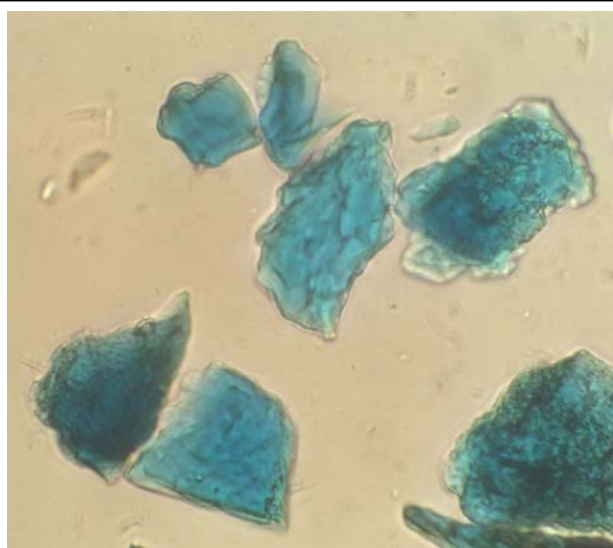
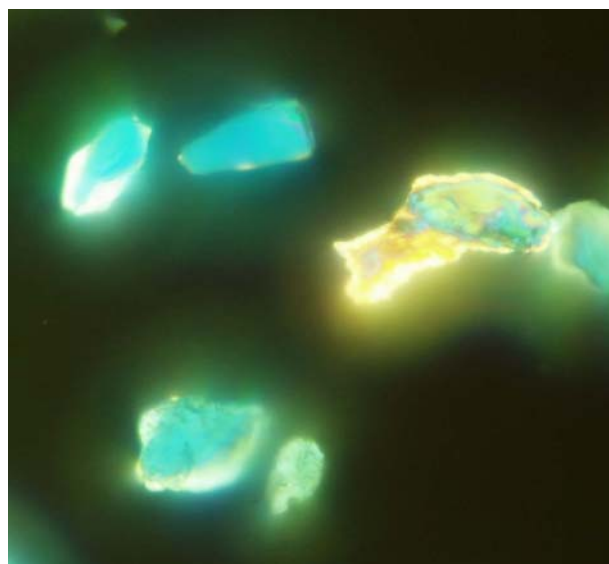


# Azurite

$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  (Derived from the mineral- Azurite)  
Mountain blue



Microscopic appearance at x500 mag



Microscopic appearance under crossed polars

## Dates of Use

Ancient times in both the East and the West but rarely used today.

## Summary of Manufacture

Derived from the mineral azurite- a basic copper carbonate, which can be found as a natural deposit in many parts of the world. Hungary seems to have provided a large source of the mineral in the sixteenth century. Like other minerals, the pigment is extracted from the stone through a time consuming process of grinding, washing, levigation and floatation.

## Brief History of Usage

The most important blue pigment in European painting from the fifteenth to the middle of the seventeenth century. Deep blue 'azure' in colour, the name 'azure' being derived from the Arabic for blue. At one time known as 'azure d'Alemagna' and the name suggests that a large amount of the pigment at that time came from Germany. Also used prolifically in the East, azurite can be found in wall paintings in Central China from the Ming and Sung Dynasties, as well as cave paintings at Tun Huang in Western China. There are records of its use also in Japan and Ancient Egypt (Gettens & Stout)

## Surface Morphology / Microscopic Description

Course, heterogenous, blue crystals with no regular shape. Crystalline particles which are more intense in colour when coarsely rather than finely ground. As a result dark painted areas of azurite look more textured and less refined in comparison to other pigments. Conchoidal fracture of transparent to larger opaque crystals with a particle size of 1-50 $\mu\text{m}$ .

## Aging Characteristics

Fine ground azurite tends to be pale and far reduced in tinting strength.

The intensity of the blue is due to the presence of copper and the way it is chemically bound to the hydroxyl (OH) and carbonate (CO<sub>3</sub>) groups. Malachite, another naturally occurring mineral, is a more oxidized form of the mineral azurite. Hence it is the increased oxidation that causes the colour change from blue to green. The formula for the change includes the addition of a water molecule to that of two azurite molecule which releases one of carbon dioxide and leaves three malchite molecules.

$2\text{Cu}(\text{OH})_2 \cdot 2(\text{CuCO}_2) + \text{H}_2\text{O} = 3\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3 + \text{CO}_2$  Oxidation is ongoing hence the slow transformation from blue to green.

## Technical Examination Techniques/ Instrumental Analysis Techniques

Particles are anisotropic and exhibit high birefringence. Crystals exhibit pleochroism, turning from blue crystals with yellow edges to navy crystals with bright blue centers.

Particles show occasional complete oblique distinction and exhibit blue/ green-blue pleochroism.

Transmission colours with the Chelsea filter = deep blue and grey/blue

See Appendices chemical test for copper(II) ions.

# Barytes

**BaSO<sub>4</sub> (Barium sulphate)**

**Barium White, Blanc Fixe, Permanent White, Barite**

Microscopic appearance at x500 mag

Microscopic appearance under slightly crossed polars

## Dates of Use

Ancient times to the present day.

## Summary of Manufacture

Mineral deposits of barite are found naturally or as the synthetic version. The name is derived from the Greek word 'barys', which means heavy. Like other minerals it is prepared by grinding, washing and levigation and then bound with a medium or glue. As a heavy inert material it is often used, like gypsum, as a base for lake pigments.

Blanc fixe was originally applied to term the synthetic variety and prepared through precipitation of barium chloride solution with sodium sulphate. A number of grades are manufactured of both the natural and synthetic barytes but most contain over 98% BaSO<sub>4</sub>.

## Brief History of Usage

Commonly used as a ground, filler or extender it has been suggested that barytes seems to have been used as a pigment in painting from around the 14<sup>th</sup> Century. It has very poor hiding power, which generally restricted its use as a base or filler only. Barytes also has a low oil absorption and so is not often seen in this medium. The largest natural deposits can be found in Germany, Italy, USA and the Czech Republic.

## Surface Morphology / Microscopic Description

Synthetic barytes (Blanc fixe) is identical to the natural version but particles should appear finer.

The crystal system is orthorhombic.

Cleavage is prismatic and fracture in the particles is uneven.

Particles are white, dull white to colourless.

The luster is vitreous.

As a ground to brightly coloured pigment crystals, barites at times forms a concentric pattern of larger crystals settling outward from smaller ones in the middle giving the appearance of a flower-like pattern.

## Aging Characteristics

An extremely inert pigment and hence very stable being unaffected by light, heat and strong chemicals. Synthetic barytes has a much higher hiding power than its natural counterpart.

## Technical Examination Techniques

Particles exhibit parallel extinction.

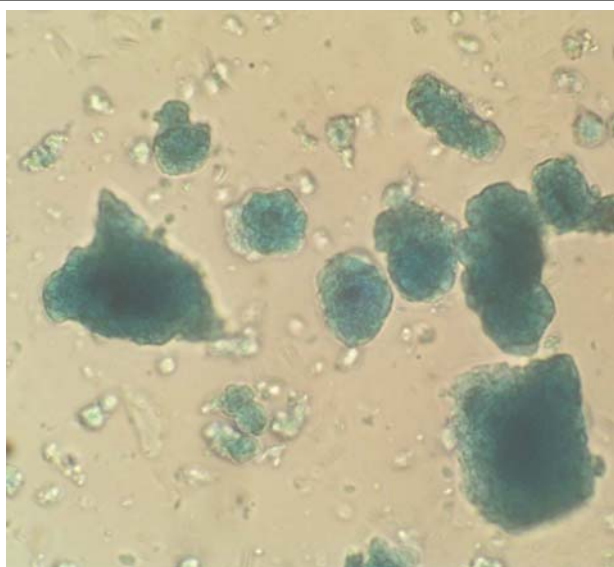
Characteristic rod-like crystals can occasionally be found and these exhibit oblique extinction.

Fluoresces purple in ultraviolet light.

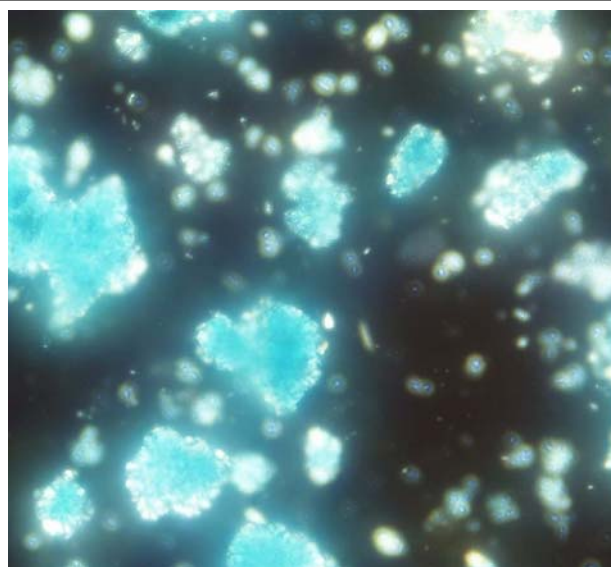
Barytes is common and can be confused with other minerals such as Celestite (SrSO<sub>4</sub>), which has the structure as barytes. Only a flame test will distinguish the two. barytes produces a pale green flame; celestite a red flame.

# Blue Verditer

$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  (Artificial basic copper carbonate)  
Blue Bice, Cendres blues d'Angleterre



Microscopic appearance at x500 mag



Microscopic appearance under crossed polars

## Dates of Use

From around the beginning of the Middle Ages up until the present day.

## Summary of Manufacture

Similar in chemical composition to the minerals malachite and azurite recipes for making the synthetic copper carbonate have been around for centuries. Commonly prepared in the Middle Ages in Europe the essence of its production is to add potash, lime and sal ammoniac to a soluble copper salt such as copper sulphate or sulphite. Its manufacture was a profitable byproduct and sideline for the metal industry and indeed company's such as the Sheffield Smelting Company took up paint making in 1781.

## Brief History of Usage

Made and used in large quantities in England in the Middle Ages its manufacture was cheap and its colour strong hence making it a good alternative to the more expensive and imported ultramarine (lapis lazuli) and azurite minerals. Found in paintings, manuscripts and illuminations prolifically in England and across Europe; the pigment enjoyed great popularity in the Middle Ages but gradually its use declined with the manufacture of synthetic substitutes. Although it can still occasionally be found in paintings today.

## Surface Morphology / Microscopic Description

An artificial basic copper carbonate; similar in composition to the mineral azurite and often mistaken for the latter.

Slightly more green in hue in comparison to azurite.

Pale blue in colour, particles are small, rounded and even in size.

Some crystals may appear colourless to slightly pale green.

Highly birefracting it can be mistaken with a finely ground azurite as they are very similar in hue.

Polycrystalline blue rosettes of fibrous aggregates.

Particles size usually 1-20µm

## Aging Characteristics

Fugitive

Particles tend to turn green due to their ammonia content.

Historically blue verditer was often mixed with smalt to create deeper shades of blue.

Stable in lime and often referred to as 'lime blue' because of the latter, consequently it was commonly used in tempera and watercolour but not in oil.

Undergoes gradual oxidation as it ages, like the other copper pigments although it seems more stable and retains its colour in tempera.

## Technical Examination Techniques

Particles do not exhibit pleochroism, are anisotropic and exhibit undulose extinction (may only be seen in some crystals). Transmission colours with the Chelsea Filter are deep blue and grey/ blue.

