 **Mass Absorption Coefficients of the Metallic Elements[a] (in cm^2 g^{-1})**

	0.25Å (W=0.24)	*0.711Å (Mo)*	*1.542Å (Cu)*
Titanium	1.20	23.3	202
Zinc	2.81	55.5	59.5
Antimony	12.08	33	267
Barium	15.66	2.4	336
Lead	7.16	123	232

a. From *Handbook of Chemistry and Physics* (1973); Bertin (1975).

Instrumental neutron activation analysis (INAA) for trace elements in titanium dioxide that produce long-lived radioisotopes can provide useful identifying data (see section 4.1). However, INAA performed by R. Hancock (personal communication, 1988) on milligram-sized samples to detect trace quantities of elements producing short-lived radioisotopes (such as vanadium, manganese, chlorine, arsenic, and antimony) proved inadequate to separate the purer grades of modern sulfate and chloride process rutile pigments. Duewer and Kowalski (1975) used neutron activation to distinguish papers made by different manufacturers. The detection limit for titanium is about 0.5 µg in a paper matrix (Grant et al., 1974).

5.3.7 ***X-radiography.*** Under the conditions commonly used in the x-radiography of paintings, with a peak in the energy distribution at about seventy nanometers (Mo tube), areas executed in anatase or rutile pigment are likely to be considerably more transparent to x-rays than those containing lead white or barium sulfate, while composites or mixtures of titanium dioxide with barium sulfate will produce an intermediate range of densities. Generally, it is not feasible to distinguish titanium dioxide and zinc oxide radiographically in a work of art (table 12).

The K absorption edges of these elements are: titanium 2.497, zinc 1.283, antimony 0.407, barium 0.331, and lead 0.141 Å.

Contact microradiography is used in industry to study the state of pigment dispersion in systems of low pigment concentration, as in some plastics (Homer & Ferguson, 1980). Examination of thicker layers such as those found in many paintings is not possible by this technique; however, laboratory samples of thin paint films and paper have been studied (Waterfield & Peacock, 1973).

In electron emission radiography, again it is the

pigments containing atoms of high atomic number that give rise to a more intense exposure of the radiographic film. A test panel containing thirty-three white pigment mixtures and two minerals gave the greatest darkening of the x-ray film for lead white, decreasing through barium sulfate, zinc white, and both forms of titanium dioxide. Thus, in an electron emission radiograph, an area of white paint that gives relatively little response is more likely to be a pigment such as titanium dioxide or zinc white. As with conventional radiography, mixtures of titanium dioxide with barium sulfate will register more dramatically on the film than pure anatase or rutile pigment.

5.3.8 ***Neutron radiography and autoradiography.*** Direct neutron radiography using thermal neutrons can provide complementary information to that of x-radiography, as the mass absorption coefficients of the elements rank in a very different order. The mass absorption coefficient of titanium for neutrons of wavelength 1.08 Å is 0.119, higher than that for zinc (0.045), antimony (0.037), barium (0.018), or lead (0.034) (Berger, 1965). However, in neutron radiography, light elements such as hydrogen, carbon, oxygen, and sulfur have effects on the radiographic opacities that can make interpretation difficult (mass absorption coefficients 48.5, 0.26, 0.15, and 0.029, respectively). In objects containing a hydrocarbon medium, the differences between pigments are swamped by the opacity due to hydrogen and carbon.

The activation reactions of titanium when exposed to a neutron flux are described in section 5.3.6. The short-lived ^{51}Ti radionuclide formed during irradiation of ^{51}Ti with thermal neutrons, has a relatively low saturation activity (Sayre & Lechtman, 1968), and does not register well in an autoradiograph. The activation of the longer-lived ^{48}Ti and ^{47}Ti isotopes would require fast neutrons, which are generally avoided in autoradiography as they can cause significant radiation damage to paintings.

5.3.9 ***Thermal analysis.*** The anatase form of titanium dioxide changes irreversibly to the rutile form on heating, a weakly exothermic transformation (Shannon, 1964; Shannon & Pask, 1965; Dachille et al., 1968; Sheinkman et al., 1984 and 1985; Dassler et al., 1988). According to Whitehead (1983), the transformation only proceeds to a significant extent at temperatures above 700°C. However, in pigment samples, depending on surface treatments, presence of impurities, and the method of synthesis, transformation can occur over a wide range of temperatures, from 400°C to 1,200°C.

Differential thermal analysis up to 1,400°C in inert and oxidizing atmospheres did not reveal any conclusive difference between anatase and rutile samples or between sulfate and chloride synthesis. Various degrees of sintering occur due to the presence of impurities in the starting material, particularly any inorganic coatings. Thermogravimetry shows low-temperature weight losses between 200°C and 300°C, which can be attributed to loss of water and of organic coating compounds (S. Mikhail, personal communication, 1988). The presence of a medium, as in a paint sample, further complicates thermal analysis at these temperatures.

