Preface

This is the resulting research project produced by Claire McBride during her Getty Trust postgraduate fellowship in paper conservation at Cornell University (Oct 2001-02). The following document is a first draft, as yet uncompleted and largely unedited in its entirety. The intention of the project was to begin compiling an accessible, practical atlas of pigments and paper fibers for the use of conservators in private practice and small studios. This year a solid ground of information was gathered from scientific and artistic sources on the most common paper fibers and pigments. The atlas design, information gathered, the microscopy and photography were researched and produced solely by Claire McBride as part of her learning and practical experience gained on this internship. However the idea of the atlas was the proposal of Tatyana Petukhova, Senior Paper Conservator at Cornell and this work could not have been produced without her constant encouragement and guidance. Much time and work was spent on the images and the image database of fibers and pigments gathered and stored at the Graphics Conservation Lab. We hope that this work will continue and the range of pigments and fibers covered will grow. Future students may make their own additions in their own specific areas of research until the more obscure pigments and fibers are included. It was with this in mind that a page template was provided at the end of each section. The atlas compiles basic reference facts on each pigment and fiber gathered from the arts and science libraries at Cornell as well as from articles and the world-wide-web. The bibliography points to further reading in specific areas but hopefully this document will reduce the excessive time spent by those of us in the conservation profession who find themselves searching for scientific and art history information from many different sources, as the latter two fields are usually kept very much apart. This document has been placed on the Cornell website, accessible through the Graphics Conservation page in its present state at the end of Claire McBride’s appointment at Cornell. Currently we are looking at publishing this atlas in hardback hopefully at the beginning of next year and as the work is refined and content checked for correctness, the copy available here will also be updated.
Introduction

This project aimed to produce a practical reference atlas for conservators in order to assist them in the identification of various pigments and paper fibers found in works of art on paper. The process of the atlas project resulted in the collection of a pigment and fiber sample library for the research use and interest of the Preservation & Conservation Department of Cornell University; for its staff, those of the Herbert F. Johnson Art Museum and Cornell students as a whole.

The atlas has four distinct sections; both Western and Eastern with each sub-splitting into pigments and paper fibers. Each section is colour coded with a border as illustrated on the following page and each section is in alphabetical order (rather than page numbered) so later additions can be easily added. The focus of the project is on the most common pigments and fibers with emphasis on Western pigments with which I am most familiar. The main function of this atlas is to become a practical reference guide, and a dictionary assisting conservators in small laboratory’s in both private practice and small institutions. Including both art historical and scientific information such as: chemical formula, manufacture, usage, dates of use, surface morphology, aging characteristics and methods of technical/ instrumental analysis.

Each sample is illustrated with a basic reflected light microscopic photograph as well as one taken through a polarizing light microscope at crossed-polars. Each with x500 magnification and with different samples aiming to encourage the reader to recognize the similarities in samples of the same type, and not to rely on exact matching to reference photographs such as those that I have recorded in the atlas and those from other sources. I aimed to record samples typical of the pigment or fiber and only slight alterations were made to the micrographs such as brightness and contrast through adobe photoshop in order to make the sample clearer in definition. Much time was spent on photography so a good image database could be compiled in the Graphics Studio for future reference. All pigments were purchased new from Kremer Pigmente so one should bear in mind, when studying and comparing samples the effects of light ageing for instance, and mediums which may inhibit clear analysis of samples from actual artworks. Be aware also that all samples are not alike! Mineral based pigments may vary greatly in size and uniformity largely as a result of the extent with which they were ground and washed during preparation. Fibers can vary from variety to plant to

The atlas also aimed to bridge the gap between practical studio conservation analysis and a more scientific approach aiding the identification process of a pigment or paper, the provenance of the object, its date and conservation treatment decisions. Although brief in data the bibliography and appendices directs users to particular reading and research documents reducing time on publication searches.

Although an ambitious project, it was intended that the work done this year would form a sound basis of information covering the most common pigments and fibers. We hope that future students will continue to add information and refine the data. With this in mind a template page has been added at the end of each section for students and conservators who wish to print out the project, make additions and work from it.
Key to Sections – Fibers split into sections and denoted by coloured borders.

Denotes a Pigment Originating from West

Denotes a Fiber Originating from the West.

Denotes a Pigment Originating in East

Denotes a Fiber Originating in the East

Denotes a Pigment Originating from Both the East & West

Denotes a Fiber Originating from Both the East & West
Eastern Pigment Atlas
Dragons Blood

Sanguis Draconis
Shrub species *Pterocarpus draco*

**Dates of Use**
Ancient times to, less commonly, the present day.

**Summary of Manufacture**
A red resin extracted from the Asian trees *Calamus draco* (a rattan palm) but occasionally also attributed to the resin from the shrub *Pterocarpus draco*. The bright dry resin looks similar to dried blood which inevitably gave rise to the legend of its originating from the blood of dragons and hence the name still used today. The resin is washed, ground and worked together with an oil or water based medium.

**Brief History of Usage**
Originating from Asia the pigment was traded Westward and was a popular red colourant in Medieval times being known as Dragons Blood. Pliny was the first to describe the myth of its source and many mythical accounts for its origination can be found since. The fashion for rich colours found in Persian art and then in Byzantine traveled home to Europe during the Crusades and with it rich reds, blues and greens from Eastern sources. It seems it found little use in the painters palette of the seventeenth century and generally after its hey day in the Middle Ages. It was expensive to import and inevitably synthetic reds took over.

**Surface Morphology / Microscopic Description**
As a resinous substance particles may be difficult to isolate or identify. It is a resin with a red/ brown surface colour changing to a red/orange hue in the center of the deposit.
Similar in appearance to cochineal and the carmine lakes, dragon’s blood is more orange in hue.

**Aging Characteristics**
As an organic of vegetable origin it has poor permanence.
Cennino Centini said of dragons blood ‘you should leave it alone and not care for it a lot as it is not in the conditions giving you much honour.’
(http://www.sebino.it/pigmenti/english/129.htm)
Highly transparent and often used for glazing, for instance mixing with varnishes or glazing silver to impart a copper tone.
Soluble in ethanol.

**Technical Examination Techniques/ Instrumental Analysis Techniques**
Particles do not exhibit birefringence as can be seen from the samples above. Particles themselves are difficult to see except at high magnifications.
With a magnification of x500 or less only a resinous substance will be seen which can only be confused with a carmine lake such as cochineal or kermes.
Raman microscopy & high powered liquid chromatography (HPLC) will distinguish each with standard samples.
Gambouge

(Gambogic Acid - Colouring Principle)
Yellow gum resin of particular tree species

**Microscopic appearance at x500 mag**

**Microscopic appearance under slightly crossed polars**

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**Dates of Use**
Since Ancient times in the Far East, spreading to the West in the 16th and 17th Centuries. Still used today.

**Summary of Manufacture**
Drawn from trees through incisions made in the bark. A milky juice exudes and hardens upon contact with the air. It was then sold in the form of hard yellow lumps, which are often covered in yellow dust.

**Brief History of Usage**
Used for centuries in the Far East in painting and quickly spread to the West as trade increased in the late 16th, 17th and 18th Centuries. Flemish painters were the first to exploit the pigment in oil paintings and importantly it was also used to impart a golden hue on the leather for which Amsterdam was famous in the 17th Century. By the 18th Century trade was such that it could be bought across Europe in lump form from the chemist. It was largely abandoned in oil painting because of its transparency but was commonly used in gold leaf and in water colours. Often mixed with Prussian Blue or Indigo to make a rich green that was known as Hooker's green. Gamboge fades however in sunlight which accounts for the blue trees, bushes etc often seen today in landscape watercolours of centuries before.

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**Surface Morphology / Microscopic Description**
Light yellow rounded particles. The majority of particles have a distinctive well-rounded shape but some will not conform to this description.

Crystals will appear translucent in reflected light but clearly cylindrical and yellow under cross polars.

Appears as a translucent resinous exudate.

Seen to have an amorphous structure.

Particles are usually between 1-50µm in size.

Gamboge = 70-80% yellow resin and 15-25% water-soluble gum. The rest is composed of esters, hydrocarbons, wax, ash residue and vegetable detritus.

**Aging Characteristics**
As a watercolour it is clear, highly transparent and warm yellow in hue with a medium tinting strength.

If powdered and ground in oil paint it tends to a fairly permanent medium, but in watercolour it tends to fade rapidly. Has a reputation for being soluble in everything and is partially soluble under heat in varnishes, linseed oil and gum arabic as well as in alcohol and some other organic solvents.

Unaffected however by sulphur compounds but bleached by strong heat.

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**Technical Examination Techniques/ Instrumental Analysis Techniques**
Particles are isotropic and show characteristic intense yellow birefringence. Some small particles, however, in our sample were not birefringent in comparison to larger cakes which glowed.

Refractive index ca. 1.58.

Test - Pigment is slowly soluble if heated in Aroclor (the pigments surface becomes globular).

Appears bright yellow in transmitted light and absorbs ultra-violet appearing purple/ black.
Indian Yellow

$C_{19}H_{16}O_{11}MgH_2O$  Magnesium or calcium euxanthate

(Alternative Names if Applicable)

Microscopic appearance at x500 mag

Microscopic appearance under slightly crossed polars

Dates of Use
Since ancient times in the Far East, traded to Europe and banned in England in 19th Century

Summary of Manufacture
Was once produced from the sun dried urine of cows fed solely on mango leaves (Mangifera indica Linn) in India. It was then exported in crude lump form called piuri to Europe where it could be powdered, washed and bound with a medium for painting. The lumps were brown on the outside and brilliant yellow-green on the inside. Synthetically produced Indian Yellow is still available however today from a few suppliers.

Brief History of Usage
Known since ancient times and used in Indian miniature painting. Exported and traded in Europe in the 18th Century but disfavoured in England in the late 19th Century when the truth about its manufacture was finally uncovered. Its production was finally prohibited in 1908 on humane grounds since mango leaves are harmful to cattle. Commonly seen in Indian miniatures. Found in European palletes from the 18th Century, particularly in water colours.

Surface Morphology / Microscopic Description
Yellow crystalline particles with a deep rich, translucent orange/yellow hue. Anisotropic and exhibiting weak birefringence. The coloring matter is principally the magnesium or calcium salt of euxanthic acid, $C_{19}H_{10}O_{11}Mg.5H_2O$. Particles can vary greatly in shape depending upon their manufacture from rods to spherulite to appearing like a gel. Particles can vary in size from 1-30µm.

Aging Characteristics
With a low hiding power and good tinting strength it was used in both oils and water based mediums because of its good lightfastness. Although direct sunlight will result in slight photoxidation and therefore fading. The colour is discharged in excess aqueous acid and may be regenerated by aqueous alkalinity. It is only slightly soluble in water and is decomposed by hydrochloric acid with precipitation of white euxanthic acid.

Technical Examination Techniques/ Instrumental Analysis Techniques
All Indian yellows are moderately birefringent Particles exhibit extinction although the type of extinction can vary from sample to sample. Exhibits strong bright yellow fluorescence in ultra-violet light. Appears clear in infra red light.
**Indigo**

**C十6H10N₂O₂** (Colouring matter - Indigotin)

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**Dates of Use**
Known since Ancient times to the present day.

**Summary of Manufacture**
A violet blue vegetable dye derived from certain plants cultivated in India from the genus *Indigofera*, among which *I. Tinctoria*, probably of Indian origin was the main source of the dye until the process of making the synthetic variety (from coal tar) was discovered by Baeyer in 1880. From the natural source preparation involved macerating the freshly cut plants, packing them into large vats and allowing them to ferment. After the glucoside is hydrolysed into indigo and sugar the dark precipitate is strained, pressed and dried into cakes.