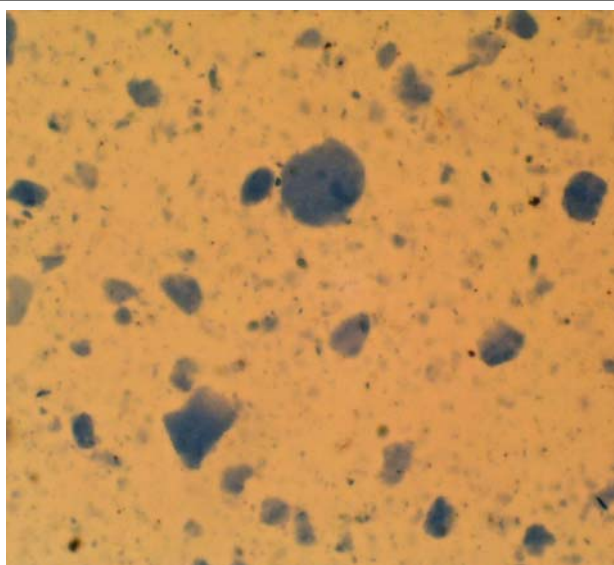
Some particles, however, do exhibit high birefringence.

Appears blue in transmitted light.

See Appendices chemical test for copper(II) ions.

# Cobalt Blue

$\text{CoO} \cdot \text{Al}_2\text{O}_3$  (cobalt aluminate) (cobalt (II) oxide, aluminium oxide)  
Thenards Blue. Dresden Blue



Microscopic appearance at x500 mag



Microscopic appearance under slightly crossed polars

## Dates of Use

1802 to the present day.

## Summary of Manufacture

The simplest form is made by calcining a mixture of cobalt oxide and aluminium hydrate to form cobalt aluminate. The composition is approximately 32%  $\text{Co}_3\text{O}_4$  and 68%  $\text{Al}_2\text{O}_3$ .

## Brief History of Usage

An inorganic oxide of cobalt and aluminium, it was discovered in 1802 by Thenard, the pigment soon increased in popularity especially in France. Its colour varies slightly depending upon its manufacture and with the amount of impurities present. It is one of the most expensive pigments and is often substituted by ultramarine and the blue lakes. Its tone resulted in its use mainly for painting areas of sky but it works well in all media and can therefore be seen in oil, water and acrylic painting. It has been identified on watercolour paintings by R.P. Bonnington (1801-1828) and in Dutch paintings from around 1840. Generally its use was widespread and extensive. Notably it has a unique hue, valuable in violet mixtures because of its red cast.

## Surface Morphology / Microscopic Description

Essentially cobalt blue is a finely ground glass with tiny pale blue crystals.

Particles are moderately fine, irregular in size, rounded, and some exhibited a crusty texture.

Its coarse particles can be mistaken with azurite or ultramarine but microscopically it does **not** have a crystalline appearance.

Occasional glassy flakes may also be noted.

Particle size is usually 1-50  $\mu\text{m}$

## Aging Characteristics

Generally cobalt blue dries to a darker blue with moderate opacity, tinting strength and good drying capacity.

Chemically it's very stable being insoluble in strong acids, alkalis and unaffected by sunlight.

Even unaffected by hydrochloric acid.

Unaffected by moisture and oxygen.

Unaffected by mixture with other pigments.

Cobalt blue, therefore, has excellent permanence.

## Technical Examination Techniques

Particles are isotropic and when examined optically particles reflect more green and violet light as well as blue. (Caveat: Some particles are anisotropic) Particles do not exhibit pleochroism, birefringence or extinction.

Transmission colours with the Chelsea Filter = bright red.

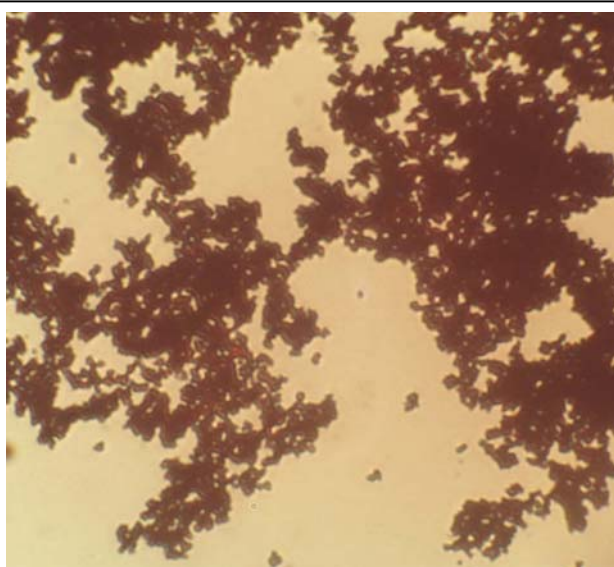
Bright blue particles by transmitted light and viewed by candlelight, it acquires a purplish hue.

Melting point of 900 - 1000°C. Medium refractive index.

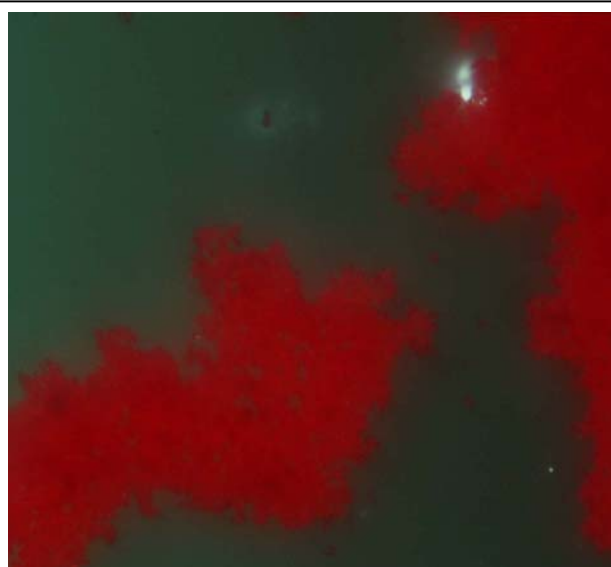


# Cadmium Red

**CdS(Se) (cadmium sulpho-selenide)**  
 Manufactured in grades light, medium & dark



Microscopic appearance at x500 mag



Microscopic appearance under slightly crossed polars

## Dates of Use

Early 1900s up until the present day.

## Summary of Manufacture

Prepared through the precipitation of calcium sulphate with sodium sulphide and selenium. Shades vary as a direct result of the manufacturing process due to the manipulation of the proportions of sulphur to selenium and by regulating the precipitation process.

A range of hues can also be obtained through varying lengths of exposure to heat. In commercial grades it is produced as light, medium and dark cadmium red.

## Brief History of Usage

A modern synthetic pigment and developed in the early 1900s along with the other cadmium pigments. According to Gettens & Stout it was mentioned by a German patent in 1892 but does not seem to have been put into commercial production as an artists pigment until around 1910. Today it is just as popular in use and has virtually taken over from vermilion as the most common red pigment in the European palette. In oil medium, it requires some wax and at least 40% oil for binding.

## Surface Morphology / Microscopic Description

Tiny rounded, homogenous particles.

Particles tend to clump together and individual rounded crystals can only be seen at high magnification of around x500 mag or more.

Varying shades can be manufactured from deep maroons to pink/reds and vermilion shades.

Particles are tiny, fine grouped masses less than  $1\mu$  in diameter.

Their strong, intense red colour is a good identity indicator as is their obvious synthetic, uniform appearance.

## Aging Characteristics

All cadmiums are chemically stable and light resistant. Nevertheless it is known to turn brown in fresco and it readily chemically reacts with copper pigments such as emerald green turning black.

Over grinding of the pigment in preparation results in the particles needing more binding medium, which can in turn make the paint quite oily in appearance and composition.

## Technical Examination Techniques

Particles are isotropic and exhibit high birefringence due to the depolarisation of light by reflection.

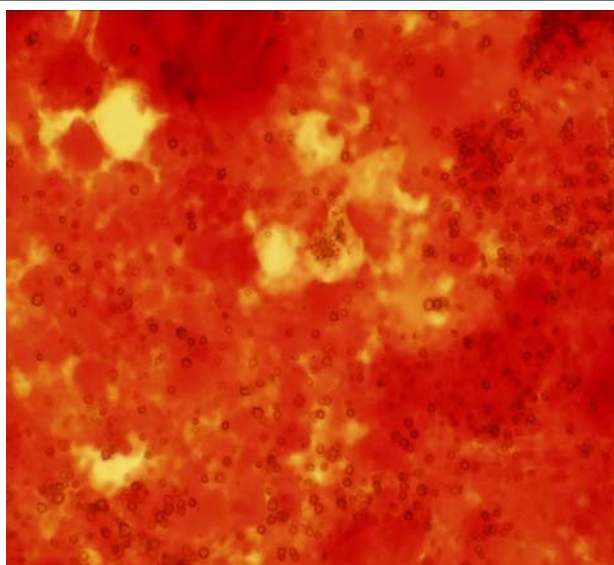
Characteristically particles exhibit bright red polarisation colours.

Particles do not exhibit pleochroism or extinction and are unaffected by the red compensator added to the microscope.

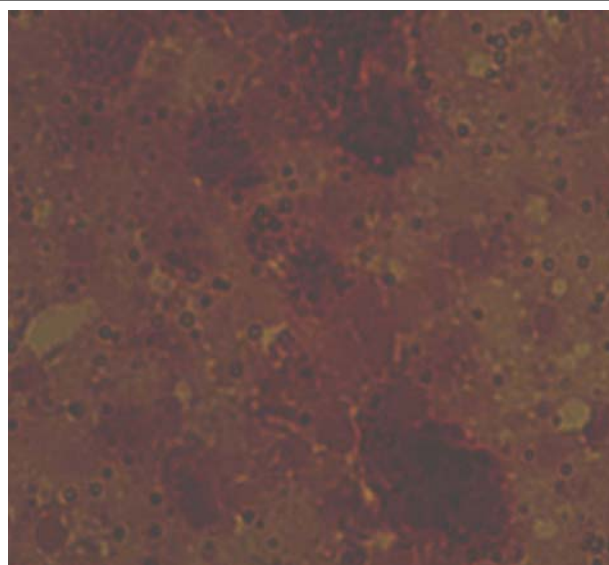
Cadmium red's refractive index is more than or equal to the medium, 'meltmount' and therefore the halo around each crystal moves inward ( $n >> 1.66$ )

# Cochineal Carmine

$C_{22}H_{20}O_{13}$  (Carmonic Acid - Colouring Principle)  
Carmine Lake or Crimson Lake



Microscopic appearance at x500 mag



Microscopic appearance under slightly crossed polars

## Dates of Use

Native to the New World and used for centuries by the Aztecs but brought to Europe in the 16th Century. Commonly used as a pigment and dyestuff today.

## Summary of Manufacture

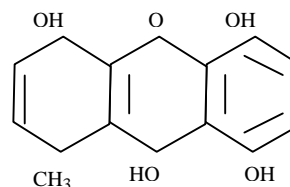
Natural organic dyestuff made from the dried bodies of the female insect '*Coccus cacti*'. The female beetles are collected 2-4 times a year and are killed with hot water. The resultant colour is dependent upon the amount of soaking, the quantity of pigment used and the chemicals added to the mordanting process. Carmine lake is obtained when hot aqueous extract of cochineal is precipitated with iron-free alum.

## Brief History of Usage

Cochineal carmine was native to the New World and was used by the Aztecs and Mayan people as a dye in textiles and as a pigment in paint. Its earliest recorded use was a textile dye in the Peruvian Paracus culture of 700BC. It was brought to Europe shortly after the discovery of the Americas and the conquest of Mexico in 1523 and was first described by Mathioli in 1549. Europeans recognised its similarity to their native 'kermes' beetle' (See Carmine). The finest quality is known as 'nacarated carmine'.