5.3.10 ***Other instrumental methods.*** Electron diffraction of pigment particles can distinguish anatase from rutile (Coupry et al., 1987). Cathodoluminescence is a phenomenon that depends on the energy difference between the valence and empty electronic bands; anatase has a smaller gap and shows the phenomenon while rutile does not (Goebel & Stoecklein, 1987). Surface analytical techniques such as secondary ion-mass spectrometry, Auger electron spectrometry, and x-ray photoelectron spectrometry can provide detailed information concerning the pigment surface layers. Ion-beam techniques are just beginning to be used in museum applications; the presence of titanium has been used to classify stamps and Chinese porcelain (Peisach, 1986), "desert varnish" (Duerden et al., 1986), and paintings (Tuurnala et al., 1986). Electron-spin resonance has been used in photochemical studies of titanium dioxide to determine the chemical species formed at the pigment surface on irradiation. The identification of organic surface treatments can be performed using pyrolysis gas chromatography, a method that allows analysis of samples as small as 10 mg (Hutton, 1984).

5.4 Criteria for Identification

A stepwise analysis can be used to establish the type of titanium pigment. The presence of titanium can first be confirmed by microchemical tests, emission spectroscopy, or x-ray energy spectrometry. Using light microscopy, it is possible to distinguish between titanium dioxide whites, which have a high refractive index, and other titanium-based pigments. Rutile of ground

mineral origin can be distinguished from the white synthetic precipitated product through observation of its color and morphology. Composite pigments can also be identified at this stage, although transmission electron microscopy of leached samples may be necessary. Ancillary materials such as lead white or zinc white can be dissolved out of the preparation using dilute acid.

X-ray or electron diffraction and Raman or infrared spectroscopy will distinguish between the anatase and rutile forms. Polarized light microscopy or cathodoluminescence can also be used to make the distinction.

Ion-beam techniques and other surface analytical methods such as x-ray photoelectron spectrometry can be used to identify inorganic surface coatings. Careful analysis using the electron microscope may also allow one to infer whether any inorganic coatings have been applied to the pigment particles. Organic coatings may be identified using gas chromatography.

Trace element analysis using a technique such as atomic absorption spectrophotometry, neutron activation analysis, or mass spectrometry will provide further information concerning the manufacturing process (sulfate versus chloride). Infrared luminescence at low temperatures may also aid in making this distinction.

6.0 **Occurrences**

It has been a matter of interest throughout this research to note how few conservation laboratories have analyzed twentieth-century works of art. Analyses carried out to confirm forgery are not documented here. As more contemporary works undergo analysis and conservation, they will reveal the variety of materials now used in works of art that contain titanium dioxide pigments.

In many cases, modern artists describing their technique indicate their use of titanium dioxide white pigments, without naming specific works. These include Arthur Dove, who used Permalba in ground layers of a series of paintings from 1930 to 1934 (Wimsatt, 1982). Other artists include Edgar Endes, Winfred Gaul (Althöfer, 1980), Frederick J. Waugh (Fischer, 1930), William Palmer (Watson, 1950), Thomas Hart Benton (Branchick & Braun, 1985), Diego Rivera (Heller, 1988), Fionnuala Boyd and Leslie Evans, Peter de Francia, Terry Frost, Patrick George, A. Gouk, Tim Head, David Hepher, Ivon Hitchens, David Hockney, Leon Kossoff, Mark Lancaster, Peter Lanyon, and Gerhard Richter (S. Hackney, personal communication, 1988).