**Brief History of Usage**
Earliest records have come from the Far East where it was used prolifically for dyeing cloth. It was known over Egypt and formerly grown all over the world but in particular India, China and Bengal indigo, which was one of the highest grades produced. It spread to Europe rapidly and was mentioned in the XII century in commercial trading documents. The pigment can also be found in Italian painting as early as the XV Century. Since 1900 and the invention of the synthetic variety natural indigo is rarely processed.

**Surface Morphology / Microscopic Description**
Deep blue, regular and slightly rounded particles.
All particles are very fine.
Some deep blue needle shaped particles often seen.
Particles are difficult to analyze and almost no distinct particles can be seen at magnification. De Wilde however, suggests that particles do appear at x1500 magnification.
Particles are usually between 1-10µm in size.

**Aging Characteristics**
Has a fair tinting strength but has poor permanence tending to fade in sunlight. Chemically stable being insoluble in water but soluble in hot water, ether, alcohol, lyes and hydrochloric acid. Nitric acid decomposes it with the formation of a yellow compound called 'isatin'. It is reduced by reducing agents to soluble indigo white, called 'leuco indigo'. The latter process is important to dyeing where the dye is taken up by the fibres and then oxidised by the air to soluble indigo blue. The pigment is also bleached by hypochlorite solutions.

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**Technical Examination Techniques/ Instrumental Analysis Techniques**
Particles exhibit slight pleochroism, are anisotropic and have a very low birefringence.
Transmission colours with the Chelsea Filter = varies from a dark blue to a red/violet.
Sublimes when heated to 300°C. Refractive index of >1.66
Looks grey under infra-red, very dark under IR False Colour and dark blue under UV light.
In thin films it is green and blue by transmitted light.
Naples Yellow

Technical Examination Techniques/ Instrumental Analysis Techniques
Particles are isotropic rounded yellow grains.
Particles do not exhibit birefringence or pleochroism.
Refractive indices of 2.535 and 2.665.
Confirmed by microchemical tests for lead and antimony.

Dates of Use
Ancient times to the modern day although its history is obscure.

Summary of Manufacture
Made from the prolonged roasting of the mixed oxides of lead and antimony; or from salts of those metals, like tartar emetic (potassium antimonyl tartrate) and lead nitrate with sodium chloride.

Brief History of Usage
(Note: Genuine Naples yellow is a lead antimoniate, however the paint tube colour of the same name is sometimes a substitute mixture of white and ochre, with or without an addition of red.) The name Naples yellow came to signify a shade of yellow rather than the actual source of the pigment. Used as a colour tint in yellow ceramic glazes in Babylon and Assyria and was also found in Egyptian glass of the XIX Dynasty. It was reputedly a pigment in the palette of the Old Masters but generally its history is unsure. Up until the watercolour period its importance is undocumented. It has been essential to the landscape tradition because it has the quality of appearing to recede into the picture's distant plains unlike other yellows which sit in front of the plain.

Surface Morphology / Microscopic Description
Essentially a lead antimonate which may be considered to be chemically combined lead and antimony oxides. It varies in colour from yelow to orange depending upon its constituent chemical proportions.
Particles are homogenous and appear very fine and finely divided, similar to what you would expect from a synthetic pigment.
No crystalline form can be detected even at high magnification.
Particles are usually between 1-5µm in size.

Aging Characteristics
Its hiding power, tinting strength and drying properties are good.
Chemically it is quite stable and is little affected by alkalis, dilute or concentrated nitric or hydrochloric acids.
It fuses only at high temperature but turns dark brown permanently.
**Orpiment**

**As₂S₃ (The yellow sulphide of arsenic)**

**Kings Yellow,** from the Latin, 'aauripigmentum' for gold/gold coloured paint

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**Microscopic appearance at x500 mag**

**Microscopic appearance under slightly crossed polars**

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**Dates of Use**

Ancient times up until the 1900s

**Summary of Manufacture**

This natural sulphide occurs widely, but in relatively small deposits. Principle Ancient sources seem to have been Asia Minor, Central Asia, Macedonia and Hungary. Natural deposits were mined, ground and washed in preparation. In modern times the artificial version can be made through a process of sublimation and precipitation.

**Brief History of Usage**

Known to the Greeks as *arsenikon* and related to the Persian *zarniikh* which is based on the word *zar,* the Persian for gold. Known since ancient times its export to Europe was at one time prolific with large supplies reportedly leaving the Shih-huang-Ch'ang in Yunnan province of China. Mentioned by Pliny and Vetrivious and found in Egyptian works, Persian and across Asia. It seems to have had little known use in Northern Europe where lead tin yellow seems to have been one of the dominant yellows in a European palette. Orpiment, (yellow arsenic sulphide) often gets confused with Realgar (the red arsenic sulphide AsS or As₂S₃) They are similar and both have been used in their natural and synthetic forms.

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**Surface Morphology / Microscopic Description**

Distinct brilliant yellow (rich lemon in colour) pigment, often coarsely ground to retain it vibrant hue particles are rich yellow. Large particles may appear to have a waxy, glazed appearance. Look for characteristic orange-red realgar particles which are often present. Crystalline yellow cleavage fragments. Occasionally a fibrous structure may be seen. Particles are usually between 1-30µm in size.

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**Aging Characteristics**

Stable to light and air. Unaffected by dilute alkalis and acids however reactive to strong acids. Burns when ignited to form arsenic trioxide. As a sulphide it is reactive with copper and often, lead based pigments.

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**Technical Examination Techniques / Instrumental Analysis Techniques**

Particles exhibit anomalous polarization colours, high birefringence and complete extinction. Has a very high refractive indices. Confirmed by microchemical tests for As and H₂S evolution.
Inorganic

Ultramarine

\[ \text{Na}_{8.16}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_2\text{S}_4 \] From the semi-precious stone - Lapis Lazuli
A mixture of the blue mineral lazurite, calcite and iron pyrites

**Microscopic appearance at x500 mag**

**Microscopic appearance under slightly crossed polars**

**Dates of Use**
Ancient times in the East, from Medieval period to modern day in the West.

**Summary of Manufacture**
There have been many documented methods for its preparation one is summarised as follows;
"Choose a rich blue stone. Pound it in a bronze mortar and sift. Melt the powder in 6 ounces of gum mastic and 3 ounces of new wax per pound of lapis. Work the resulting ball for a few days. The blue particles are extracted by the addition of lye and the ball kneaded like brad to extract them. The first particles of pigment 'given up' by the kneading are the purest. Cennini Cennino (1437)'To Purify Ultramarine' from the Craftsman's Handbook.

**Brief History of Usage**
Ancient sources are said to include Persia, Tibet and China; and is believed to have been brought to Europe in medieval times from Badakshan mines originating in Afghanistan. At one time it was more expensive than gold and although traded in the medieval period to Europe it has in fact been found in earlier works in England a France in the 12th Century and the year 1000 respectively.

**Surface Morphology / Microscopic Description**
Conchoidal blue flakes.
(Synthetic - Tiny rounded blue grains)
Particles size can vary greatly however depending upon the extent and skill in preparation.
Microscopically it is extremely difficult to tell apart from the synthetic French ultramarine. However, as you would expect, synthetic particles tend to be more uniform and finely divided.
Particles are usually between 1-50µm in size.

**Aging Characteristics**
(Note: A close approximation of this colour can be obtained by mixing Phthalocyanine blue and white.)

**Technical Examination Techniques/ Instrumental Analysis Techniques**
Particles are isotropic and exhibit **high colourless birefringence.???? McCrone says no birefringence!**
Transmission colours with the Chelsea Filter = Bright red.
Looks semi-transparent under infra-red light, red in IR False colour and blue under ultra-violet light.
See Appendices for chemical spot test for ultramarine (caveat: result will be the same for synthetic French ultramarine).
Inorganic

Vermilion

**HgS (Red mercuric sulphide)**

Cinnabar

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**Technical Examination Techniques/ Instrumental Analysis Techniques**

Particles are anisotropic and appear to turn darker with pleochroism. Particles exhibit birefringence and some crystals exhibit characteristic undulose extinction. With the red compensator in the microscope they appear colours other than red and their polarisation colours are bright orange to red/brown depending upon their manufacture. Semi-transparent under infra-red, yellow-brown in false colour and purple-blue under UV light. When heated it sublimes at about 580°C and at higher temperatures it burns with a bluish flame. Insoluble in alkalis.

**Dates of Use**

Known and used in China since prehistoric times, it spread across Europe and was the principle red in painting until the manufacture of its synthetic equivalent, cadmium red in .

**Summary of Manufacture**

The natural deposits of cinnabar, the principle ore of mercury, was crushed and ground in early history. Tow methods however emerged in its manufacture; that of the dry method, which was used by Ancient alchemists and the wet method, which was developed in England, Germany and America.

**Brief History of Usage**

Used in China since Ancient times and found on cartouches, stamp seals, silk and scrolls. The pigment was known to the Greeks and Romans and was mentioned by Pliny who called it 'minium'. According to Pliny the whole supply of vermilion came from Sisapo in Spain. The pigment quickly spread Westward and was used up until the discovery of cadmium red, when its use dramatically reduced due to its known blackening upon reaction to hydrogen sulphides in the air. The main source is Almaden, Spain but deposits can also be found across Europe, China, Japan, California, Mexico and Peru.

**Surface Morphology / Microscopic Description**

Artificial cinnebar does not differ chemically or physically from the natural ore but manufactured vermilion tends to have finer, more uniform particles. Course and broken shard particles are more likely to be natural. The particles are highly birefracting (\(\varepsilon_{Li} = 3.14, \omega_{Li} = 2.81\)).

Particles manufactured by the wet process appear as tiny, homogenous particles. They are evenly separated, transparent with a glassy appearance and light red in colour. Particles are usually between 1-30\(\mu\)m in size.

**Aging Characteristics**

Vermilion is, largely, a permanent pigment, its body and hiding power are stronger than those of cadmium red. However in the presence of hydrogen sulphides and sunlight the pigment reacts chemically darkening to a black physically. Although it is a sulphide, it is so inert that it does not darken lead white when they are mixed and as a result they have often been mixed for flesh tints.

**Microscopic appearance at x500 mag**

**Microscopic appearance under slightly crossed polars**

HgS

Cinnabar
Both East and West Pigment Atlas
Carbon Black

C (Carbon, Oxygen, Hydrogen)  Lamp Black
Bone Black  Ca$_3$(PO$_4$)$_2$+

Dates of Use
From Ancient times up until the present day.

Summary of Manufacture
Made by collecting the soot of wood burning fires. Graphite is also made today by collecting the soot from burning natural gas by impingement, flames impinge on metal surfaces from which the soot is scraped.

It is not until fairly recently that different forms of carbon soot were distinguished; such as lamp-black and bone-black, collected as their names suggest. Mars-black and lamp-black are also other well-known forms. In the USA 'carbon black' is specifically used to term the product produced by allowing a smoky flame from natural gas to impinge against a cooled, revolving metal drums from which the black is removed by industrial scrapers. (Gettens & Stout)

Brief History of Usage
Has been used since prehistoric times as a pigment for drawing and writing. Recent discovery of a number of types of carbon has been manipulated in printmaking for their slightly different hues. Today the pigment is widely used in both the art and industrial industry and is known to have excellent hiding power in all its forms.