## Surface Morphology / Microscopic Description

The colouring principle of cochineal extract is carmonic acid and used to make true carmine it gives a scarlet-red solution with water and alcohol, and a violet solution with sodium hydroxide. The pigment is a protein containing an aluminium-based lake of carmonic acid.



Carminic Acid

## Aging Characteristics

It is soluble in water and alcohol but not in ether. It has a tendency to change to a more orange hue on exposure to acids and a more purple hue on exposure to alkalis. The cochineal lakes are not permanent to light. They turn brownish and then fade rapidly in strong sunlight, particularly when used in water-colour. They are, however, fairly stable in oil.

## Technical Examination Techniques

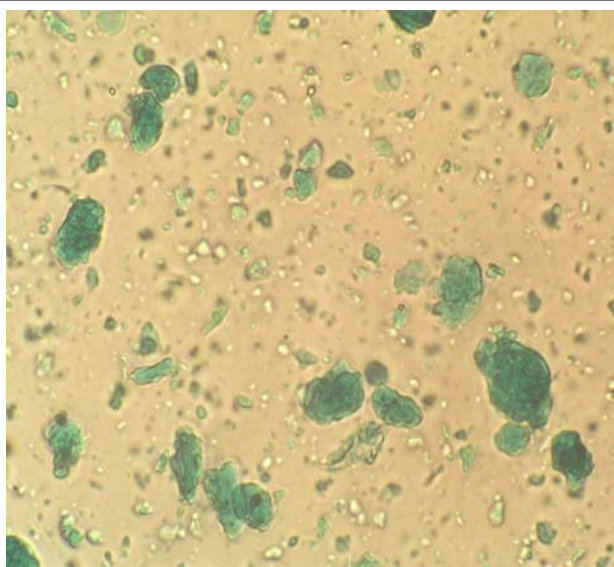
Appears quite transparent in transmitted light.

Does not exhibit birefringence or polarization colours and therefore dulls and darkens to black under cross-polars.

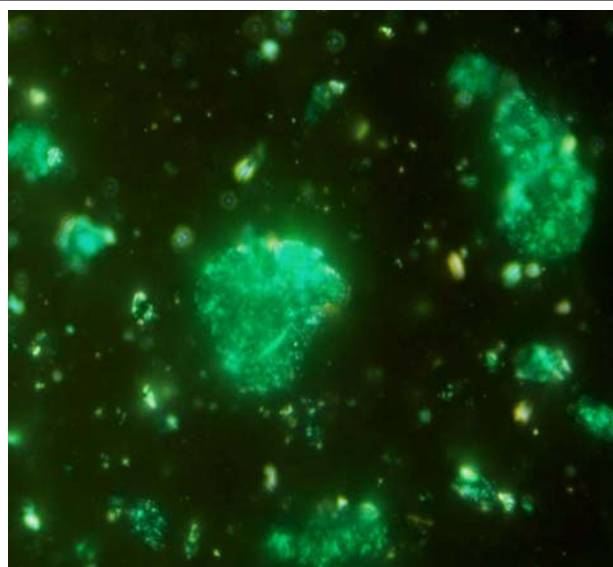
Cochineal varieties can be definitively distinguished from each other as well as from other insect dyes such as Kermes through thin layer chromatography and comparison to known standards.

# Emerald Green

$\text{Cu}[\text{C}_2\text{H}_3\text{O}_2]_2 \cdot 3\text{Cu}[\text{AsO}_2]_2$  (copper (II) aceto-arsenite)  
Schweinfurt Green, Paris Green, Veronese green



Microscopic appearance at x500 mag



Microscopic appearance under slightly crossed polars

## Dates of Use

1814 to the early 1900s.

## Summary of Manufacture

Artificial aceto-arsenite, which can be made in several ways. However a method was not published until 1822 when Braconnot and Liebig wrote papers on the subject. Generally copper, acetic acid (or verdigris), white arsenic and sodium carbonate are mixed in hot solution and the precipitate is then washed and dried.

## Brief History of Usage

First produced commercially in Schweinfurt, Germany in 1814. Use of the material as an artist's pigment had a short life span due to its rapid blackening upon reaction with hydrogen sulphides in the atmosphere. Emerald Green is poisonous and its toxic nature makes it difficult to handle, and as a result, impractical for use by artists. It had uncommon use in the art world and can perhaps be seen more in watercolour medium particularly sea and landscapes. Also used to colour wall papers and dressing screens etc of the late 1800s to Early 1900s when the intense green was employed with the fashion for Botanical and Oriental designs. Was also occasionally employed to tone repairs on bronzes.

## Surface Morphology / Microscopic Description

Bright blue-green particles, which are small, rounded and uniform in size.

May be seen to be radial in structure at high magnifications.

Some crystals may appear to have a pit or dark spot at their center.

Course leafy 'spherulites'.

Some samples, however, may vary greatly in size and shape depending upon the manufacturing process.

Particles may also seem like green flower-like rosettes.

Particle size is usually 1-10µm

## Aging Characteristics

Emerald green has a fair hiding power.

Has a tendency to blacken upon reaction to hydrogen sulphides in the air just as with the other copper-based greens.

Readily reactive with acids and alkalis.

Blackened by heat although it is fairly permanent in oil medium.

## Technical Examination Techniques

Particles are highly birefracting and exhibit undulose extinction.

Transmission colours with the Chelsea Filter = lime green.

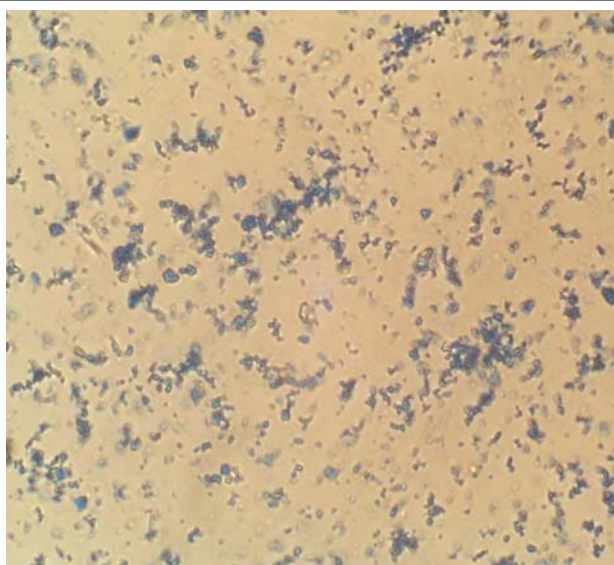
Confirm with microchemical tests for copper and arsenic and the stannous chloride test for Scheele's green.

Turns blue in weak sulphuric acid and into an ochre shade in potassium hydroxide.

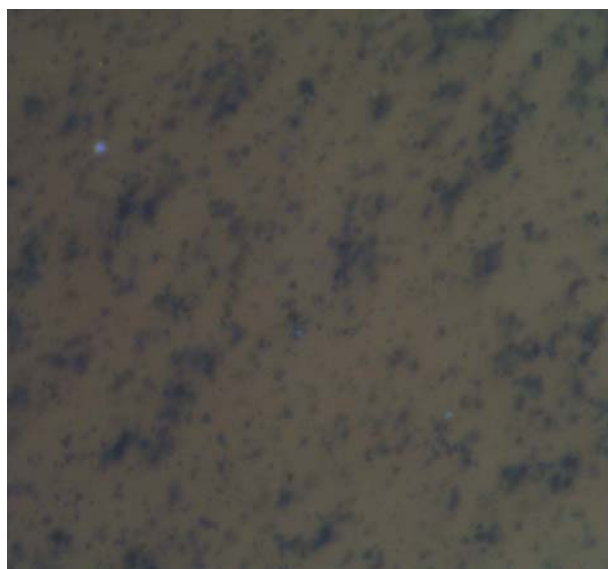


# French Ultramarine

$\text{Na}_{8-10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$  Alumno Silicate  
Synthetic Ultramarine (Natural - Lapis Lazuli)



Microscopic appearance at x500 mag



Microscopic appearance under slightly crossed polars

## Dates of Use

From around 1830 to the present day.

## Summary of Manufacture

Artificial ultramarine is a complex compound of sodium, silica, aluminium and sulphur. It's prepared by heating china clay with sulphur, soda, carbon and Gauber's salt. The resulting chemical composition is very similar to that of lapis, its fine uniformity of particles only indicating it as the synthetic version. Although varying hues of ultramarine are produced from a dark blue to a lilac/ purple hue.

## Brief History of Usage

Synthetic ultramarine was first introduced in France and was available commercially from about 1830. Sometimes referred to as 'permanent blue', its hue is close to that of the natural lapis but its retail cost made it a cheap alternative to the expensive original. Since its discovery the pigment quickly became a lapis substitute and was used prolifically as a main blue in the water-colour palette and other water based mediums. The commercially produced oil colour has a purplish hue, neutral blues closer to that of lapis can be obtained in a dry form, which can then be mixed with white to seem almost indistinguishable to the lapis blue seen in early Master paintings.

## Surface Morphology / Microscopic Description

Clusters of small blue transparent particles seen at x100mag.

Individual crystals only seen at x400 plus magnification and appear as fine uniform, rounded particles.

Particle size is usually from 1-50µm

Larger particles of the synthetic ultramarine may be confused with the natural lapis if the lapis has undergone extensive grinding. The finest grades of lapis have small particles but generally they should appear still larger than those of the synthetic variety.

## Aging Characteristics

Has excellent hiding power.

Becomes quickly discoloured by the action of weak acids, which attack it forming hydrogen sulphide.

Discoloured by alum and vinegar, which were often used in tempera.

It has a melting point of 300°C.

It may form a white coating/ blanching on its surface as a result of hygroscopic action. The so-called 'ultramarine disease' is said to be the result of decomposition of the varnish in oil paintings.

## Technical Examination Techniques

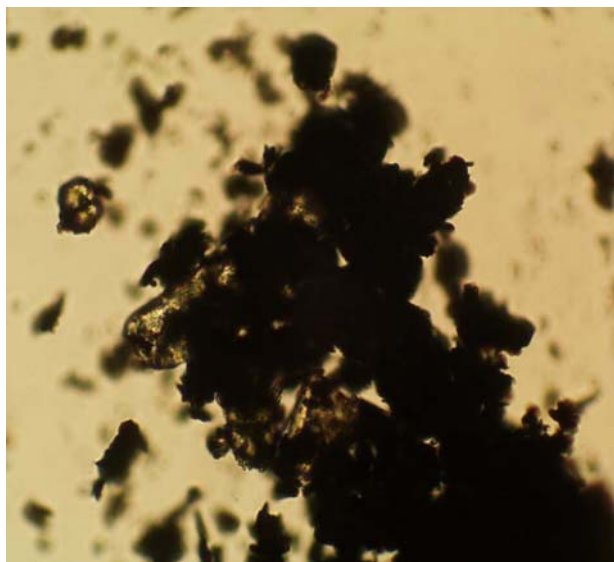
Particles do not exhibit pleochroism but do exhibit high colourless birefringence (although none was seen in the sample photographed above). Transmission colours with the Chelsea Filter = Bright red. Particles do not exhibit extinction. Has a high refractive index. Both the synthetic and the natural ultramarine are bleached by acetic acid. The pigment should be free of sodium sulphate but if not it will exhibit effervescence.

See Appendices chemical spot test for ultramarine (caveat: the same result will occur for lapis lazuli)



# Graphite

**C (Carbon - A crystalline form)**  
(named from the Greek, γράφειν - to write)



Microscopic appearance at x500 mag



Microscopic appearance under slightly crossed polars

## Dates of Use

From ancient times in areas where it is found as a natural mineral and commonly used today in both its natural and manufactured form.