Occurrences of Titanium Dioxide Whites

Date	*Artist, Title or Description, Collection or Location*	*Analyst and Method of Identification*
1920–1930	Fessenden fathometer National Museum of Science and Technology, Ottawa	R. S. Williams, 1981** IR (anatase)
c.1924	Jean (Hans) Arp *Shirt Front and Fork* Australian National Gallery	Byrne (1985) SEM/XES (Ti, Ba, Zn, Pb, Ca, S)
1928	Georgia O'Keeffe *Yellow Hickory Leaves with Daisy* Stieglitz Collection, Art Institute of Chicago	Fiedler, 1990* micr. (gypsum), SEM/XES (Ti, Si, Al, Ca, S [upper layer] Ti, Ba, Si, Al [lower layer])
1929	Arthur Dove *Silver Sun* Stieglitz Collection, Art Institute of Chicago	J. Sirois, I. Fiedler, 1987* XRD (anatase $BaSO_4$), SEM/XES (Ti, Ba, Zn, S)
1943	Otto Dix *Sand Pit* Private collection	Baudisch (1986) micr. (titanium dioxide) ES (Ti)
1943	Pablo Picasso *The Rocking Chair* Musée National d'Art Moderne Centre Georges Pompidou, Paris	Coupry et al. (1987) Raman micr. (anatase $BaSO_4$), XRF (Ti, Zn, Pb, Sr, Ba)
1944	Otto Dix *Winter in the Village* Otto-Dix-Stiftung, Vaduz Liechtenstein	Baudisch (1986) micr., ES, XRD (anatase)
1945	Arshile Gorky *Country Landscape* Musée National d'Art Moderne Centre Georges Pompidou, Paris	Coupry et al. (1987) Raman micr. (anatase) XRF (Ti, Ba, Zn, Sr)
1946	Otto Dix *Job*, Otto-Dix-Stiftung, Vaduz Liechtenstein	Baudisch (1986) micr. (titanium dioxide) ES (Ti)
1946–1947	Frans Mars *Landscape with Mill* Molenmuseum te Koog-Zaandijk Northern Netherlands	De Keijzer (1989b) micr., XRD (anatase)

*Personal communication
**Unpublished analytical report available from Canadian Conservation Institute, Ottawa
chem.=Chemical or microchemical tests
EBM=Electron beam microprobe
ES=Emission spectroscopy
FTIR=Fourier transform infrared spectroscopy
IR=Infrared spectroscopy
LSA=Laser emission spectroscopy
micr.=Light microscopy
Raman=Raman spectroscopy
Raman micr.=Raman microspectroscopy
SEM/XES=Scanning electron microscopy with energy-dispersive spectroscopy
XRD=X-ray diffraction
XRF=X-ray fluorescence spectroscopy

Occurrences of Titanium Dioxide Whites Continued

Date	*Artist, Title or Description, Collection or Location*	*Analyst and Method of Identification*
1948	Willem de Kooning *Painting* Museum of Modern Art, New York	J. Sirois, E. Ordonez, 1987* micr., XRD (rutile), SEM/XES (Ti, Al, Si)
1950	Franz Kline *Chief* Museum of Modern Art, New York	J. Sirois, E. Ordonez, 1987* micr., XRD ($CaSO_4$ $CaCO_3$, rutile) SEM/XES (Ca, Ti, S)
1951	Josef Albers Study for *Homage to the Square* Josef Albers Foundation, Hartford	J. Sirois, 1988* XRD (anatase, ZnO $BaSO_4$)
1951	Stuart Davis *Visa* Museum of Modern Art, New York	J. Sirois, E. Ordonez, 1987* micr., XRD (anatase $BaSO_4$, ZnO) SEM/XES (Ti, Zn, S)
1951	Serge Poliakoff *Composition in Gray and Black* Musée National d'Art Moderne Centre Georges Pompidou, Paris	Coupry et al. (1987) Raman micr. (anatase) XRF (Ti, Ca, Sr, Zn Ba, Pb)
1953	Franz Kline *New York, N.Y.* Albright-Knox Art Gallery Buffalo, N.Y.	L. Potoff, 1987* chem., micr. (TiO_2 ZnO, lead carbonate)
1953	Jackson Pollock *The Deep* Musée National d'Art Moderne Centre Georges Pompidou, Paris	Coupry et al. (1987) Raman micr. (anatase) XRF (Ti)
1955	Willem de Kooning *Gotham News* Albright-Knox Art Gallery Buffalo, N.Y.	L. Potoff, 1987* micr., EBM (TiO_2)
1955–1956 (attrib.)	Vilmos Huszár *Composition 6* Private collection, Netherlands	De Keijzer and Mosk (1985) micr., LSA, XRD (rutile)
1956	Jean Paul Lemieux *Noon Train* National Gallery of Canada, Ottawa	R. S. Williams and I.N.M. Wainwright, 1985** FTIR (TiO_2) SEM/XES (Ti, Zn [?])
1956	Lucio Fontana *Spatial Concept 1956*—with spangles Civico Museo d'Arte Contemporanea Milan	Barcilon and Galassi (1987) A. Gallone, 1988* chem., SEM/XES (Ti, S, Zn)
1956	Lucio Fontana *Spatial Concept 1956*—with yellow and green glass Civico Museo d'Arte Contemporanea Milan	Barcilon and Galassi (1987) A. Gallone, 1988* chem., SEM/XES (Ti, Si S, Fe)
1956	Josef Albers Study for *Homage to the Square* Josef Albers Foundation, Hartford	J. Sirois, 1988* XRD (anatase, $BaSO_4$)
1956	Oscar Cahen *Black Trophy* Robert McLaughlin Gallery, Oshawa	E. Moffatt, 1982** FTIR, IR (rutile)