Technical Examination Techniques
Particles are opaque under the microscope so no light properties can be observed. They also have no birefringence properties and will therefore be invisible at cross-polars. Ivory and bone blacks may be distinguished from other carbon blacks by heating. A grey ash is left which is composed of phosphates. Does not fluoresce in Ultra Violet Light. Under-drawings in carbon can be seen with the use of infrared light.

Surface Morphology / Microscopic Description
Particles can vary greatly in shape and size although opaque flakes with fractures are generally observed. Particles can vary greatly but usually fall between 1-100µm in size
Bone black particles are usually 1-20µm

Aging Characteristics
All carbon blacks are very stable being unaffected by light, air or hot concentrated acids or alkalis. They can only be destroyed by burning which converts them to carbon dioxide.
In terms of solubility they are fairly stable and also have a good permanence. Carbon oil paints are sometimes slow drying, the freer they are from impurities, the better they dry.

Microscopic appearance of lamp black at x500 mag
Micro appea of bone black under slightly crossed

Crystalline carbon (graphite)  Carbon black  Charcoal
soot  animal  vegetable
oils  bone  vine
methane  ivory  carbon
peach stone

Microscopic appearance of lamp black at x500 mag
**Chalk**

**CaCO₃ (Calcium Carbonate)**

Chalk, Whiting (usually precipitated), Lime white, Limestone

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**Dates of Use**

From Ancient times up to the present day, in both Europe and the Far East.

**Summary of Manufacture**

Natural chalk is a rock derived from marine and plant life and largely composed of fossils from unicellular algae. Natural deposits can be found on the English Coast, on Northern France, Belgium, Denmark and across Europe, with poorer qualities found in the USA. The white, yellowish or greyish chalk lumps are quarried and ground with water, separating the courser material through levigation. A very fine variety is known as 'guilders whiting'. Artificially made chalk is known as 'precipitated chalk' and is calcium carbonate in its whitest, finest and purest form.

**Brief History of Usage**

The earliest known white pigment used since Ancient times in drawing and painting. Commonly found in Northern European painting and mixed with glue to form the ground. Found in Chinese and Japanese painting the source of which was chalk ground from oyster shells. Marble was also ground to form the pigment.

**Surface Morphology / Microscopic Description**

Small colourless crystals with no regular shape and some may appear pale pink in hue. Heterogenous. Coccoliths (Fossil shells) can be seen at 500x mag in a sample of natural chalk. They are distinctive and highly birefracting due to their composition of tiny calcite crystals. Precipitated chalk is finer, more homogenous and whiter than the natural material with fine uniformly sized particles with no impurities as with natural chalk. Looks similar to plaster of Paris under the microscope. Long needle shaped crystals that have a tendency to mat or felt with each other. Whiting (limestone) particles are usually 1-30µm in size whereas chalk and precipitated chalk particles are usually 1-10µm.

**Aging Characteristics**

Very stable in normal environmental conditions. Excellent lightfastness. Incompatible with alkali-sensitive pigments such as Prussian blue. (Pigments through the Ages)

**Technical Examination Techniques**

Anisotropic and pleochroic with the surface of the crystals becoming red and green upon rotation. See Appendices for chemical spot test for calcium in chalk. Particles do not exhibit pleochroism. Polarisation may result in a green or red tint on the surface of some crystals. Confirm natural chalk by the presence of coccoliths or limestone rhombohedra.
Charcoal
(See carbon blacks)

Dates of Use
Since ancient times beginning with cave drawings by Prehistoric man, used and made in the same way to this day.

Summary of Manufacture
Historically, charred wood from the fire was used by Prehistoric man as a tool to draw outlines of animals on cave walls. Today charcoal is produced from vine and willow twigs in special kilns from which air has been excluded. The sticks come in varying thicknesses, averaging $\frac{1}{4}$" in diameter. The degree of softness also differs. Charcoal types are so-called 'stick' (vine or willow), compressed (powdered and compacted with a binder), pencil and powder form.

Brief History of Usage
Known since ancient times and is the oldest and most versatile drawing pigment. Commonly used in sketches and preparatory drawings before the paint layer. From the watercolour tradition developing in the 18th Century up until the present day, drawing has become a high art form in itself and with it the importance of charcoal. Honoré Daumier (1808 - 1879), Edgar Degas, Renoir (1841- 1919) and Lautrec (1864 - 1901) exploited the medium in their drawing and combined it with other media. Its use today is as prevalent as ever it was.

Surface Morphology / Microscopic Description
Particles look small, opaque, elongated and splintery. Charcoal is light, inert and porous and may retain some of the fine structure of the wood it was made from. The particles are not bound to the surface of the paper, making them easy to smudge and blur. All charcoals are hydroscopic and therefore need to be dried before being bound in oil. Charcoal withdraws the majority of organic colouring matters from suspension, and even from solution in water. All are bluish-black in hue. (This has often been imitated by mixtures of lamp black and indigo.)

Particles can vary greatly in size but are usually between 1-100µm.

Aging Characteristics
Excellent permanence
Although charcoal is an extremely permanent pigment if it has been badly washed or imperfectly carbonised it may become greyer or less brown following prolonged exposure to light.
Non-toxic

Technical Examination Techniques
Particles are opaque therefore no microscopic effects can be seen.
Infrared light can detect under-drawings in paintings such as graphite and carbon.
Bogus pigments which may appear to look like charcoal (i.e. mixtures of lamp black & indigo) can be detected by heating in a test tube (indigo will give off a purple vapour).
**Malachite**

**CuCO₃·Cu(OH)₂** (basic copper carbonate)

**Mountain Green**

**Dates of Use**
Ancient times up until but rarely in the present day. Occasionally still used in the East but rarely in the West.

**Summary of Manufacture**
Naturally occurring mineral similar in composition to azurite but essentially containing more combined water. Occurs across the world where secondary copper ore deposits are found and like most mineral pigments it is prepared through a series of grinding, washing and sieving to extract the pure green particles. (Gettens & Stout) (Meyer)

**Brief History of Usage**
Large deposits can be found in Egypt and Sinai as well as smaller deposits being found across the world. Close in relation and history to azurite, malachite is one of the oldest bright green pigments found in paintings in both the East and West. Found commonly in China from Ancient times and in Europe more prolifically in the Middle Ages. Today its use continues in the East, but rarely in the West as synthetic greens took over in popularity and quality of colour. As a mineral particles are large and like azurite dramatically and characteristically granular in comparison to the finer synthetic version of today.

**Surface Morphology / Microscopic Description**
Bright green, crystalline and fairly characteristic microscopically. Crystals are homogenous and some may appear to be clear to pale green.
As can be seen in the photographs, crystals vary greatly in size. Their size will also depend upon the manufacturing process and the amount of grinding carried out.
Bottle green, glass-like cleavage fragments.
Particles are usually between 1-50µm in size.

**Aging Characteristics**
Moderate permanence
As a carbonate it is decomposed by acids but is unaffected by light.
More often seen in oil than in tempera medium

**Technical Examination Techniques**
Particles exhibit high birefringence and are anisotropic. Particles exhibit parallel extinction, no pleochroism.
Transmission colours with the Chelsea Filter = dark grey-green
The halo on each crystal does not appear to move and therefore its refractive index is around that of the mount medium, meltmount. See Appendices chemical test for the presence of copper(II) ions.
**Massicot**

PbO (yellow monoxide of lead) lead oxide

**Litharge**

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**Dates of Use**
Ancient times up until, but less commonly, today.

**Summary of Manufacture**
Both massicot and litharge often terms used for the same pigment, but more correctly each are lead monoxides derived from different sources. **Massicot** is the unfused monoxide of lead made by the gentle roasting of white lead at 300°C. The white lead reacts upon heating and gives off carbon monoxide and water. Massicot, the soft, sulphurous yellow powder is left.

**(Litharge is the fused and crystalline oxide, which is formed from the direct oxidation of molten metallic lead. Today the molten lead is atomized by whirling propellers and allowed to oxidize through contact with the air. It is essentially the byproduct of refining silver by the cupellation process.)**

**Brief History of Usage**
Litharge is more orange in comparison to massicot due to the content of some red lead. Litharge is rarely seen used as a pigment in comparison to massicot but was more commonly employed in varnishes and glazes. The manufacture of yellow monoxide has been known since Ancient times and found in Egypt, Italy, Germany, across Europe in general and in the North and South Americas.

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**Surface Morphology / Microscopic Description**
Light yellow rounded particles
Colour can vary from yellow to a reddish yellow.
Litharge is usually more orange in hue.
Appears to possibly be amorphous.
Generally difficult to identify as particles vary greatly depending upon the manufacturing process.
Massicot and litharge are furnace products and therefore particles can appear 'fluffy', uniform, small and rounded.
Particle luster is greasy to dull.
Crystals are generally opaque but some can be transparent as can be seen in the samples above.
Cleavage is distinct in two perpendicular directions but difficult to see.

**Aging Characteristics**
Good permanence
Good hiding power.
Dissolves in nitric and acetic acids and has similar properties as all lead pigments.

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**Technical Examination Techniques**
Particles exhibit high anomalous birefringence and anomalous polarization colours but do not exhibit pleochroism. Refractive indices of 2.51 (x) to 2.71 (γ).
Confirm with a microchemical test for lead.
Massicot is the orthorhombic variety of PbO whereas litharge is the tetragonal variety of PbO.
Inorganic

Smalt

CoO (Cobaltous oxide) K, Co(Al), silicate (glass)

Cobalt

Microscopic appearance at x500 mag

Microscopic appearance under slightly crossed polars

Dates of Use
Ancient times up until the nineteenth century.

Summary of Manufacture
Artificial in nature it is a potash silicate, highly coloured with cobalt oxide and reduced down to a powder. It seems to have been manufactured in Ancient Times by roasting cobalt minerals such as cobaltite and smaltite to form cobaltous oxide. The oxide was then added to molten glass and the mixture poured into cold water. The resulting broken particles were then ground and washed and allowed to settle repeatedly in order to separate out the finer particles.

Brief History of Usage
The earliest of the cobalt pigments, in painting and, particularly in the colouring glass in Ancient Egypt, in Venetian glass making and even across to Asia and the Far East. Laurie in 'The Pigments and Mediums of Old Masters' mentions the word, smalto, as being used as early as 1492 and a glass pigment called, azzuro di smalto, being described in 1584. As a pigment it has been suggested that smalt has been used since the late sixteenth century in Europe. However with the introduction of French ultramarine and other artificial blues its use decreased in the 19th Century and it is rarely used today.

Aging Characteristics
Excellent permanence
Poor hiding power and a tendency to streak or settle in application of the paint film due to it course particles and the necessity to use it in thick application.
Arguably insoluble, even in most acids but gradually pales becoming grey with reaction to moisture and carbonic acid in the air. (Artists Materials & Techniques)

Technical Examination Techniques
Particles are isotropic and do not exhibit pleochroism or birefringence.
Transmission colours with the Chelsea Filter = rose-red or bright red.
Refractive index ca. 1.55
Confirm with a test for potassium.

Surface Morphology / Microscopic Description
Smalt particles are essentially glass particles with a conchoidal fracture and quite distinctive in appearance.
Large particles can exhibit a purple-blue hue while small ones may appear pale blue.
Despite their glassy characteristic, they can have varying shapes, some appearing like sharp splinters or shards of glass; others are more square and angular.
Tiny air bubbles are common and a good indicator of the pigments identity.
Particles are usually between 1-50µm in size.

Dates of Use
Ancient times up until the nineteenth century.