## Summary of Manufacture

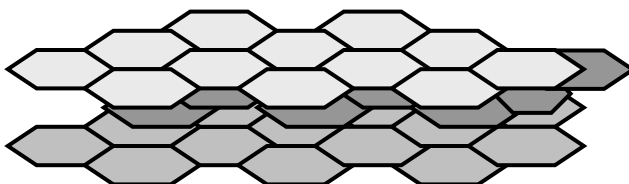
Mined directly or artificially by a furnace process (Acheson process) since about 1891. Manufacturer's grade graphite pencils according to their relative softness of hardness. The common scale runs from 8B - F, HB, H-8H.

## Brief History of Usage

Used directly in its mineral form and mined in various parts of the world. Discovered in Bavaria in approx 1400 and England in 1504 at Borrowdale in Cumberland. (Getten & Stout) The main modern sources are to be found in Ceylon, Cumberland, Bavaria and Bohemia. Used in pencils, crayons and transfer paper graphite is named from the Greek, γράφειν ('to write'). Often confused with lead which was also used for writing. (The first discovery in England was in fact thought to be lead deposits. Graphite was only discovered to be a separate pigment, hence the confusion, although even then it did not receive its name until 1789.)

## Surface Morphology / Microscopic Description

Semi-crystalline with a flaky, greasy texture and dull-grey colour. Its structure is similar to that of metals; the carbon atoms are joined by covalent bonds into planar networks of hexagonal rings.



## Aging Characteristics

It is one of the most stable and refractory of all materials. Although physically it is 'flaky' and friable because of its layers of sliding sheets of atoms (as seen above).

Extremely stable at high temperatures.

Conducts electricity like the metals in moving electrons.

## Technical Examination Techniques

Has a high refractive index and reflective power of about 37%.

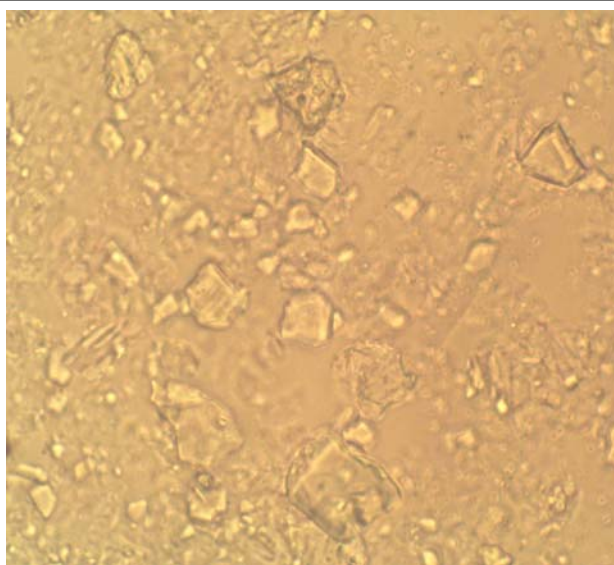
Microscopically it appears opaque with a dull but shiny surface. Particles are dense and usually difficult to separate. Particles exhibit relection pleochroism and birerectance but do not exhibit birefringence becoming black under cross-polars.

The element is conductive and thermal.

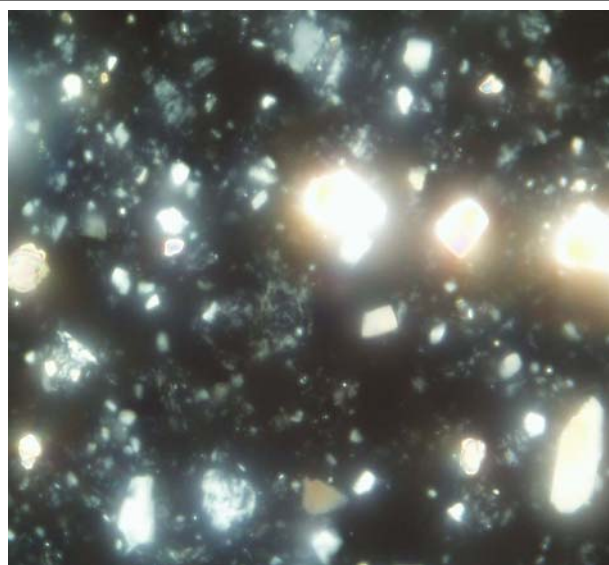
# Gypsum

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (calcium sulphate dihydrate)

**Terra Alba, Gesso, Alabaster**, from the Greek γύψος (the mineral)



Microscopic appearance at x500 mag



Microscopic appearance under crossed polars

## Dates of Use

Ancient times to the present day

## Summary of Manufacture

Naturally occurring in a number of varieties and often associated with salt deposits. Deposits are found all over the world but mainly in Europe, USA and Canada. Gypsum is found in crystalline form (selenite), transparent and foliated (satin spar). Alabaster can differ in white hue and particle size depending upon its country of origin. Rock gypsum is a dull white, granular and often found with impurities such as clay, silica and calcium carbonate. The mineral in all its forms was ground and combined with a medium or glue to form an inert white pigment. Today terra alba is ground to a 200 fine mesh and sized by air separation to produce the finest of gypsum grades.

## Brief History of Usage

Fine grades were commonly used as prime coats on bases of paintings and as a filler or bulking agent. Very important in the preparation of Plaster of Paris and cements. Occasionally utilized as a base for lake pigments and is found as a constituent in some artificial oxide reds such as Venetian Red. Rarely used with oils because of its low refractive index.

## Surface Morphology / Microscopic Description

Heterogenous clear crystals.

Colourless to white tabular rhombs.

Characteristic glass-like crystals, which show distinctive birefringence under cross-polars, some appearing luminous white while others appear duller.

Particles are usually 5 - 50µm in size.

## Aging Characteristics

A very stable pigment only drying in the presence of heat.

Slightly soluble in water and can often be seen to effervesce particularly on wall paintings where damp is often present.

Soluble in dilute hydrochloric acid.

Precipitates in weak acid to form very characteristic needle-like crystals which mass together.

## Technical Examination Techniques

According to Gettens & Stout particles exhibit low birefringence, however in the sample photographed some particles were highly birefringent at cross polars.

Oblique extinction of some particles should also be seen.

Does **not** exhibit pleochroism. Halo around the particles moves outward therefore  $\mu = < \text{ or } = 1.66$ .

# Kermes Carmine

$C_{22}H_{20}O_{13}$  (Kermesic Acid - Colouring Principle)  
Carmine Lake or Crimson Lake

Microscopic appearance at x500 mag

Microscopic appearance under slightly crossed polars

## Dates of Use

Native European insect equivalent of the New World cochineal beetle, known since Ancient times and revived in popularity after the discovery of the Americas. Still used today.

## Summary of Manufacture

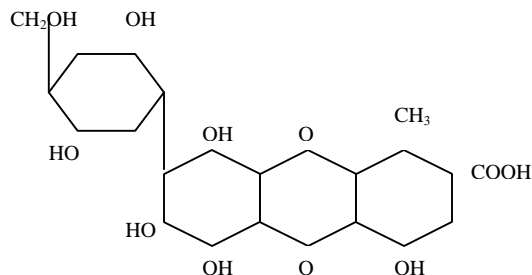
A crimson-red lake is obtained through the precipitation of the extract of the kermes scale insect with iron free alum. Usually found in the form of a lake, which principally may include substances such as calcium, tin or magnesium in addition to alum. The name 'Carmine', however is also given to a synthetic and manufactured substitute for the natural source.

## Brief History of Usage

Harvesting the beetle in Europe was revived from the middle of the 16<sup>th</sup> Century after the discovery of the Americas. However the pigment is one of the oldest known, was mentioned in the bible, in the writings of Pliny and Dioscorides and used in Ancient Egypt. Recipes for its manufacture were published as early as 1656. It was also one of the principle colours in the palettes of portrait miniature painters from the middle ages and onwards. All carmine lakes tend to be translucent when used in oil painting and as a result were often used in glazes in this medium.

## Surface Morphology / Microscopic Description

Almost indistinguishable to cochineal under the microscope.



Kermesic acid

## Aging Characteristics

Generally lakes made with the insect tend to have a better light-fastness than their manufactured counterparts. Light-fastness being between 1 and 2 on the British Standard. Not affected by hydrogen sulphides. Possesses a strong aromatic smell, which is often imparted to cloth.

## Technical Examination Techniques

Kermesic acid is distinguished from carmonic by its solubility in ether.

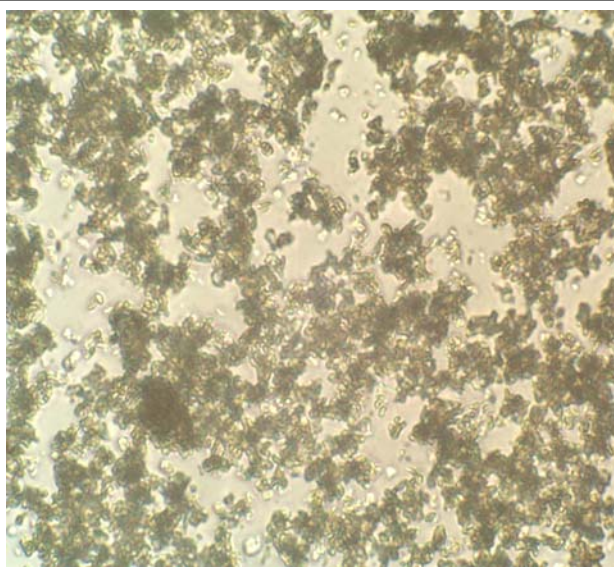
Readily soluble in methanol, ethanol and glacial acetic acid. Soluble without decomposition in concentrated sulphuric acid giving a violet-red solution.

Carmine lakes can vary in hue from wavelengths of 497c-of a purplish hue; to a strong red or deep yellowish pink with a wavelength around 612nm.

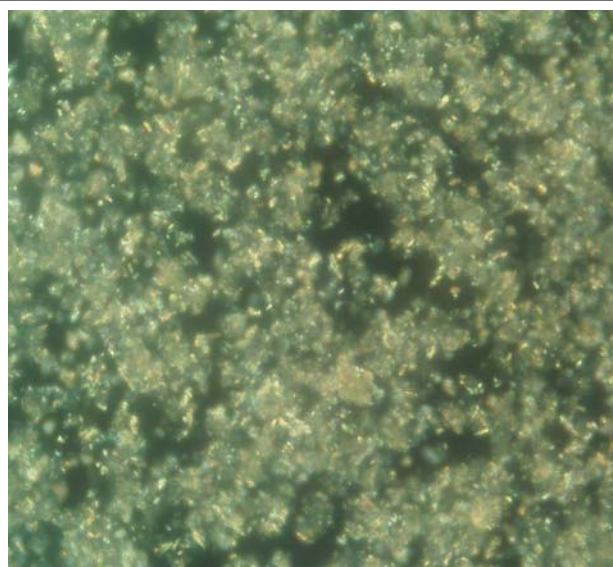


# Lead White

$2\text{PbCO}_3\text{Pb}(\text{OH})_2$  (Lead, Carbon, Oxygen, Hydrogen)  
(*Flake White*)



Microscopic appearance at x500 mag



Microscopic appearance under crossed polars

## Dates of Use

Since ancient times up to 19<sup>th</sup> Century when its poisonous lead content restricted its manufacture and sale as an artist's pigment.

## Summary of Manufacture

Many recipes for the pigments manufacture have been recorded over the centuries. Since lead white is a poisonous compound if inhaled as a dust or ingested, grinding in manufacture was a dangerous industry and as a result the process was banned after legislative action. Today, however, improved processes and safety standards have revived its manufacture today, but it is still no longer produced as an artist's paint. Cremnitz white is a special kind of lead white prepared by the action of acetic acid and carbon dioxide on litharge. It is favoured by artists and considered to be whiter variety.