Occurrences of Titanium Dioxide Whites Continued

Date	*Artist, Title or Description, Collection or Location*	*Analyst and Method of Identification*
1956	Pablo Picasso *Two Women on the Beach Before the Sea* Musée National d'Art Moderne Centre Georges Pompidou, Paris	Coupry et al. (1987) Raman micr. (anatase $BaSO_4$), XRF (Ti, Zn, Sr, Ba)
1956	Ulysse Comtois *Untitled* National Gallery of Canada, Ottawa	R. S. Williams, 1983** IR (TiO_2, $BaSO_4$)
1957–1961	Robert Motherwell *Elegy to the Spanish Republic* Museum of Modern Art, New York	J. Sirois, E. Ordonez, 1987* micr., XRD (rutile) SEM/XES (Ti, Al, Si, S)
1958	Sam Francis *Towards Disappearance II* Museum of Modern Art, New York	J. Sirois, E. Ordonez, 1987* micr., XRD (ZnO, $CaCO_3$ anatase), SEM/XES (Ca, Zn, Ti)
1962	Barnett Newman *Not There, Here* Musée National d'Art Moderne Centre Georges Pompidou, Paris	Coupry et al. (1987) Raman micr. (rutile) XRF (Ti, Zn, Ba)
1963	Otto Dix *Portrait of Eleonore Frey* Otto-Dix-Stiftung, Vaduz, Liechtenstein	J. Baudisch (1986) micr., ES (titanium dioxide)
1963	Niki de St. Pholle *The Bride* Musée National d'Art Moderne Centre Georges Pompidou, Paris	Coupry et al. (1987) Raman micr. (rutile) XRF (Ti, Ca, Zn)
1964–1965	Jo Baer *Primary Light Group: Red, Green, Blue* Museum of Modern Art, New York	E. Ordonez, 1992* micr., SEM/XES, XRD (rutile)
1966	Robert Motherwell *New England Elegy* J. F. Kennedy Federal Building, Boston	A. J. Quint, 1988* [method not given]
1967	Barnett Newman *Who is Afraid of Red, Yellow, and Blue III,* Stedelijk Museum Amsterdam	M. de Keijzer, 1987* micr., LSA, XRD (rutile with chalk, $BaSO_4$)
1967	Jack Bush *Colour Field* Government House, Ottawa	N. Adair, 1979* IR, XRD, XRF (rutile)
1968–1970	Raoul Dubuffet *The Winter Garden* Musée National d'Art Moderne Centre Georges Pompidou, Paris	Coupry et al. (1987) Raman micr. (rutile) XRF (Ti, Zn)
1968	Lucio Fontana *Spatial Concept 1968*—with spangles and glass Galleria d'Arte Moderna, Milan	A. Gallone, 1991* micr., SEM/XES (Ti)
1969–1970	Max Bill *Eight Groups of Lines around the Space* Musée National d'Art Moderne Centre Georges Pompidou, Paris	Coupry et al. (1987) Raman micr. (rutile) XRF (Ti, Zn, Pb)

Occurrences of Titanium Dioxide Whites Continued

Date	*Artist, Title or Description, Collection or Location*	*Analyst and Method of Identification*
1970–1971	David Hockney *Mr. and Mrs. Clark and Percy* Tate Gallery, London	J. Sirois, 1989* XRD (rutile, calcite)
1972	Robert Bradford *Action at Shwebo* Canadian War Museum, Ottawa	E. Moffatt, 1988** FTIR (rutile, $CaCO_3$)
1972	Max Bill *Condensation towards Yellow* Collection of the artist	Bosshard (1978) XRD or ES ("titanium white")
1974	Joan Miró *People, Birds in the Night* Musée National d'Art Moderne Centre Georges Pompidou, Paris	Coupry et al. (1987) Raman micr. (anatase) XRF (Ti, Zn, Pb, Sr, Ba)
1976	A. R. Penck *TM 1976* Musée National d'Art Moderne Centre Georges Pompidou, Paris	Coupry et al. (1987) Raman micr. (rutile) XRF (Ti, Zn, Ba, Sr)
1978	Philip Guston *Tomb* Museum of Modern Art, New York	E. Ordonez, 1987* micr. (TiO_2), SEM/XES (Ba, Ti, Zn, S)
c.1980s	Norval Morrisseau *Animal Environment* Glenbow Museum, Calgary	E. Moffatt and D. Moffatt, 1987/1988* FTIR, Raman (rutile $CaCO_3$[?])
c.1980s	Norval Morrisseau *Poppy Tree* (see fig. 20) Glenbow Museum, Calgary	E. Moffatt and D. Moffatt, 1987/1988* FTIR, (rutile, $CaCO_3$[?])

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