Aging Characteristics
Excellent permanence
Poor hiding power and a tendency to streak or settle in application of the paint film due to it course particles and the necessity to use it in thick application.
Arguably insoluble, even in most acids but gradually pales becoming grey with reaction to moisture and carbonic acid in the air. (Artists Materials & Techniques)
Western Pigment Atlas
Azurite

2CuCO₃·Cu(OH)₂ (Derived from the mineral- Azurite)
Mountain blue

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 as 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 1-50µm.

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 (CO₃) 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 malachite molecules.

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.
BaSO₄ (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 barites but most contain over 98% BaSO₄.

Brief History of Usage
Commonly used as a ground, filler or extender it has been suggested that barites seems to have been used as a pigment in painting from around the 14th Century. It has very poor hiding power, which generally restricted its use as a base or filler only. Barites 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 barites (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 barites 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.
Barites is common and can be confused with other minerals such as Celestite (SrSO₄), which has the structure as barites. Only a flame test will distinguish the two, barites produces a pale green flame; celestite a red flame.
Blue Verditer

2CuCO$_3$.Cu(OH)$_2$ (Artificial basic copper carbonate)
Blue Bice, Cendres blues d'Angleterre

Microscopic appearance at x500 mag

Microscopic appearance under crossed polars

**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.

**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 is 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 small 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 its seems more stable and retains its colour in tempera.
# Cobalt Blue

**CoO.Al₂O₃ (cobalt aluminate) (cobalt (II) oxide, aluminium oxide)**

Thenards Blue. Dresden Blue

<table>
<thead>
<tr>
<th>Microscopic appearance at x500 mag</th>
<th>Microscopic appearance under slightly crossed polars</th>
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## 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% Co₃O₄ and 68% Al₂O₃.

## 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 course 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 1-50µm.

## 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

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 commercially 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 1µ 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 are 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_{38}O_{13} (Carmonic Acid - Colouring Principle)

Carmine Lake or Crimson Lake

**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 Paracut 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 'nacarat 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.

**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

Cu[C_2H_3O_2]_2\cdot3Cu[AsO_2]_2 (copper (II) aceto-arsenite)
Schweinfurt Green, Paris Green, Veronese green

**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**

**Inorganic**

**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).

**Surface Morphology / Microscopic Description**

Clusters of small blue transparent particles seen at x500 mag. 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 hydroscopic action. The so-called 'ultramarine disease' is said to be the result of decomposition of the varnish in oil paintings.

**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.

**Dates of Use**

From around 1830 to the present day.

**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.

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

Graphite

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

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, γραφεῖν ('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 reflection pleochroism and bireflectance but do not exhibit birefringence becoming black under cross-polars.
The element is conductive and thermal.
Gypsum

CaSO₄·2H₂O (calcium sulphate dihydrate)

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

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 µ = < or = 1.66.
### 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 America's. 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 16th 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.

### Technical Examination Techniques
Kermesic acid is distinguished from carminic 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.

### 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.
**Lead White**

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

Microscopic appearance at x500 mag

Microscopic appearance under crossed polars

**Dates of Use**
Since ancient times up to 19th 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. Creemnitz 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 1-50µm.

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**

C₁₄H₈O₄ (Colouring Principle - alizarin- 1,2 dihydroxyanthraquinone, derived from the herbaceous root of *Rubia tinctorium*) Madder lake, Alizarin

**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 ore 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)₃ 1,2dioxyanthraquinone,

**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.

---

Microscopic appearance at x500 mag

Microscopic appearance under slightly crossed polars
**Prussian Blue**

Fe₄(Fe(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 copper(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 0.5µm  
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°C at which point it darkens. See Appendices chemical test for prussian blue.

Prussian Blue
**Red Lead**

<table>
<thead>
<tr>
<th>PbO₄</th>
<th>Red tetraoxide of lead</th>
</tr>
</thead>
</table>

**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 (PbO) in air or oxidizing molten atomized white lead for a number of hours at a temperature of 480°C.

**Brief History of Usage**  
Known in antiquity as 'minium', 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.

**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 PbO₂ functions as an oxidising agent within the whole structure of PbO₂. 2PbO₂ resulting in the change in hue over time.

**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 1-50µm 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.

**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\textsubscript{1},Fe\textsuperscript{III}), (Fe\textsuperscript{II}Mg)(AlSi\textsubscript{3},Si\textsubscript{4}) O\textsubscript{10}(OH)\textsubscript{2}**  
Green Earth  
(Composed of the minerals celadonite & glauconite)

**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 viridian can often be confused with the pigment.

**Surface Morphology / Microscopic Description**  
Terre verte can often appear as a confusing mixture of particles.  
Crystals are course 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**

**TiO₂** (Ilmenite, originally menachanite - principal ore)  
Titanium Dioxide, titanox

### 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 - FeTiO₃) 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 1µm 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

Fe$_2$O$_3$·MnO$_2$·nH$_2$O  Iron(III)oxide containing manganese(IV)oxide

Raw Umber, Burnt Umber

**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

<table>
<thead>
<tr>
<th>Technical Examination Techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>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.</td>
</tr>
</tbody>
</table>

Dates of Use
- Probably discovered in the late 16th/early 17th Century.
- Prepared as a medium for painting from the 17th Century. 19th 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 19th 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.

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

<table>
<thead>
<tr>
<th>Microscopic appearance at x500 mag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microscopic appearance under slightly crossed polars</td>
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</tbody>
</table>

Inorganic
### Verdi

**Cu(C₂H₃O₂)₂·2Cu(OH)₂**  *(An acetate of copper)*

**Vert de Grece**

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#### 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.

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<table>
<thead>
<tr>
<th>Dates of Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufactured since Ancient times up until the present day, although it is rarely sold as an artists pigment today due to its toxic nature.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Summary of Manufacture</th>
</tr>
</thead>
<tbody>
<tr>
<td>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 &amp; Stout)</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Brief History of Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>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)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Surface Morphology / Microscopic Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intense green crystals of different shapes and sizes. Particles can vary greatly depending upon the method of manufacture, for instance well-crystalised 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.</td>
</tr>
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<table>
<thead>
<tr>
<th>Aging Characteristics</th>
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<tbody>
<tr>
<td>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 &amp; 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 gambouge or saffron, often in these cases the pigment remains green being possibly protected by the resinous yellow.</td>
</tr>
</tbody>
</table>
**Inorganic**

**Viridian**

Cr₂O₃·2H₂O (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 1-10µm

**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.

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**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

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, Leclaire in France showed that the latter could be overcome by adding an oil that had been rendered siccative by boiling with pyrolusite (MnO₂) 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 1µ in diameter. Its refractive index of 2.00 is about the same as lead white but unlike the latter it is birefracting.
Particles are very fine and can only, therefore, be observed at high magnifications.
Zinc oxide is a pure, cold white, is non-poisonous but 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 2µm in size

Aging Characteristics
The paint has a tendency to dry brittle and crack. Untouched 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 µ=<or=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.
Eastern Fiber Atlas
## Dates of Use
Ancient times up to the present day in Japan and the Far East in general.

## Summary of Manufacture
**Plant family** Thymelaeaceae. The plant grows in mountain regions where it grows up to 1 - 1.5m in height. It cannot be cultivated which makes the resulting paper very expensive. Gampi is regarded as one of the most refined Japanese fibers. Harvested fibers are around 2.5 to 5.3 mm in length. Fibers are used from the branches which are harvested from the plant in the Spring. As with most paper fiber preparation, the leaves are removed and the fiber stripped from the cored of the branch. The inner bark is removed from the outer by scraping and/or peeling and the fibers soaked and cooked depending upon their intended use.

## Brief History of Usage
Used for copy paper, tracing paper and for woodblock printing since 850 AD. The paper is also easily dyed and decorated and can be found as the support for screens, fans and parasols. Phillipene gampi is almost identical to Japanese but the fiber is courser due to the climate, producing an off-white, tan paper. Naturally grows in Japan, Nepal and Hawaii. (India??)

## Surface Morphology / Microscopic Description
The paper is fine but strong with a warm tone, sheen and a pronounced rattle when handled. The sheet has visible chain and laid lines. The fibers are long, thin and regular in width with occasional markings or nodes. Cross striations are fine and well spaced but may group and extend across the fiber. The lumen is wide and has narrow, defined walls. The cell ends are roundish. The white bark comprises about twenty-two percent hemicellulose and 3 per cent lignin.

## Aging Characteristics
Gampi fibers make strong paper with a lustrous sheen and a warm greenish/yellowish hue. Paper which appears quite green probably contains more fibers from the inner bark only. That which appears tan in hue with flecks is likely to be a mixture of outer and inner bark. Gampi has strong adhesive power between the fibers and the sheet is acid free. The paper also reputedly has a strong resistance to insects. The latter properties make the paper resilient deterioration. It is also reputed to need less addition of binding mucilage added to the pulp as the fiber seems to retain a great deal of its own even after cooking.

## Technical Examination Techniques/ Chemical Staining Tests
Turns green/yellow with the Hertzberg stain.
Hemp

Chemical Formula
From the stem of *Cannabis sativa*

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**Dates of Use**
Ancient times to the present day.
For cloth, paper and today, illegally as a drug.

**Summary of Manufacture**
Plant family *Moraceae*
Derived from the bast fibers of the plant *cannabis sativa*.
Harvested fiber length is around 25 mm
Fibers are harvested from the stems of the weedy perennial or annual herb in the Autumn.
The leaves are removed, then the stems are usually steamed and the fibers stripped apart. Commercial preparation of the fibers, like with most others, the fibers usually undergo retting before being boiled with the addition of lye into the vat. The preparation differs slightly for hemp being made into cloth as opposed to paper. Usually cloth preparation undergoes further cooking in a solution of lye.

**Brief History of Usage**
Course varieties have been used for centuries as the main fiber in sail and rope making. Finer fibers were used in cloth and textiles and occasionally it was used as a support for paintings. Commercial varieties are grown in Russia, China, Italy and Saudi Arabia, but the plant will grow in almost any conditions.

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**Aging Characteristics**
Original paper colour is usually off-white.
Chinese paper was often fermented during fiber preparation giving it a finer quality and hence the main source of fine paper in China and as paper currency.

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**Technical Examination Techniques/ Chemical Staining Tests**
Kozo

Technical Examination Techniques/ Chemical Staining Tests

Dates of Use
Ancient times to the present day.

Summary of Manufacture
Family Moraceae.
Fibers yielded from the mulberry tree. As opposed to paper mulberry which is manufactured from the fibers of *Broussonetia papyfera*, the main source of kozo is derived from *Broussonetia kazinoki*. There are however many varieties of mulberry from which kozo is made but the latter one is considered to yield the best fibers. The tree is cut into section and cut branches left to steam in a pot of boiling water. After several hours when the bark has softened it is stripped by hand and hung to dry. The bark is then later soaked and stripped down from the outer balck bark into the inner green and white bark depending upon the yield desired for papermaking.

Brief History of Usage
The most widely used bast fiber in Japan; Kozo originates from around 105AD, from a mountain wilderness of Shikoko and Kyusu province of China. The kozo mulberry is closely related to the white and red mulberry trees commonly found in North America. The leaves of the variety, Moras alba L. are fed to silkworms in Japan.