## Brief History of Usage

Known since ancient times and was mentioned by Pliny and Vestruvius who describe its preparation from metallic lead and vinegar. Commonly used in Medieval times in both oil and watercolour, as a ground and for opacity in 'body' colour used in miniature painting. Lead white is almost the only white used in easel painting up until the XIX Century.

## Surface Morphology / Microscopic Description

Tiny, fine, colourless crystals of slightly differing size. Appear as rounded, hexagonal plates at high magnification. Homogenous crystals with an average size of 1-50 $\mu\text{m}$ .

A finely divided crystalline compound, comprising of the basic carbonate of lead and ordinarily contains about 70% of the latter and 30% lead hydrate.

Some appear as powdery particles; others like shards of glass.

## Aging Characteristics

Has a tendency to yellow when not exposed to sunlight. Its surface is blackened on contact with sulphides in the air causing the chemical reaction of lead carbonate to black lead sulphide. The lead hydroxide part of the white lead molecule is able to partially 'saponify' linseed oil to form with it a lead soap called lead linoleate. This fact has been used to explain why lead white in oil forms has such a hard and porous paint film. It is also a given reason for the transparency of aged lead white paint films. Readily soluble in dilute mineral acids and in acetic acid producing effervescence.

The siccative or drying action of lead white upon oils is another reason for its being so widely used.

## Technical Examination Techniques

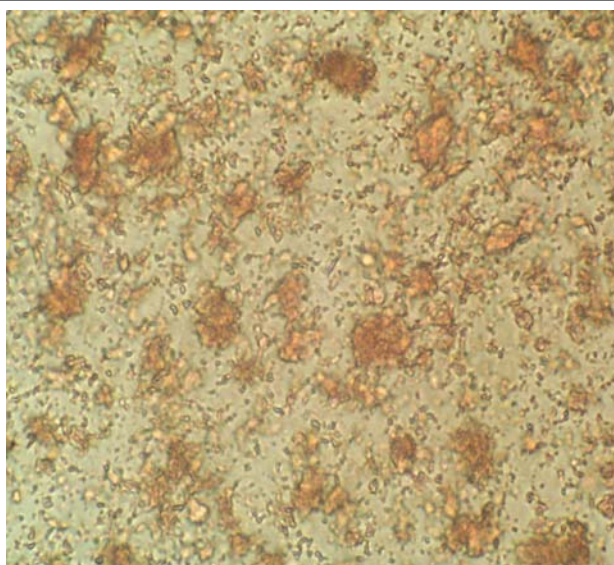
Appears transparent under infrared light, white under IR False colour film.

Fluoresces bright white under Ultra Violet light.. Particles exhibit pleochroism turning pale green. The halo around each crystal moves inward therefore  $\mu = >> 1.66$

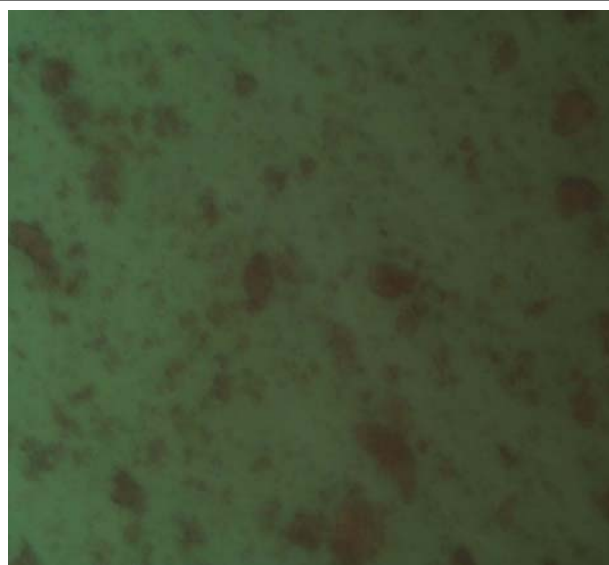
Particles exhibit high birefringence Polarisation shows bright white crystals, a few may appear to be orange or red.

# Madder

$C_{14}H_8O_4$  (Colouring Principle - alizarin- 1,2 dihydroxyanthraquinone, derived from the herbaceous root of *Rubia tinctorium*) **Madder lake, Alizarin**



Microscopic appearance at x500 mag



Microscopic appearance under slightly crossed polars

## Dates of Use

Ancient times to the present day.

## Summary of Manufacture

Mass cultivated in Europe and Asia Minor, prior to synthetic production, the root is harvested from plants 18 to 28 months old. The alizarin dye is extracted through fermentation of the root with sulphuric acid: The pigment is made by adding alum to the root and precipitating the mixture in an alkaline solution. The root also yields another dye called purpurin which makes the lakes produced more of a red/ orange hue compared to that of those made from synthetic madder

## Brief History of Usage

The plant is native to Greece and was probably first used as a dye for cloth. The dye produced was often referred to as Turkey Red and was widely used to dye cloths such as French military cloth. Found in artifacts from both Ancient Egypt and Greece. As a pigment it was prominent in the palettes of the seventeenth and eighteenth century's and often seen mixed with a white such as lead white to make flesh tones, particularly in portrait miniatures. Alizarin was chemically isolated in 1826 by Colin and Robiquet and synthesized in 1868 by Graebe and Lieberman.

## Surface Morphology / Microscopic Description

Alizarin lake particles are small bright pink and heterogenous.

They often clump together making distinction difficult.

Crystals generally appear a translucent pink like stained glass.

Particle size is usually 1-20µm

Both the natural and the synthetic madder are indistinguishable even at high magnification.

Halo around each particle moves inward indicating its refractive index is more than or equal to the medium, 'meltmount' ( $n > 1.66$ ).

## Aging Characteristics

One of the most stable organic pigments/ dyestuffs, although it can be quite soluble.

Turns purple upon reaction with dilute sodium hydroxide. Synthetic madders should be more stable and more intense in colour than natural madder.

Both madder and its lake are soluble in hydrochloric acid.

Chemical formulae for the alizarin lake;

***e+Al(OH)<sub>3</sub> 1,2dioxanthraquinone,***

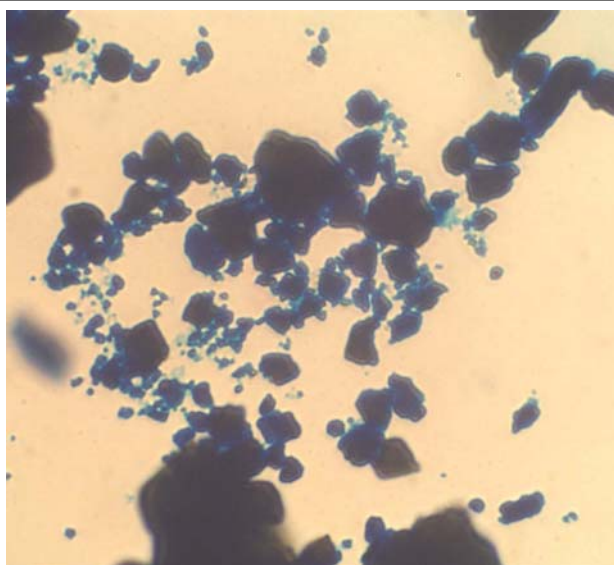
## Technical Examination Techniques

Particles are isotropic although confusingly occasionally one or two crystals can still be seen (for those crystals birefringence is low). Particles do not exhibit extinction, pleochroism and are unaffected by the red compensator. Crystals do, however, appear pink under cross polars (polarisation colours).

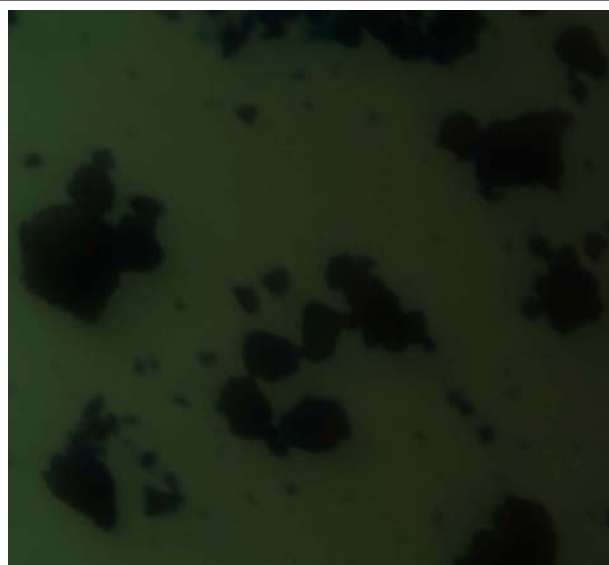
Natural madder fluoresces a bright yellow/ red due the purpurin constituent in ultra-violet light whereas synthetic madder shows a slight violet fluorescence. Appears purple/ red in transmitted light.

# Prussian Blue

$\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$  (ferric ferrocyanide) Iron(III)-hexacyanoferrate(II)  
Berlin Blue, Paris Blue



Microscopic appearance at x500 mag



Microscopic appearance under slightly crossed polars

## Dates of Use

Produced from the middle of the eighteenth century to the present day.

## Summary of Manufacture

Now commonly made by the action of an oxidising agent, such as potassium bichromate and sulphuric acid, upon a mixture of coppera (ferrous sulphate) and sodium ferrocyanide. Slight variations in shade and physical composition can be produced by controlling the conditions of precipitation and oxidation.

## Brief History of Usage

The first manufactured pigment, made by Diesbach in Berlin around 1704. He accidentally made the pigment while experimenting with the oxidation of iron. It was widely available to artists by 1730 widely used in Europe by 1750. The darkest of all the blues Prussian blue was known for its intense hue and greenish tint. Extensively used in water-colour, and first recorded by J.E. La Farque from 1770. Since then it has been extensively used pigment across the world.

Its use in acrylic painting has been largely replaced by today's 'phthalo blue'.

## Surface Morphology / Microscopic Description

Small particles with a greenish hue.

Particles clump in amorphous aggregates.

Technically the pigment is a ferric ferrocyanide and is so finely divided that it resembles a dye.

A deep blue colour in powder and lump form but when pressed shows a coppery lustre.

Soft particles with an average size of  $0.5\mu\text{m}$

Crystals form agglomerate spheres, which tend to clump together making single particle study difficult.

The pigment has a cubic crystal system.

## Aging Characteristics

Possesses an excellent drying capacity.

Transparent in colour, but has a high tinting strength.

Fairly permanent in light and air.

Unaffected by dilute mineral acids.

Extremely sensitive to alkalis which causing the particles chemically react and turn brown.

## Technical Examination Techniques

Particles are isotropic and do not exhibit pleochroism, birefringence or extinction.

Transmission colours with the Chelsea Filter = blue-grey

Green-blue in transmitted light.

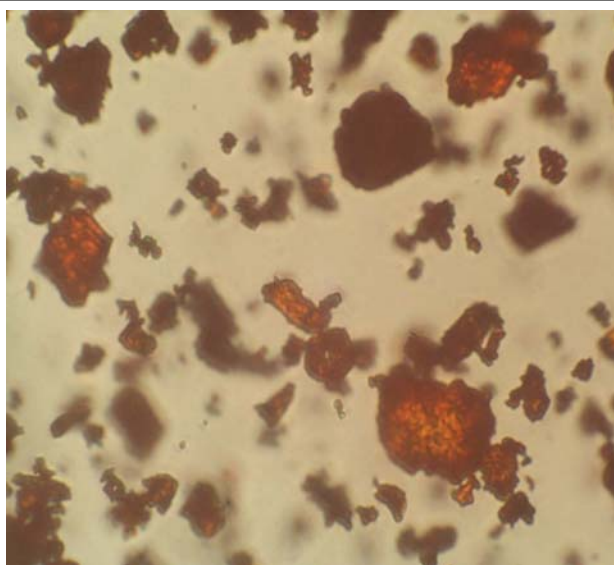
Soluble in 10% oxalic acid. Decomposes rapidly on ignition and leaves a residue of ferric oxide.