Surface Morphology/ Microscopic Description
Known for its long, sinewy and strong fibers. Fibers vary in length between three and twenty-five mm. Fiber diameter averages .025mm. The material constituents of the white bark of kozo averages approximately nine per cent and the lignin content about 4 per cent. Thai kozo is less expensive than kozo grown in Thailand. The plant is identical botanically to the Japanese kozo, but due to the warmer climate they have different fiber characteristics. Chinese kozo is less expensive than Thai kozo and similar to Japanese in appearance.

Aging Characteristics
Generally kozo fiber contains very little lignin and therefore little inherent acidity. The fibers are long and physically strong and as a result the paper is durable and only mainly at risk from external factors of degradation. Over time however, the fiber furnish or surface of the paper can become fluffy as the long fibers undergo physical damage and abrasion across the surface of the sheet, the fibers twist and protrude from the surface.

Chemical Formula *Broussonetia kazinoki Sieb Diplomorpha canescens, family Moraceae*

Microscopic appearance at x500 mag

Microscopic appearance under slightly crossed polars

Technical Examination Techniques/ Chemical Staining Tests
Manilla

Chemical Formula
*Manila Hemp, Abaca, Musa textiles Née*

**Surface Morphology/ Microscopic Description**
- Its colour varies from yellow/ pink to a golden brown
- Fiber tips tend to be tapering to a point or rounded end
- Fibers are unicellular and approximately 5-10mm in length.
- Cells appear oval in shape or circular in cross-section and with a distinct central canal which may often be less than half of the diameter of the fiber.
- The fibers are tough and flexible and the nodes are usually not obvious.
- The degree of lignification present depends on the individual fiber and can vary greatly.

**Aging Characteristics**
- Generally fibers have a higher lignin content than other bast fibers resulting in higher inherent acidic content and therefore papers have a higher potential for acidic degradation and visible discolouration.
- Original paper colour can vary from a tan/ buff if fresh leaf stems were used, to a pale yellow if rope was used; to a cream if dry fibers were prepared.

**Technical Examination Techniques/ Chemical Staining Tests**

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**Dates of Use**
- Ancient times to the present day.

**Summary of Manufacture**
- Plant family *Musaceae*
- The leaf stem of tall perennial herbs are harvested and hence the fiber is a leaf fiber not a bast one. Fibers are around 3-7mm in length and are harvested in the summer months. The plants roots lie near the soil surface while above ground the plants commercial fiber is the sclerenchyma of the leaf bases. The plant can be cut after 3 years of growth but its yield decreases after approx 5 years of harvesting. The fibers are cut into pieces and soaked in water for a day. If being prepared for paper the fibers are then often boiled for a couple of hours in a solution of lye, beaten and made into sheets.

**Brief History of Usage**
- There are 35 species of manila and of these *M. textilis* is the main source for fibers. The plant originates in the Philippine Islands where it was made into cloth from the sixteenth century and exported to Japan. From the seventeenth century paper was being made in Japan from the variety Musa sapientum (Basho). Varieties found in the Philippines, Uganda, Malaya, Bolivia and Japan.

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Mitzumata

Technical Examination Techniques/ Chemical Staining Tests
Fibers turn light green/ yellow with the Herzberg stain.

Dates of Use
Ancient times to the present day.

Summary of Manufacture
Plant family Thymelaeaceae, genus Edgeworthia
Harvested fiber length is around 3mm.
The branches from the shrub are harvested for paper manufacture in late spring or early summer.
Preparation involves the removal of leaves from the branches, which are then steamed and, as like most methods the fibers are then stripped apart. Outer bark is then removed from that of the inner by scraping and peeling it away; after which it is then soaked and cooked. Fibers intended for mitzumata paper production is then usually boiled for a couple of hours in a solution of soda ash and beaten to further separate the fibers.

Brief History of Usage
Introduced in the Yedo period (1603-1867) in Japan it believed to have originated in China. It has also had a long history of use in Nepal and has probably been around for a much longer time than is documented. Today it is harvested and produced in much the same way as it has for centuries and is exported from these countries to the West.

Surface Morphology / Microscopic Description
Known for its fine-grained, lustrous, soft and pliant fibers.
Glossy thin and smooth paper with distinct chain and laid lines.
The sheet is flexible and lightweight.
Fibers are shorter than kozo fibers and thin and regular in width.
Fibers have fewer markings or nodes than kozo with frequent fine cross striations. The latter sometimes group to form a V shaped pattern.
Some rectangular parenchyma cells often seen.
The walls of the lumen are pronounced and thick.
Cell ends are blunt and roundish.

Aging Characteristics
Original paper colour is usually off-white.
The paper has a natural resistance to insects.
With no additives and with traditional manufacture the paper is acid-free.

Mitzumata

Chemical Formula Edgeworthia papyrifera or Edgeworthia chrysanthemum

Microscopic appearance at x500 mag

Microscopic appearance at x500 mag
Dates of Use
Ancient times to the present day.

Summary of Manufacture
Plant family Moraceae
Fiber length is around 10mm.
Plants are harvested in the late autumn after the leaves have fallen.
The fibers of the tree are separated from the inner bark by scraping, soaking and macerating in water. Often they are then further boiled in a weak alkaline solution to rid them of most impurities. After treating they are then rinsed, drained and added to the pulp to make handmade papers. Fibers are often long and unbroken.

Brief History of Usage
Used for centuries from Ancient China as both paper and for clothing. Also prepared by the Polynesians where it was known as 'Tapa' or 'bark paper'. The name is apt for the tougher variety of mulberry grown and harvested there. Attributed possibly to the environmental differences between China and Polynesia, the latter having a much higher annual humidity than the former resulting in faster growth cycles of the plant. Today it is still as well used and harvesting has changed little over the centuries.

Surface Morphology / Microscopic Description
Fibers vary in length from approximately 6 - 20mm and are long slender and mostly unbroken fibers. Very long fibers generally with tapered ends, some may appear chopped or blunt.
Incomplete parallel extinction may be seen on wider fibers.
Their width varies slightly but generally is around 0.0030mm.
Most fibers appear almost transparent under the microscope and many show transverse markings or joints as well as longitudinal striae.
The central canal of the fiber is usually obvious and the ends of the fiber are usually rounded and blunt in appearance.

Aging Characteristics
Paper colour can vary dramatically following sheet formation due to the additives to the pulp and also mainly due to the part of the plant from which the fibers came from. White paper usually contains fibers from the inner bark only; white paper with a green tint will probably contain a majority of fibers from between the inner and outer bark; and tan/buff paper often with flecks of brown may contain fibers from both the inner and outer bark.

Technical Examination Techniques / Chemical Staining Tests
The herzberg stain will turn fibers red. Note however that cotton, linen, ramie, hemp and manila fibers will also turn a shade of red. Some wood fibers that have undergone partial or mechanical and chemical treatment may also turn red with the herzberg stain.
Chemical Formula
*Diplomorpha canescens*

**Microscopic appearance at x500 mag**

**Microscopic appearance under slightly crossed polars**

**Dates of Use**

**Summary of Manufacture**

**Brief History of Usage**

**Surface Morphology / Microscopic Description**

**Aging Characteristics**

**Technical Examination Techniques / Chemical Staining Tests**
Western Fiber Atlas
The Herzberg staining test turns cotton fibers red/brown.

Surface Morphology / Microscopic Description
Fiber length varies from 2 to 5.6 cm and the diameter from 0.0163 to 0.0215 mm. Fibers are smooth and ribbon-like with twists along the length. Mercerized cotton has few twists, however, due to chemical processing, making identification more difficult. The walls are thick and the lumen in the central canal is broad, making the fiber appear like a collapsed, twisted tube.

Aging Characteristics
The paper produced can vary in color from a white if bleaching agents have been added to the pulp to a yellow/brown if little or no chemicals have been added in paper manufacture. Cotton itself is over 90% cellulose. Fiber preparation usually involves a long cooking process with the addition of lye. Lye itself is ………. Cotton is very reactive with acids and moderately strong oxidizing agents but relatively unaffected by alkali hypochlorites.

Technical Examination Techniques / Chemical Staining Tests
The Herzberg staining test turns cotton fibers red/brown.
Despite its lesser content in comparison to mechanical pulps, lignin can be detected with the phloroglucinol test. Fibers will become red with the herzberg stain. Note however that cotton, linen, ramie, hemp, manila and paper mulberry fibers will also turn a shade of red. The 'sellengers' stain will turn sulphite treated woodpulp red.

Surface Morphology / Microscopic Description
Chemical pulps are cleaner in appearance to mechanical pulps and have a slightly higher strength. Blunt and chopped edges can, however still be seen depending upon the amount of mechanical action used to initially break down the fibers. Often wood varieties were mixed and esparto grass added to increase paper strength. Soda pulp is made from deciduous or broad-leafed trees such as poplar. As high as a 70% yield of cellulose can be produced. Sulphite and sulphate pulp separates the pure cellulose from the impurities in coniferous woods such as pine and spruce. The process produces a stronger paper particularly as the paper is usually left unbleached but as a result the colour quality is poor.

Aging Characteristics
This is dependent upon the chemicals used and coatings, fillers and sizes added. Chemicals from the process are always left in the paper. Acidic chemicals accelerate the breakdown of cellulose and additives intended to aid paper strength may be reactive. Alkaline processes such as the sulphate one however results in a more stable and stronger paper than other processes and mechanically produced pulps.

Technical Examination Techniques/ Chemical Staining Tests
Despite its lesser content in comparison to mechanical pulps, lignin can be detected with the phloroglucinol test. Fibers will become red with the herzberg stain. Note however that cotton, linen, ramie, hemp, manila and paper mulberry fibers will also turn a shade of red. The 'sellengers' stain will turn sulphite treated woodpulp red.
Esparto

Esparto grass, Stipa tenacissima

Dates of Use
Since Ancient times to the present day as a fiber for ropes and mats etc and not commonly, paper.

Summary of Manufacture
A spear grass plant with long leaves. The stems and leaves are cut into smaller pieces and soaked in clean water for at least a day prior to cooking. The fibers are very strong and are separated by a process of boiling with caustic soda.

Brief History of Usage
Used particularly in England in the manufacture of paper more prolifically when paper makers were finding rags in short supply and other possible fibers were being tested and added to supplement the pulp prior to the invention of wood-pulp paper. Use of esparto was has a longer history of use for papermaking in the Mediterranean where it had already been used for centuries in the manufacture of ropes, mats and sails. Stipa comata is a variety of esparto growing in the USA where it is used in the Western States for cattle forage.

Technical Examination Techniques/ Chemical Staining Tests
Turns green/ yellow with the Hertzberg stain.

Surface Morphology / Microscopic Description
Fibers are very strong and flexible.

Aging Characteristics
**Technical Examination Techniques/ Chemical Staining Tests**

**Dates of Use**
Prehistoric times to the present day.

**Summary of Manufacture**
Plant family *Linacea*

The stems from the perennial weed or annual herb are harvested from the plant.
Fibers are harvested in the summer or autumn when the stems are turning yellow.
The fibers (length approx 33mm) are obtained from the green bark which undergoes rotting, retting, cleaning and bleaching. Each flax plant yields about 8% linen fibers. The fibers are tough and can be bleached or dyed more easily than cotton.

**Brief History of Usage**
Prehistoric remains of linen have been found across Europe and in the wrappings of many Egyptian mummies fine weaves have been discovered. Scotland, Ireland and Belgium produce some of the finest linens today and Russia the largest amount of flax. Linen cloth for clothes was largely abandoned in favour of commercially produced cotton in the 20th Century but it has always been used as the most common support for easel painting. Today flax is grown widely across the world and various species exist, prolifically throughout the USA.

**Surface Morphology / Microscopic Description**
Fibers are 6 to 60mm long and 0.012 to 0.026mm wide.
The cellulose content is between 70 to 80% cellulose.
Linen can be distinguished from cotton fibers by cross-markings, twists and in particular joints across the width of the fiber and striation markings along the length between the joints.
The stem hollow is filled with pith but in older plants it breaks down so stems become empty.

**Aging Characteristics**
Linen can range in colour from a white to a grey or a light brown and even white if it has been bleached.
The aging of the material is largely due to the additives within it following the manufacturing process. Bleaching agents, for instance, added to make the material white are inherently acidic causing acidity within the fibers themselves, loss of strength and brown/buff discoloration.

**Chemical Formula**
Flax, *Linum Usitatissimum*
Mechanical Woodpulp

Microscopic appearance of coniferous wood at x500

Microscopic appearance of non-coniferous wood

**Dates of Use**
1780s to present day

**Summary of Manufacture**
Produced by the mechanical action on wood in the presence of water. Pulp is produced by cutting wood logs into shorter lengths which are then ground, most commonly against a rotating abrasive stone in the presence of freely floating water. The paper produced has limited strength in comparison to handmade papers because of impurities left in the pulp particularly lignin. Ground-wood pulps contribute absorbency, bulk and opacity and are lower in cost than chemical wood pulp.

**Brief History of Usage**
In the late 1700s (80s-90s) a French scientist investigated the use of other materials to solve the increasing demand for paper. His use of wood to make pulp stemmed from experiments with the woody pulp produced and used by wasps to make their nests. The process is inexpensive and speedily produces cheap, satisfactory paper used for newsprint, wallpapers and wrapping papers.

**Surface Morphology / Microscopic Description**
Short, thick fibers with broken, choppy ends. Signs of mechanical damage should be fairly apparent. Packing vessels (parenchinal) may be seen. The fibers tend to break rather than fibrilate and as a result tend to have broken straight edges. Paper has a high lignin low cellulose content and impurities such as dirt and metal particles can often be seen. Fillers and sizing agents are often added to aid strength.

**Aging Characteristics**
The high lignin content accelerates the aging of the paper through acidity. Some fillers, coatings and sizing agents such as alum rosin can also contribute acids to the deterioration process.

**Technical Examination Techniques / Chemical Staining Tests**
Phloroglucinol test for lignin as the pulp contains more of the latter with very little cellulose. Should become yellow with the herzberg stain. Note however that straw, grass of jute fibers that have undergone little or no chemical treatment will also turn yellow.
Vellum

Chemical Formula
Usually used to term *calfskin or skins from the aborted foetus.*

Dates of Use
Used since ancient times along with parchment (general skins from the hides of animals). Used as a support in medieval times particularly for the production of monastic writings, illuminations and choir books etc as other hides were not large enough.

Summary of Manufacture
The carcass of the calf is skinned and de-haired. The flesh side is then scraped down to remove fat and the hide stretched on a frame. The skin is repeatedly washed, often with lime and scraped to remove grease. Followed by drying under tension and the surface smoothed with pumice or burnishing tool.

Brief History of Usage
Vellum is and was a higher quality parchment with a smoother velvety surface, making it preferable for illuminated manuscripts although it was as a result more expensive. Vellum made from the foetus of an aborted calf was favoured by portrait miniature painters in the 16th and 17th Centuries because of its superior fine quality. Its manufacture was largely abandoned as paper production increased. Along with general parchments it is still used in bookbinding, but the skills used to produce fine quality skins have largely been lost.

Surface Morphology / Microscopic Description
Velvety smooth texture.
A network of tensioned protein fiber (collagen) in a matrix of binding mucous (muco-polysaccharide) with a high water binding capacity. The tightness of the fibre network varies from hide to hide and animal but generally the mesh is tighter and finer in comparison to parchment skins. Vellum skins often have finer, less detectible hair follicles with the skins made from aborted foetus's with little evidence of hair growth. Sometimes skins were coated with an animal or fish size and some with a glaze of egg white.

Aging Characteristics
Oils spots and stains can often be seen arising to the surface over time through the skin. Bad curing of the skin as it was prepared also results in spots or blotches forming from the salts used in putrification. All skins are extremely sensitive to humidity. They are hydroscopic the extent of which depends upon their age. Skins absorb and desorb water in sympathy with their changing environment. Prolonged exposure can result in breakdown of the fibrous mass; whereas too dry an atmosphere shrinks the material leaving its surface character dry, cockled and hard.

Technical Examination Techniques/ Chemical Staining Tests
Extremely sensitive to humidity changes.
Notes on Pigments
# Chronology of Artist's Pigments

<table>
<thead>
<tr>
<th>First recorded date</th>
<th>Pigment</th>
<th>Fell into Disuse</th>
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<tbody>
<tr>
<td>Before 1300</td>
<td>Asphaltun (Bitumen)</td>
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<td>Azurite</td>
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<td>Blue Verditer</td>
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<td>Bone White</td>
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<td>Bone Black</td>
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<td>Calcined Bone</td>
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<td>Chalk</td>
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<td>Charcoal</td>
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<td>Cinnebar (Vermilion)</td>
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<td>Copper Resinate</td>
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<td>Egyptian Blue</td>
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<td></td>
<td>Gambouge</td>
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<td>Green Earth (Terre Verte)</td>
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<td>Gypsum</td>
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<td>Indigo</td>
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<td>Iron Earths (ochres &amp; sienna's)</td>
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<td></td>
<td>Ivory Black</td>
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<td>Lead Tin Yellow</td>
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<td>Massicot</td>
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<td>Minium (Red Lead)</td>
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<td>Mosaic Gold</td>
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<td>Terre Verte</td>
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<td>Ultramarine (Lapiz Lazuli)</td>
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<td>Verdigris</td>
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<td>1550</td>
<td>Vermilion</td>
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<td>1550</td>
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<td>1549</td>
<td>Graphite</td>
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<tr>
<td>1565</td>
<td>Van Dyke Brown</td>
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<tr>
<td>1565</td>
<td>Naples Yellow</td>
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<tr>
<td>1600s (late)</td>
<td>Prussian Blue &amp; Yellow Ochre</td>
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<tr>
<td>1610</td>
<td>King's Yellow, Sepia, Bistre</td>
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<td>1700</td>
<td>Scheele's Green</td>
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<td>1778</td>
<td>Vermilion (wet process)</td>
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<td>1780</td>
<td>Cobalt Green synthesised</td>
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<tr>
<td>c.1780</td>
<td>Turner's Yellow</td>
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<td>Zinc Oxide</td>
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<tr>
<td>1781</td>
<td>Discovery of Chromium</td>
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<tr>
<td>1797</td>
<td>Indian Yellow</td>
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<td>c. 1800</td>
<td>Cobalt Blue</td>
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<td>1802</td>
<td>Cerulean Blue</td>
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<td>1809</td>
<td>Calcium Carbonate (precipitated)</td>
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<td>1800s</td>
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<td>1814</td>
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<td>Chrome Yellow</td>
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<td>1818</td>
<td>Synthetic Ultramarine</td>
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<td>c.1824</td>
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<td>Alizarin</td>
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<tr>
<td>1826</td>
<td>Cobalt Green (known since 1786)</td>
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<tr>
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<td>Strontium Yellow</td>
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<td>Barium Sulphate</td>
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<td>1842</td>
<td>Zinc yellow</td>
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<td>1847</td>
<td>Prussian Blue &amp; Cadmium Yellow</td>
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<tr>
<td>1850</td>
<td>Iron Oxides (mars yellow)</td>
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<td>1850</td>
<td>Ultramarine Green</td>
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<td>1850</td>
<td>Coal Tar Pigments (mauvre)</td>
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<td>1854</td>
<td>Cobalt Violet</td>
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<td>1856</td>
<td>Chromium Oxide</td>
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<td>1861</td>
<td>Carbon Blacks (Commercially produced)</td>
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<td>1864</td>
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<td>Pigment/ Filler etc</td>
<td>Refractive Index</td>
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<td><strong>Whites</strong></td>
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<td>Titanium White</td>
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<td>Lead White</td>
<td>1.94 - 2.09</td>
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<td>Zinc White</td>
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<tr>
<td>Plaster</td>
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</tr>
<tr>
<td><strong>Blues</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalk</td>
<td>1.50 - 1.64</td>
<td></td>
</tr>
<tr>
<td>Aluminium Hydrate</td>
<td>1.50 - 1.56</td>
<td></td>
</tr>
<tr>
<td>Cerulean Blue</td>
<td>1.84</td>
<td></td>
</tr>
<tr>
<td>Azurite</td>
<td>1.73 - 1.84</td>
<td></td>
</tr>
<tr>
<td><strong>Greens</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cobalt Blue</td>
<td>1.74</td>
<td></td>
</tr>
<tr>
<td>Prussian Blue</td>
<td>1.56</td>
<td></td>
</tr>
<tr>
<td>Lapis Lazuli (Ultramarine)</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td><strong>Yellows</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smalt</td>
<td>1.49 - 1.52</td>
<td></td>
</tr>
<tr>
<td>Green Earth</td>
<td>2.50 - 2.70</td>
<td></td>
</tr>
<tr>
<td>Chromium Oxide</td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td>Cobalt Green</td>
<td>1.94 - 2.00</td>
<td></td>
</tr>
<tr>
<td>Malachite</td>
<td>1.65 - 1.88</td>
<td></td>
</tr>
<tr>
<td>Orpiment</td>
<td>2.40 - 3.02</td>
<td></td>
</tr>
<tr>
<td>Cadmium Yellow</td>
<td>2.35 - 2.48</td>
<td></td>
</tr>
<tr>
<td>Naples Yellow</td>
<td>2.01 - 2.28</td>
<td></td>
</tr>
<tr>
<td>Yellow Ochre (natural)</td>
<td>2.00 - 2.40</td>
<td></td>
</tr>
<tr>
<td>Raw Sienna</td>
<td>1.87 - 2.17</td>
<td></td>
</tr>
<tr>
<td>Indian Yellow</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td><strong>Reds</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vermilion</td>
<td>2.81 - 3.14</td>
<td></td>
</tr>
<tr>
<td>Realgar</td>
<td>2.46 - 2.61</td>
<td></td>
</tr>
<tr>
<td>Pigment/ Filler etc</td>
<td>Refractive Index</td>
<td></td>
</tr>
<tr>
<td>--------------------</td>
<td>-----------------</td>
<td></td>
</tr>
<tr>
<td>Red Lead</td>
<td>2.42</td>
<td></td>
</tr>
<tr>
<td>Cadmium Red</td>
<td>2.64 - 2.77</td>
<td></td>
</tr>
<tr>
<td>Raw Umber</td>
<td>1.87 - 2.17</td>
<td></td>
</tr>
<tr>
<td>Van Dyck Brown</td>
<td>1.62 - 1.69</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>1.330</td>
<td></td>
</tr>
<tr>
<td>Oil of Turpentine</td>
<td>1.470</td>
<td></td>
</tr>
<tr>
<td>Gum Arabic</td>
<td>1.344</td>
<td></td>
</tr>
<tr>
<td>Egg Tempera</td>
<td>1.346</td>
<td></td>
</tr>
<tr>
<td>Poppy Oil</td>
<td>1.477</td>
<td></td>
</tr>
<tr>
<td>Walnut Oil</td>
<td>1.480</td>
<td></td>
</tr>
<tr>
<td>Linseed Oil</td>
<td>1.484</td>
<td></td>
</tr>
<tr>
<td>Dammar</td>
<td>1.515</td>
<td></td>
</tr>
<tr>
<td>Mastic</td>
<td>1.536</td>
<td></td>
</tr>
<tr>
<td>Shellac</td>
<td>1.516</td>
<td></td>
</tr>
</tbody>
</table>
Historical Notes on Some Pigments;

'How to make an Excellent Ultramarine Blue'
Libri colorum (The Book of Colours) compiled by Jean Lebègue, 15th Century

Take lapis lazuli and grind it fine on a porphyry stone. Then make a mass or paste of the following ingredients: for a pound of lapis, 6 ounces of Greek pitch, two of mastic, one of spike or linseed oil, and half an ounce of turpentine; bring it all to the boil in a pot until almost melted, then filter and gather the product in cold water. Stir and mix well with the powdered lapis lazuli and let sit for a week or so. The longer it rests the better and finer the blue will be. Next knead the paste with the hands, sprinkling it with warm water; the blue will come out with the water. The first, second and third rinsing should be done separately. When you see the blue fall to the bottom of the container, throw out the water and keep the blue. (The difficulty rests in extracting only the blue element, the lazurite, from the minerals that make up lapis lazuli.)