Melting point at  $120^\circ\text{C}$  at which point it darkens. See Appendices chemical test for prussian blue.

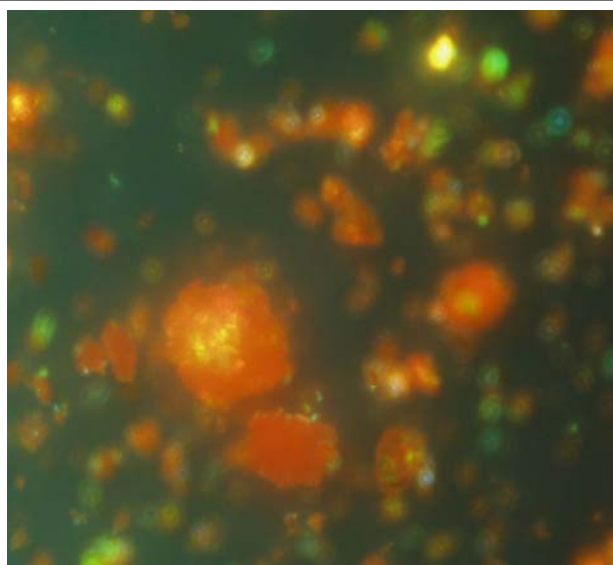


# Red Lead

$\text{Pb}_3\text{O}_4$  Red tetraoxide of lead



Microscopic appearance at x500 mag



Microscopic appearance under crossed polars

## Dates of Use

Ancient times until recently in industry.

## Summary of Manufacture

One of the earliest artificially prepared pigments still in use today.

Produced by various methods of roasting litharge ( $\text{PbO}$ ) in air or oxidizing molten atomized white lead for a number of hours at a temperature of  $480^\circ\text{C}$ .

## Brief History of Usage

Known in antiquity as 'inimum', red lead has probably been manufactured since the discovery of lead itself. It was a favourite of Byzantine and Persian illuminators and commonly used in European manuscripts and paintings. It is seen less on wall paintings and wood panels although widely used in the wall paintings of China and Central Asia. Up until recently and the manufacture of other anti-corrosives, red lead was often used as a primer in industry on steel bridges etc. No longer manufactured for artists due its toxic nature and its colour change upon ageing. The colour was matched instead by adding cadmium yellow to venetian red.

## Surface Morphology / Microscopic Description

Tiny homogenous particles often clumped together. Often dark brown in colour to a deep red or orange red.

Microscopically particles tend not to be very characteristic but some particles appear transparent and orange -red by transmitted light.

Crystals are usually  $1\text{--}50\mu\text{m}$  in size.

High refractive index but only slightly birefringent according to Gettens & Stout. Most crystals in the sample photographed exhibited high birefringence although some were less bright.

## Aging Characteristics

Has a good hiding power.

Moderate permanence and stability.

Initially orange-red in colour it is photooxidized to a light pink in the sun or a brownish red depending upon the environmental influences. Browning has more notably occurred when it has been applied in water colour or tempera medium.

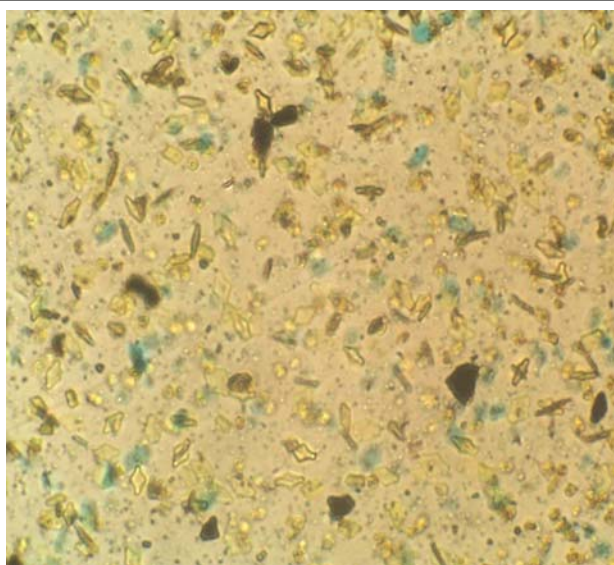
Favoured because it has good hiding power and a thick texture. The  $\text{PbO}_2$  functions as an oxidising agent within the whole structure of  $\text{PbO}_2 \cdot 2\text{PbO}$  resulting in the change in hue over time.

## Technical Examination Techniques

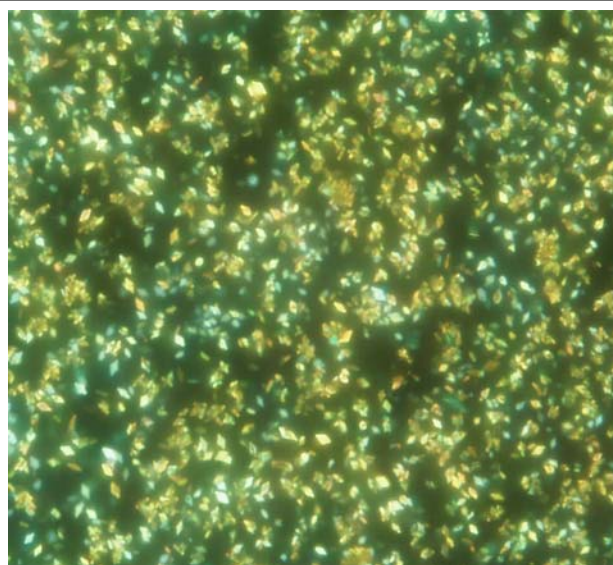
Particles are isotropic, do not exhibit birefringence, extinction or pleochroism. Unaffected by the red compensator and most do not exhibit polarisation colours although sometimes second order blue or green colours are seen in elongated transparent particles. Chemically reactive turning brown with nitric or acetic acid resulting in the formation of brown lead oxide. Hydrochloric acid turns it white (lead chloride) and sulphides blacken it. Semi transparent under infra-red light, yellow-brown under IR false colour and dark red in UV light.

# Terre Verte

$K(Ca_{1/2}Fe^{III})_2(Fe^{II}Mg)(AlSi_3Si_4)O_{10}(OH)_2$  **Green Earth**  
(Composed of the minerals celadonite & glauconite)



Microscopic appearance at x500 mag



Microscopic appearance under crossed polars

## Dates of Use

Since Ancient times to the present day.

## Summary of Manufacture

Natural deposits can be found throughout Europe but good quality sources are few and include Cornwall in England, France, Cyprus, Germany and Monte Baldo near Verona in Italy. Most seem to have originated as marine clays as the natural deposits are mined, ground and washed in order to be used as pigments. Naturally their colour varies in shade from yellowish to sage green to greyish with the purest green being more sought after. The clay is essentially a mixture of the minerals celadonite and glauconite, but it is a complex mixture of magnesium, hydrous iron and aluminium potassium silicates.

## Brief History of Usage

Used widely across Europe grades and hence hues differ with the best, purer green sources naturally found in England, Germany, France and Italy. Identified on Roman wall paintings at Pompeii and Dura-Europos. The bodies and faces in Italian wall paintings were often primed with green earth for flesh tones hence the sometimes apparent hue today. In modern times a substitution mixture of red earth and viridan can often be confused with the pigment.

## Surface Morphology / Microscopic Description

Terre verte can often appear as a confusing mixture of particles.

Crystals are coarse and rounded.

Most appear a grayish-green but many characteristic translucent, angular silica particles are usually apparent.

Some distinctive yellow or brown crystals may also be seen.

Its natural variations in hue as seen by the naked eye can probably be attributed to the varying amounts of iron in the ferrous state of the pigment.

Polycrystalline aggregates

Colours can vary from yellow to green-blue

Particles are usually 1-30µm in size.

## Aging Characteristics

Earth pigments and in particular, green earth, are generally considered the most permanent of the natural pigments.

Low hiding power hence it is rarely seen mixed with oil but often in tempera painting.

Turns reddish-brown upon heating.

Unaffected by atmospheric conditions including light or air.

Unaffected by dilute alkalis and acids.

## Technical Examination Techniques

Particles exhibit moderate birefringence and undulose extinction.

Transmission colours with the Chelsea Filter = green to grey. (Imitation terre verte appears bright red.)

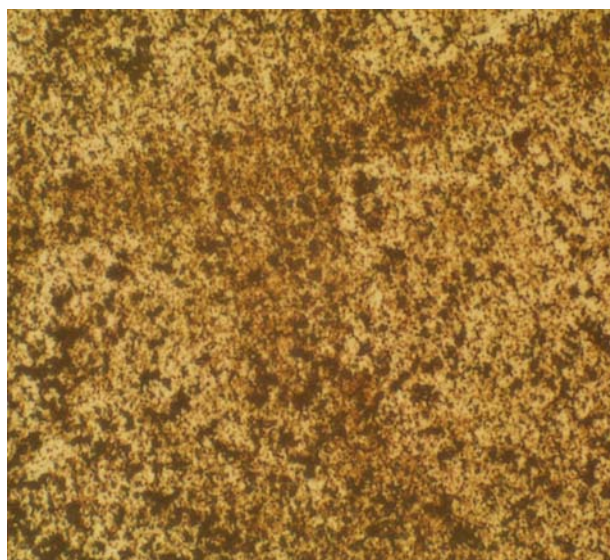
Refractive indices from 1.61 to 1.64

Confirm with microchemical tests for ferric and ferrous iron as long as the ions are put into solution by the treatment with acid. The organic base reacts ferrous salts in acid solutions to give a stable, deep red cation.

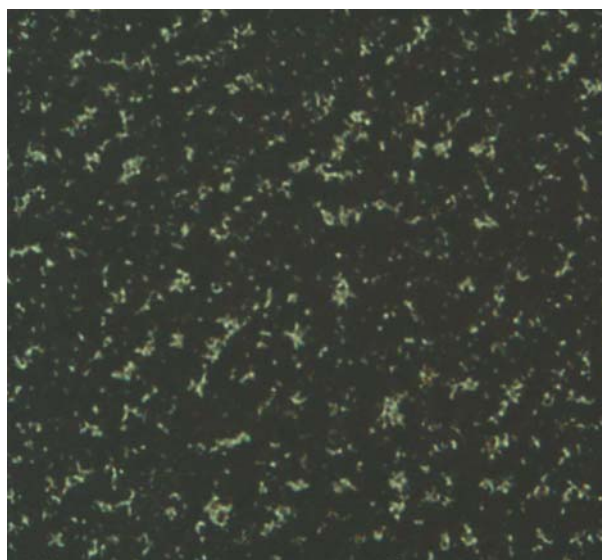


# Titanium White

$\text{TiO}_2$  (Ilmenite, originally menachanite - principal ore)  
Titanium Dioxide, titanox



Microscopic appearance at x500 mag



Microscopic appearance under crossed polars

## Dates of Use

Approx 1916/19 to the present day.

## Summary of Manufacture

The ore is chemically broken down with concentrated sulphuric acid. The result is a deposit of iron and titanium sulphate, which is then dissolved in water and boiled to result in the precipitation of the titanium as metatitanic acid and its separation from the iron. Barium carbonate is added to the precipitate to neutralize the acid after which it is calcined. Titanium oxide is usually manufactured with approximately 30% titanium oxide and 70% barium sulphate.