Experiment 2: A Simple Test for Copper (II) Ions

Test on suspected malachite CuCO₃.Cu(OH)₂

<table>
<thead>
<tr>
<th>Sample Conclusion</th>
<th>Test</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 suspected malachite</td>
<td>A small drop of dilute (2M) hydrochloric acid was added to the crystals</td>
<td>effervescence was seen at 100x magnification under to microscope</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Conclusion</th>
<th>Test</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 suspected malachite</td>
<td>A crystal of potassium hexacyanoferrate (II) was added to the solution</td>
<td>A pink – brown precipitate Formed</td>
</tr>
</tbody>
</table>

Experiment 3 Simple chemical test for ultramarine

- Crystals of sample 1, suspected of being ultramarine, were placed on a microscope slide
- With the addition of 3M hydrochloric acid the sample turned white immediately
- This indicated the presence of S₃ ions which are converted to H₂S by the acid
- The characteristic sulphur smell was also noted
Experiments 1: Confirmation of lead in a Lead White

1. A few crystals of the unknown white pigment were placed on a microscopic slide with a dissecting needle.
   *In order to discover if the sample was a carbonate the following test was carried out;*
2. A tiny drop of dilute (1M or 2M) nitric acid was placed near the crystals. The slide was then observed under incident light of a microscope set to 100x magnification. The acid coming into contact with the crystals was observed and any changes noted.
3. The solution was then evaporated off on the hot plate.
4. Once dry the sample was once again viewed under the microscope any observations recorded.
5. *Finally in order to confirm or discount the presence of lead the following test was carried out;*
6. The sample was redissolved with a drop of distilled water and with the aid of a microspatula, a crystal of potassium iodide was dropped onto the sample.
7. Any changes in the sample were recorded.

<table>
<thead>
<tr>
<th>Sample Conclusion</th>
<th>Test</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>B (Suspected to be lead white from week 3)</td>
<td>A small drop of dilute (2M) nitric acid was added to the crystals</td>
<td>effervescence was seen at 100x magnification under microscope</td>
</tr>
</tbody>
</table>

- After placing the solution on the hot plate and evaporating off the liquid, the sample was looked at again under the microscope and crystals observed. Fine dendritic (finger-like), colourless crystals were seen and drawn as seen below;

The drawing was referenced with images of Lead nitrate crystals and the sample confirmed as the latter.

Experiments 1: Confirmation of a carbonate and lead in lead white

\[
\text{lead white} + \text{dilute nitric acid} \rightarrow \text{lead nitrate} + \text{carbon dioxide} + \text{water} \\
PbCO_3\cdot2\text{H}_2\text{O} + \rightarrow + \text{CO}_2 + \text{H}_2\text{O} \\
\text{Lead nitrate} + \text{water} \rightarrow \text{potassium iodide} + \text{water} (?)
\]
Experiment 3 Simple chemical test for ultramarine

- Crystals of sample 1, suspected of being ultramarine, were placed on a microscope slide
- With the addition of 3M hydrochloric acid the sample turned white immediately
- This indicated the presence of $S_3$ ions which are converted to $H_2S$ by the acid
- The characteristic sulphur smell was also noted

Experiment 4: Simple Test for Prussian Blue

- Crystals of sample 5, suspected of being prussian blue, were placed in a microscopic slide
- To test for $Fe^{3+}$ ions, a drop of sodium hydroxide (NaOH) was added to the sample and the results observed under the microscope
- After a few seconds the sample turned a red/brown colour
- The colour change was due to the $Fe^{3+}$ ions being converted to $Fe(OH)_3$ by the NaOH as follows

\[
Fe_4[Fe(CN)_6]_3 + 18NaOH \rightarrow 4Fe(OH)_3 + 18Na^+ + 3Fe(OH)_2
\]

Experiment 2: A simple test for copper (II) ions

1. A few particles of the sample suspected of being malachite were mounted on a microscopic slide.
2. These were placed on a Vickers M10 microscope with 45º incident light focus on the sample.
3. A drop of dilute (3M) hydrochloric acid was placed on the pigment sample and observations recorded.
4. A dissecting needle was then used to place a crystal of hexacyanoferrate (II) (potassium ferrocyanide) onto the latter solution. The reaction was observed and conclusions drawn.

8. A few crystals of the unknown white pigment were placed on a microscopic slide with a dissecting needle.
   In order to discover if the sample was a carbonate the following test was carried out;
9. A tiny drop of dilute (1M or 2M) nitric acid was placed near the crystals. The slide was then observed under incident light of a microscope set to 100x magnification. The acid coming into contact with the crystals was observed and any changes noted.

The solution was then evaporated off on the hot plate.

Experiment 2: Spot tests for Calcium in Chalk

1. 
2. 
3. 
4. As Before
   1. Once the presence of a carbonate was confirmed the following test was carried out to detect the presence of calcium ions:
   2. The sample was re-dissolved in a drop of distilled water and a tiny drop of dilute (2M) sulphuric acid was added.
3. The sample was then looked at under the microscope at 100x magnification and results recorded. 

**Experiment 2: Spot Tests for Calcium in Chalk**

- **Identifying the presence of a carbonate**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Test</th>
<th>Result</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>D (Suspected to be chalk white from week 3)</td>
<td>A small drop of dilute (2M) nitric acid was added to the crystals</td>
<td><strong>Effervescence</strong> was seen at 100x magnification under to microscope</td>
<td>The presence of a carbonate in the pigment sample.</td>
</tr>
</tbody>
</table>

- **Identifying calcium nitrate**

<table>
<thead>
<tr>
<th>Test</th>
<th>Result</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>The solution was then evaporated to a dryness on the hot-plate and the slide then examined under the microscope</td>
<td>No crystals were seen but a gel-like precipitated was observed in a droplet formation</td>
<td>Calcium nitrate is so hygroscopic all you should see are tiny droplets of liquid.</td>
</tr>
</tbody>
</table>

- **Recognising acicula crystals of calcium sulphate dihydrate to confirm that the pigment sample contained calcium ions.**

Calcium carbonate + dilute nitric acid → calcium nitrate + carbon dioxide + water

CaCO3

Calcium nitrate + water + dilute nitric acid → calcium sulphate dihydrate + water

**Experiment 2: A simple test for copper (II) ions**

5. A few particles of the sample suspected of being malachite were mounted on a microscopic slide.

6. These were placed on a Vickers M10 microscope with 45° incident light focus on the sample.

7. A drop of dilute (3M) hydrochloric acid was placed on the pigment sample and observations recorded.

8. A dissecting needle was then used to place a crystal of hexacyanoferrate (II) (potassium ferrocyanide) onto the latter solution. The reaction was observed and conclusions drawn.

**Experiment 2 A simple test for copper (II) ions**

Sample 2 suspected of being malachite effervesced when dilute hydrochloric acid was added to it. The reaction for the equation is as follows;
Malachite + dilute hydrochloric acid → copper chloride + water + carbon dioxide (effervescence)

Experiment 2: A simple test for copper (II) ions

Sample 2 suspected of being malachite effervesced when dilute hydrochloric acid was added to it. The reaction for the equation is as follows;

<table>
<thead>
<tr>
<th>Test</th>
<th>Result</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>The residue from the previous test was dissolved by adding a drop of de-ionised water and a tiny drop of dilute (2M) sulphuric acid.</td>
<td>Acicula crystals of calcium sulphate dihydrate seen</td>
<td>The pigment contained calcium ions.</td>
</tr>
</tbody>
</table>

Experiment 2: Spot Tests for Calcium in Chalk

• A few pigment particles of Sample 4 (suspected of being yellow ochre) were placed on a microscope slide
• A Vickers M10 microscope with 45° incident light was focused on the sample
• A drop of concentrated (3M) hydrochloric acid was placed on the sample and observed as it touched the particles
• After the results were recorded a crystal of potassium hexacyanoferrate (II) (Potassium ferrocyanide) was placed on the sample and observations noted

Malachite + dilute hydrochloric acid → copper chloride + water + carbon dioxide (effervescence)

Experiment 3: Confirmation of Iron (III) ions in yellow ochre

Experiment 3: Confirmation of Iron (III) ions in yellow ochre

• A few pigment particles of Sample 4 (suspected of being yellow ochre) were placed on a microscope slide
• A drop of concentrated (3M) hydrochloric acid was placed on the sample and observed as it touched the particles
• Most of the particles were seen to dissolve under the microscope but no other observations were noted. A possible reaction for the addition of the hydrochloric acid could be as follows: Showing that another compound has
• After the results were recorded a crystal of potassium hexacyanoferrate (II) (Potassium ferrocyanide) was placed on the sample and observations noted
Experiment 2: Confirmation of Iron (III) ions in red ochre

METHOD 1

- The sample suspected of being red ochre was viewed under the Vicker's microscope with 45° incident light.
- A drop of concentrated (3M) hydrochloric acid was placed on the sample and the results observed.
- No reaction appeared to be taking place so the sample was placed on the hot plate until it dissolved.
- A drop of distilled water was then placed on the sample.
- Using a microspatula a crystal of potassium hexacyanoferrate(II) (potassium ferrocyanide) was placed on the sample and any results recorded.

METHOD 2

- The sample suspected of being red ochre was again set up on the Vickers microscope.
- A drop of concentrated hydrochloric acid was placed on the pigment particles and observations noted.
- The sample was then diluted with a drop of distilled water.
- A crystal of potassium thiocyanate was placed on the sample and the reaction and results noted.

- A drop of distilled water was then dropped on the sample.
- Using a microspatula a crystal of potassium iodide was placed in the solution and any reactions/observations noted.

Experiment 1: Microscopical Analysis

- It was relatively simple to distinguish the red pigments analysed and the Becke test seemed to be more clear for these crystals as compared to the yellows.