## Brief History of Usage

First described by William Gregor in England around 1791. It was, however, recognized as an element later, in 1795 by a German chemist called Kalproth. The pigments natural ore is rutile, but titanated iron ore (ilemnite -  $\text{FeTiO}_3$ ) can be found in its largest natural deposits on the coast of Norway. Manufacturing it as a pigment presented difficulties and it was not until the early 1900s that American and Norwegian companies began to develop its production for painting. Most supplies of its ore come from Norway today.

## Surface Morphology / Microscopic Description

The strongest most brilliant of the white pigment available to artist's ever. Microcrystalline in nature with fine particles.

Very fine pseudo-opaque but generally colourless crystals. Often rounded rhomboids.

The crystals are so small that they often appear cream to a light brown opaque colour under normal incident light on the microscope.

Whereas they are supposed to be highly birefracting and should appear bright white at crossed polars. The particles in the sample photographed here appear white but only moderately birefracting. Perhaps being less obvious or bright to the naked eye due to the size of the crystals

Particles are usually up to  $1\mu\text{m}$  in size.

## Aging Characteristics

Titanium white has excellent all round chemical stability.

Excellent hiding power and with twice the opacity of pure lead white. Very stable being unaffected by heat (hence it is commonly used in pottery glazes and enamel). Unaffected by dilute alkali's, acids, light and air. Non-reactive with drying oils and therefore has a very slow drying time. High oil absorbing nature.

## Technical Examination Techniques

The tiny round particles and their high birefringent property is characteristic of this pigment and so makes it distinctive from the other whites.

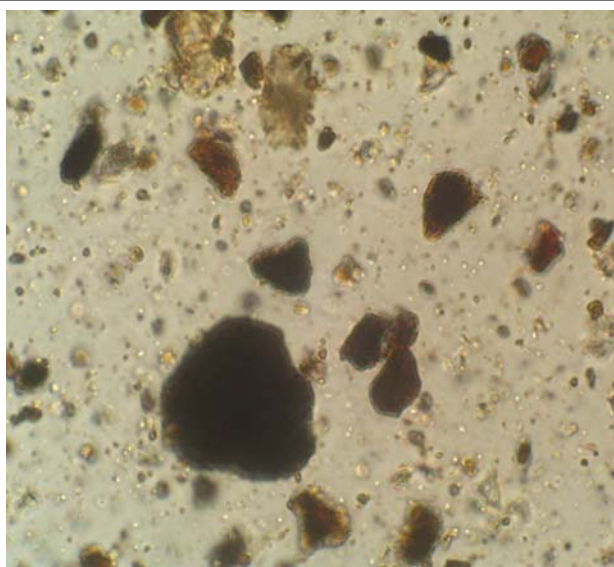
Confirm identity with a microchemical test for Ti.

Analytical examination with Raman microscopy and IR spectra.

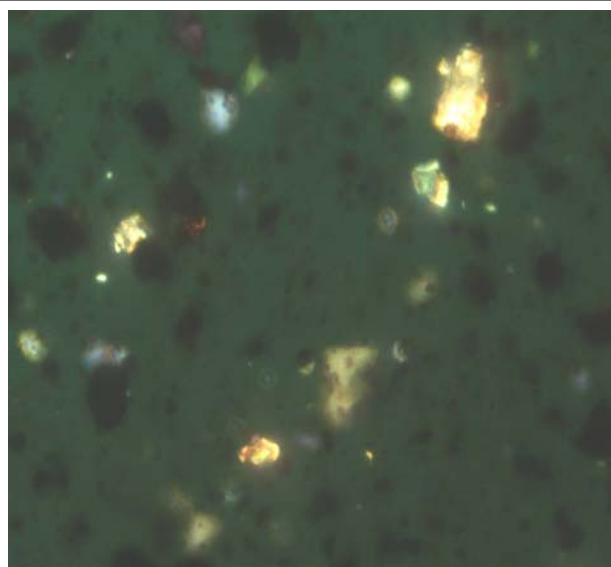


# Umber

$\text{Fe}_2\text{O}_3 \cdot \text{MnO}_2 \cdot n\text{H}_2\text{O}$  Iron(III)oxide containing manganese(IV)oxide  
Raw Umber, Burnt Umber



Microscopic appearance at x500 mag



Microscopic appearance under slightly crossed polars

## Dates of Use

Ancient times until the present day

## Summary of Manufacture

Found in natural deposits across Europe including England, Germany, France, USA and Cyprus. It is found naturally in many shades from browns, to yellows and even pale blue. Mined as a crude lump and like other minerals the lumps are ground, washed and sieved in preparation for use as a pigment. Burnt umber is made by roasting raw red earth, which chemically turns the compound from the ferric hydrate state to ferric oxide. The latter process results in a warmer, redder umber in comparison to the pigment known as raw umber. Compositionally the umbers contain around 45 to 55% iron oxide, 15% manganese oxide and lesser proportions of silica, alumina etc.

## Brief History of Usage

Probably used as a pigment since prehistoric times but prolifically in and since the Middle Ages where its use can be commonly noted in easel painting. Generally they are the main source of brown pigment for artists paints. Umbers dry well in oil because of their manganese content and as a result can often be found in oil medium and varnishes.

## Surface Morphology / Microscopic Description

Umbers range in hue from a deep brown to reddish and greenish browns depending upon their provenance.

Generally particles are heterogeneous and characteristically rounded as can be seen in the photographs above.

Burnt umber particles are almost identical to that of the raw umbers.

Burnt umber particles, however, do tend to be redder and sometimes appear more transparent.

Particles size of all umbers is usually between 1-50µm. Crystal faces are sometimes described as globular.

## Aging Characteristics

Grades and therefore permanence varies and poor grades, which contain humus matter are fugitive.

Generally, however, all umbers are considered to have excellent permanence and all are non-toxic.

All umbers are unaffected by alkalis and dilute acids.

All have high oil absorption requiring around 18% oil to grind them in oil paints. As a result the latter oil films tend darken with age.

## Technical Examination Techniques

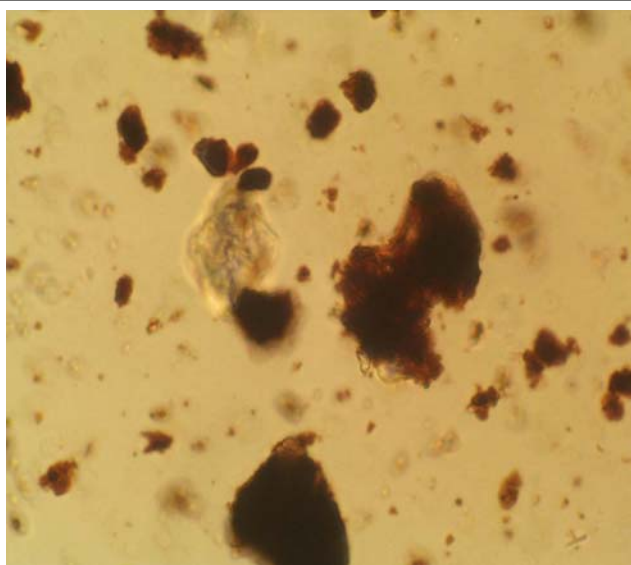
Particles are isotropic, not birefringent (Gettens & Stout) nor do they exhibit pleochroism. (Although in the sample photographed above, some particles were moderately birefringent.)

Transmission colours with Chelsea Filter = Burnt umber appears from a grey to a red-brown, while raw umber appears dark grey to colourless.

Each has a specific refractive index: raw umber is 1.80. burnt umber is 2.20.

# Van Dyke Brown

Humic substances, Soft Coal  
(Cassel Earth, Cologne Earth)



Microscopic appearance at x500 mag



Microscopic appearance under slightly crossed polars

## Dates of Use

Probably discovered in the late 16<sup>th</sup>/ early 17<sup>th</sup> Century.

Prepared as a media for painting from the 17<sup>th</sup> Century. 19<sup>th</sup> Century for both oils and watercolours.

## Summary of Manufacture

Derived from earth compounds such as soil and peat, similar in composition to lignite brown or coal. Generally it has over 90% constituent organic matter with small amounts of iron, alumina or silica.

It is prepared first by heating to drive off excess moisture and then by the common process for earth pigments. Essentially the matter is dried and homogenized.

## Brief History of Usage

So called, it is said, after 'the famous artist who was partial to the use of brown in his pictures.' (Weber, p115) It is suggested that the brown 'lignite' colours came into use in the late XVII and XVIII Century's when brown backgrounds and dark decor became popular in Europe.

Extensively used in the 19<sup>th</sup> Century in both oils and watercolour. Partially transparent in oil and as a result, has been used for staining woods and glazing in pictures.

## Surface Morphology / Microscopic Description

Heterogenous in particle size and composition and the particles appear more opaque and crystalline than ochres and umbers.

Particles look more like flakes and some appear fibrous.

The pigment appears to dissolve in oil and in varnish to stain it as a result it is difficult to identify in such mediums.

Particles are usually 1-50µm in size.

## Aging Characteristics

It fades on exposure to strong light and develops a cold, grey tone.

Does not solidify in mixtures with oil, but is stable in varnish solutions. More permanent in oil than in water colour.

Partially transparent in oil so was often used for staining woods and for glazes on paintings.

Solidify's in mixtures with oil but is stable in varnish solutions.

## Technical Examination Techniques

Particles are questionably birefringent depending upon the sample (no birefringence was noted in our sample). Crystals do not exhibit pleochroism.

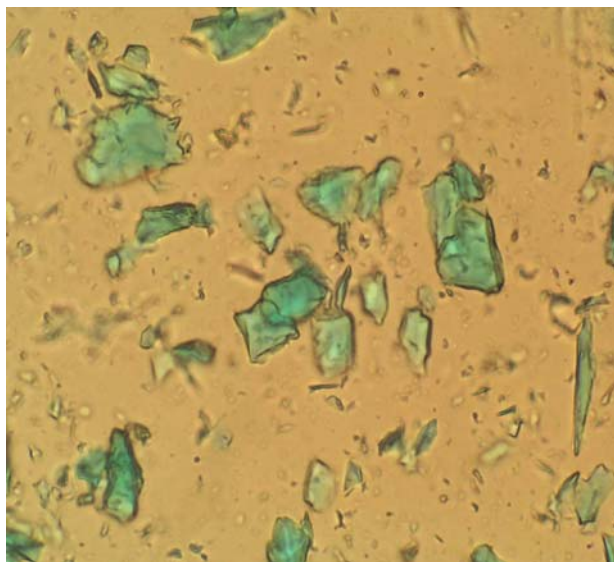
Transmission colours with the Chelsea Filter = red to a red/brown.

When ignited it burns and leaves a grey ash, and when heated in an ignition tube, tarry vapours are given off.

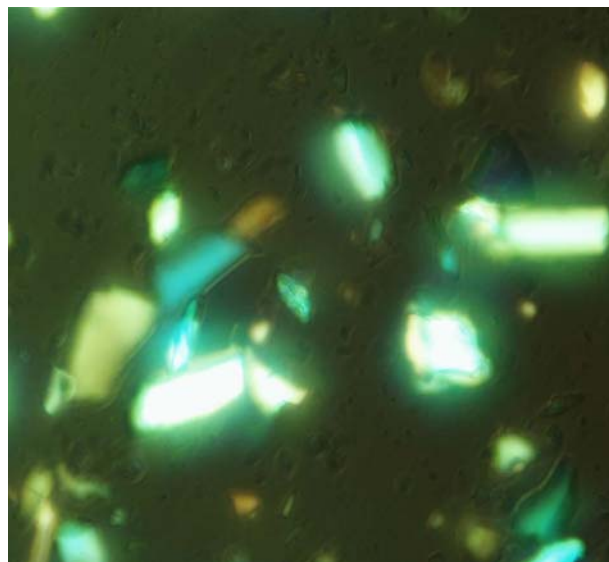
Dissolves in sodium hydroxide to a deep brown solution.

# Verdigris

$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{Cu}(\text{OH})_2$  (An acetate of copper)  
Vert de Grece



Microscopic appearance at x500 mag



Microscopic appearance under slightly crossed polars

## Dates of Use

Manufactured since Ancient times up until the present day, although it is rarely sold as an artists pigment today due to its toxic nature.

## Summary of Manufacture

Produced by the action of acetic vapours on strips of metallic copper, which can then be lixiviated and the product recrystallised from the reacted acetic acid. Many historical recipes for its manufacture can be found, but Pliny described exposing copper to the vapours of fermenting grapes or in closed casks over vinegar. (Gettens & Stout)

## Brief History of Usage

Ancient recipes can be found in the writings of Theophrastus and Pliny. The most well-known production methods have been associated with Montpellier in France, but its manufacture has also been documented in the Flemish and Italian Schools from Medieval times. Noted uses in Early Italian landscapes in oil where today the pigment has browned. Often seen in illuminations, book illustrations and maps where it fell in and out of favour due to its fugitive nature. Later it can be seen in the palettes of the followers of Van Dyke. (Meyer)

## Surface Morphology / Microscopic Description

Intense green crystals of different shapes and sizes. Particles can vary greatly depending upon the method of manufacture, for instance well-crystallised verdigris particles appear like shards of pointed needles; Whereas, particles that have not undergone crystallisation may appear like transparent grains. Due to its varying states, particles are difficult to distinguish, their distinct green colour and resinous quality are the main clues to its identity. Particles are usually 1-30µm in size.

## Aging Characteristics

The most reactive and unstable of all the copper pigments often aging to a dark brown or black. Verdigris is fugitive and reacts upon contact with hydrogen sulphides turning black. It is slightly water soluble and very soluble in all acids. With heat it decomposes to form acetic acid, water and leaves a black residue. Gettens & Stout state that 'the colour is destroyed by dilute alkali and by heat'. Warmer green tones in paintings may have been made by mixing verdigris with a yellow such as gamboge or saffron, often in these cases the pigment remains green being possibly protected by the resinous yellow.

## Technical Examination Techniques

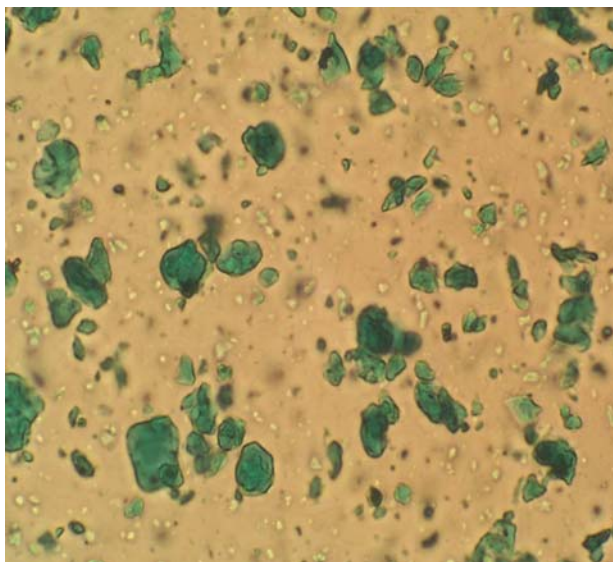
Particles exhibit pleochroism, some becoming colourless upon rotation at crossed polars, although some may appear to turn a deep bluish green.

Particles exhibit weak birefringence, undulose extinction and are isotropic appearing white and pale green at cross-polars. There is no change in particles as seen with the chelsea filter. Refractive index is less than the medium. meltmount. so therefore the halo around each crystal will move inward towards the crystal.

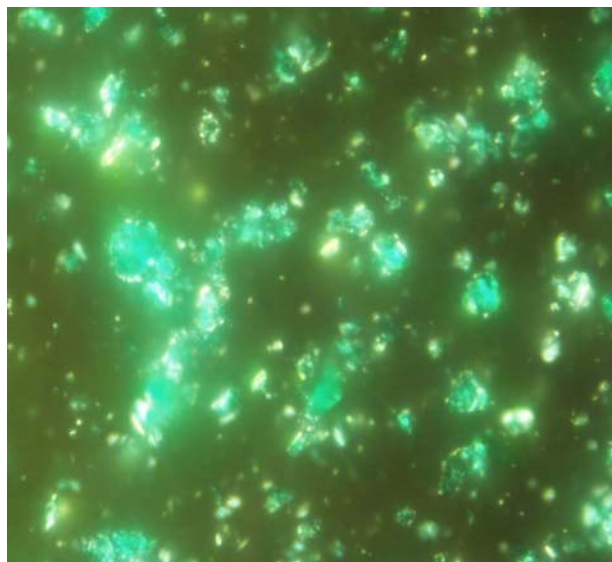


# Viridian

$\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  (Transparent oxide of chromium)  
Guignet's green, vert emeraude



Microscopic appearance at x500 mag



Microscopic appearance under slightly crossed polars

## Dates of Use

1838 to the present day.

## Summary of Manufacture

Prepared by heating a mixture of an alkali chromate with excess boric acid to a dull red heat. Once the mixture has been reduced it is raked into vats containing cold water and is left to cool and hydrate. The resulting pigment is then washed by decantation, ground while wet, washed again to free it of soluble salts and dried. The resultant pigment usually contains boric acid, some of which may be chemically combined with the chromium oxide.

## Brief History of Usage

Despite the fact the element chromium was discovered by Vauquelin in 1796 it seems that it was not manufactured as a pigment until 1838. When Pannetier, a colour maker in Paris began to make the chromium green. He and his successor Binet produced it for many years keeping its recipe a secret. Guignet was responsible for making a patent of a method of its manufacture in 1859. Viridian soon replaced Emerald Green particularly in industrial printing processes and quickly became a popular pigment in watercolour due to Emerald (Scheels) Green's poisonous nature.

## Surface Morphology / Microscopic Description

Bright green, transparent particles.

Homogenous emerald green crystals.

Some can be quite large depending upon the manufacturing process.

Some literature sources say large round crystals are a good indicator for this pigment although note that some samples may not provide characteristic crystals. Their intense colour is characteristic and should be true for all crystals.

Particles are fairly large, can be irregular in size and slightly rounded.

Particle size is usually 1-10 $\mu\text{m}$

## Aging Characteristics

Good permanence

Excellent tinting strength and stability in all mediums.

Unaffected by dilute alkalis and acids.

Unaffected by light.

Strong heat however chemically changes it to the opaque, anhydrous oxide.

## Technical Examination Techniques

Particles exhibit high birefringence with a bright intense emerald green colour.

Particles are anisotropic appearing emerald green in colour.

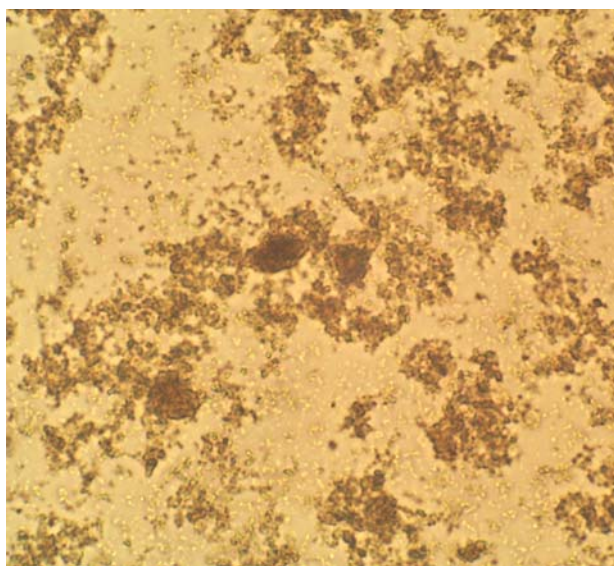
Particles do not exhibit pleochroism but do exhibit slight undulose extinction.

Transmission colours with the Chelsea Filter range from a grey to a claret red.

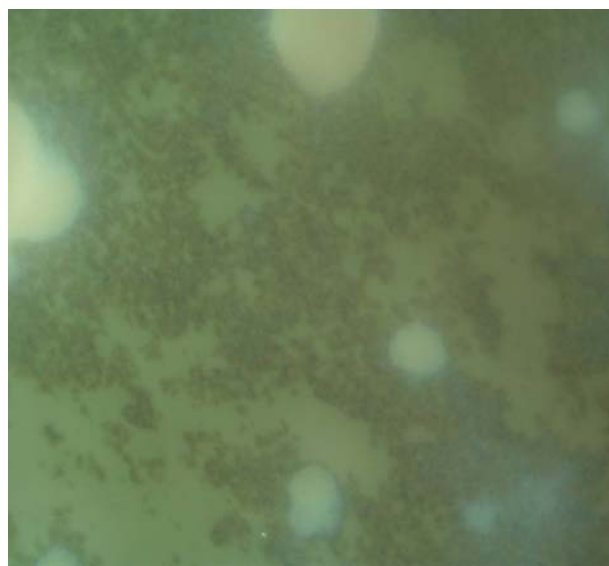


# Zinc White

Zn O (Zinc Oxide - Zinc & Oxygen) Zinc (II) oxide  
(Chinese White)



Microscopic appearance at x500 mag



Microscopic appearance under slightly crossed polars

## Dates of Use

As a pigment - from about 1830

First describes as an element by Margraaf, a German chemist, in 1746.

## Summary of Manufacture

The French processing of zinc oxide involves the manufacture of zinc vapour from the molten metallic zinc, and burning it in an oxidising atmosphere at a temperature of about 950°C. The fumes of white oxide are collected in a series of chambers.

## Brief History of Usage

Suggested as a substitute for lead white by Courtois of Dijon in 1782, but more than fifty years passed before it became commercially available. According to Church, a dense form of zinc oxide was introduced in 1834, as a watercolour pigment by Messrs Winsor and Newton Ltd of London. The main difficulty in its use at the time was its poor drying qualities in linseed oil. During 1835-1844, Leclair in France showed that the latter could be overcome by adding an oil that had been rendered siccative by boiling with pyrolusite ( $\text{MnO}_2$ ) and in 1845 he began, near Paris, to produce zinc oxide on an industrial scale. By 1850 it was commonly made as an oil paint.

## Surface Morphology/ Microscopic Description

The pigment originates as a smoke and has finely divided grains; the pigment from the French process is said to have grains less than  $1\mu$  in diameter. Its refractive index of 2.00 is about the same as lead white but unlike the latter it is birefracting.

Particiles are very fine and can only, therefore, be observed at high magnifications.

Zinc oxide is a pure, cold white, is non-poisonous but and a mild antiseptic.

Dry zinc is sold in varying forms of 'whiteness'. For example 'white seal' and 'green seal' contain over 90% zinc oxide. Green seal has the best hiding power whereas 'red' and 'gold seal' are less pure.

Acicular zinc oxide is a special form in which the particles are needle-shaped and joined in pairs to form X's.

Particles are usually up to  $2\mu\text{m}$  in size

## Aging Characteristics

The paint has a tendency to dry brittle and crack. Uffected by sunlight. Readily soluble in dilute alkalis, acids and ammonia without foaming.

Chemically reactive with hydrogen sulphide to form zinc sulphide, it is not darkened as zinc sulphide itself is white.

## Technical Examination Techniques

Appears bright yellow in Ultraviolet light.

Particles do **not** exhibit pleochroism. Halo around each crystal moves outward therefore  $\mu = \leq 1.66$

Particles exhibit slight undulose extinction.

Particles exhibit high birefringence (although in this sample only some particles exhibited moderate birefringence). Confirm with microchemical tests for zinc.