Experiment 2: Confirmation of Iron (III) ions in red ochre

Method I

- Sample 1 was suspected of being red ochre.
- A few particles of the pigment were placed on a microscopic slide and a drop of 3M hydrochloric acid was added to the sample.
- No reaction appeared to take place so the sample was placed on the hotplate for a few minutes.
- After this time it appeared that the pigment sample had dissolved slightly but no other change was noted. The reaction for the reaction could have been as follow:

Experiment 3: Confirmation of led in red lead

- A few crystals of the sample suspected of being red lead were placed on a microscope slide and looked at on the Vickers microscope using 45° incident light.
- In the fume cupboard a drop of hydrochloric acid was then placed on the pigment particles and observations noted

\[
\text{Red Ochre} + 3\text{M hydrochloric acid} \rightarrow \text{Iron Chloride} + \text{Water}
\]

\[
\text{Fe}_2\text{O}_2 + \text{HCL} \rightarrow \text{Fe}_2\text{Cl} + \text{H}_2\text{O}
\]

- A drop of distilled water was then added to the latter sample
- A crystal of potassium hexacyanoferrate (II) (potassium ferrocyanide) was added to the sample and a dark blue precipitate formed. The dark blue precipitate formed was prussian blue or \(\text{Fe}_4\left[\text{Fe(CN)}_6\right]_3\)

\[
\text{Fe}_2\text{Cl} + \text{water} + \text{potassium hexacyanoferrate (II)} \rightarrow \text{prussian blue} + \\
\text{Iron chloride} + \text{water} + \text{potassium hexacyanoferrate (II)} \rightarrow \text{prussian blue} + \\
4\text{FeCl} + 3\text{K}_4\left[\text{Fe(CN)}_6\right]_3 + 12\text{KCl}
\]

**Method II**

- As before a few crystals of sample 1 were placed on a microscope slide
- A drop of concentrated hydrochloric acid was placed on the sample and then on the hotplate
- The sample partially dissolved on the hotplate. The result appears to be the same reaction that took place in the first part of method 1, however a more obvious reaction took place when concentrated hydrochloric acid was used instead of 3 molar.
- The sample was then re-dissolved in a drop of distilled water and a crystal of potassium thiocyanate added to the sample with a microspatula. The sample immediately turned a blood red colour indicating the presence of iron (III) ions in the original sample. The red coloured compound made was made as follows;

\[
\text{Iron Chloride} + \text{water} + \text{potassium thiocyanate} \rightarrow \text{Potassium iron chloride} + \text{water} + \text{Hydrogen chloride}
\]

\[
4\text{FeCl} + \text{H}_2\text{O} + \rightarrow [\text{Fe(III)}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}
\]

\[
\text{potassium chloride} + \text{water} + \text{potassium iodide} \rightarrow \text{potassium iodide} + \\
\text{potassium chloride} + \text{water} \rightarrow \text{potassium chloride} + \text{water}
\]

\[
\text{Pb}_3\text{Cl} + \text{H}_2\text{O} + \text{KI} \rightarrow \text{KI} + \text{KCl} + \text{H}_2\text{O}
\]
Instrumental/Analytical Analysis Techniques for Pigments

Methods which Identify Elements:
- EDX (Energy Dispersive X-Ray Analysis)
- XRF (X-Ray Fluorescence)
- NAA (Neutron Activation Analysis)
- LMA (Laser Microanalysis)
- PIXE (Particles Induced X-Ray Emission)
- PIGE (Particle Induced Gamma Radiation Emission)

Methods Which Identify Compounds:
- HPLC (High Powered Liquid Chromatography)
- Raman Microscopy
- FTIR (Fourier Transform Infra-Red Analyser)
- Reflectance Spectroscopy
- XRD (X-Ray Diffraction)
# Chronology of Paper

<table>
<thead>
<tr>
<th>Approx Date of Intro</th>
<th>Fiber / Pulp</th>
<th>Fell into Disuse</th>
</tr>
</thead>
<tbody>
<tr>
<td>From 15th Century (?)</td>
<td>Rags (Cotton &amp; Linen)</td>
<td>To the Present Day</td>
</tr>
<tr>
<td>From 1800s</td>
<td>Books with rag pages</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>1845</td>
<td>Rags &amp; soda woodpulp</td>
<td>1890</td>
</tr>
<tr>
<td>1800</td>
<td>Straw</td>
<td>1870 - 90</td>
</tr>
<tr>
<td>From 1853</td>
<td>Soda woodpulp</td>
<td>To the Present Day</td>
</tr>
<tr>
<td>USA 1875</td>
<td></td>
<td>To the Present Day</td>
</tr>
<tr>
<td>From 1869</td>
<td>Mechanical woodpulp (ground pulp)</td>
<td>1869 - 80</td>
</tr>
<tr>
<td>USA 1875</td>
<td>Mechanical pulp with rags added</td>
<td>1890 (UK)</td>
</tr>
<tr>
<td>1857 (UK)</td>
<td>Esparto</td>
<td>Approx 1883</td>
</tr>
<tr>
<td>Early 1860</td>
<td>Esparto with rags added</td>
<td>To the Present Day</td>
</tr>
<tr>
<td>From 1880</td>
<td>Esparto with woodpulp</td>
<td>1890</td>
</tr>
<tr>
<td>From 1872</td>
<td>Sulphite woodpulp</td>
<td>Approx 1883</td>
</tr>
<tr>
<td>1889 USA</td>
<td></td>
<td>To the Present Day</td>
</tr>
<tr>
<td>1884</td>
<td>Sulphate woodpulp (Kraft pulp)</td>
<td>To the Present Day</td>
</tr>
<tr>
<td>From 1907 in North America</td>
<td>Bagasse</td>
<td>To the Present Day</td>
</tr>
<tr>
<td>From 1884</td>
<td>Cotton Linters</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>From 1920</td>
<td></td>
<td>&quot; &quot;</td>
</tr>
</tbody>
</table>
Important Dates in the History of Western Papermaking

European first production of paper approx 1150 (Spain)
1580 (Holland)
Double watermarks added 1483
Blotting paper introduced 1465
Cardboard produced From 1580
Stamping Mills for fiber preparation developed From 1760
Hollander beater for fiber preparation developed From 1760
Blotting paper revival after slump in its manufacture 1800
Paper machines developed From 1803
Esparto Grass paper 1861

Japanese paper;
Caveat;
Commonly today woodpulp and unbleached kraft pulps in particular are often added to the more expensive native Japanese bast fibers.

The Manufacture of Washi

General procedure for white bark in all bast fibers (e.g. kozo, gampi, mitsumata etc) as follows;

1. Soaking in water
2. Boiling
3. Washing and bleaching by exposure to the sun
4. Speck and particle removal
5. Beating
6. Papermaking
7. Removing water from the sheet through pressure
8. Drying on boards

(From the 'Handbook on the Art of Washi')

**Shrinkage Test Indicating Ages in Years of Various Parchments**

(Mc Crone Research Institute Microscopy Course for Art Conservators, taken from Appendices of Handouts, 2820 South Michigan Avenue, Chicago, IL 60616)

**Method**
1. Tweeze a few individual parchment fibers from the edge of the sheet of tear site.
2. Place the fibers on a microscope slide and add a drop of water and a coverslip.
3. Heat the slide on a hotplate at a rate of 2-4 °C/ min.
4. Between room temperature and 70°C the fibers will quickly shrink to around a half of their original length.

McCrone's Parchment shrinkage graph!!!!!!!
Pb₃O₄ + HCL $\rightarrow$ Pb₃Cl + H₂O

- The sample was then diluted with a drop of distilled water
- A crystal of potassium iodide was added to the solution and the formation of a bright lime green precipitate was observed. The production of a strong smelling gas was also noted. After a few seconds the green precipitate then turned yellow. The possible equation for the reaction is as follows:

### Electron Microprobe Analysis

**Basic Principle**

The basic principle of Electron Microprobe analysis is essentially the same as XRF. The difference is that the detector is fitted to a scanning electron microscope. The analysis is a part of Energy Dispersive X-ray Analysis (EDX). The technique can be used to analyse extremely small samples or to analyse specific parts of a sample, by utilising the resolving power of the SEM. In modern SEMs resolving power down to 4 nanometers is typical. The beam of electrons is focused on the spot required to study the composition of a single feature such as a pigment particle. Alternatively, it can be moved across the surface of the specimen for example to determine the variation in concentration of chemical elements in the layers of a cross-section.

**Questions**

Sample C was a green pigment from a polychrome sculpture. It contained particles which had a refractive index of less than 1.66 and appeared as coarse pleochroic rods, pale to deep bluish green and clearly anisotropic. There were also traces of colourless particles which had a refractive index of less than 1.66 and appeared as rounded hexagonal anisotropic plates and rods with higher birefringence.

The description of the sample above seems to correspond to the characteristics of Verdigris based on the findings in microscopic analysis of green pigments. The colourless particles mentioned could be a filler, clay, chalk or another inert white pigment. The EDX spectrum shows a large peak for copper. This would confirm Verdigris as the green pigment as it contains copper in its structure; $\text{Cu(H₃C₂O₂)₂}·\text{2Cu(OH)₂}$. The presence of aluminium and silicon strongly suggest that the colourless crystals belong to a clay. There also seems to be Calcium and sulphur present. This suggests the presence of gypsum (calcium sulphate) either in the ground or as an additive to the clay.
The most effective instrumental analysis available to conservators today to confirm crystalline compounds presence in pigment samples. It is not a method of elemental analysis but a method of identifying the compound(s) present by investigating its/their crystal structure(s).

The modern XRD machine needs little translation of data by scientists/conservators as the instrument is connected to a computer. Simply the sample is placed under the beam of x-rays, this then refracts off the sample and the results read by the computer. The description of the sample above seems to correspond to the characteristics of Verdigris based on the findings in microscopic analysis of green pigments. The colourless particles mentioned could be a filler, clay, chalk or another inert white pigment. The EDX spectrum shows a large peak for copper. This would confirm Verdigris as the green pigment as it contains copper in its structure; \( \text{Cu(H}_3\text{C}_2\text{O}_2)_2\cdot2\text{Cu(OH)}_2 \). The presence of aluminium and silicon strongly suggest that the colourless crystals belong to a clay. There also seems to be Calcium and sulphur present. This suggests the presence of gypsum (calcium sulphate) either in the ground or as an additive to the clay. The computer can then be set to match up our results to known samples from its database. The diffraction of an x-ray beam, passed through a crystal, in certain directions (determined by the von Laue condition or Braggs law) in which the path difference between the beams scattered by the adjacent atoms differs by a whole number of wavelengths. This allows both the structure and the lattice spacing to be determined. The necessary experiments can be carried out with a crystal of fixed orientation, or by observing the diffraction of an x-ray beam from a powdered sample which contains pieces of the crystal in all orientations (>powder photography). The latter technique determines the lattice spacing directly and allows the structure to be deduced.

Samples should ideally be no smaller than \( \frac{1}{2} \) cm. In the case of works of art on paper this is rather a large sample and it is unlikely that we could ever take such a large sample from an object. However smaller samples can be analysed but this increases the time of analysis by the instrument (often overnight) and as the samples get smaller then the accuracy of test results decreases. If a sample is too small the results may be inconclusive.

Taking samples of pigments from works of art has to be done only if it is necessary to identify the pigment and no other ‘in situ’ analysis available has been effective. Also if an object is suitable enough to have a sample taken from it then it is likely that a large enough sample can be taken for instrumental analysis. The taking of tiny samples for a high chance of inconclusive instrumental results is hard to justify in the name of conservation.
Gas chromatography (GC) and Liquid chromatography (LC) depend upon the equilibrium set up when a compound distributes itself between two phases; The stationary phase (contained within a column) and the moving or mobile phase. Different compounds distribute themselves between the two phases to different extents, and so move along the mobile phase at different speeds. The time a compound is held on a column under given conditions is characteristic of the compound and is called the retention time. A detector on the outlet tube monitors compounds coming off the column. The area under each peak depends on the amount of compound present. If the peaks are very sharp, their relative heights can also be used. Therefore compounds can be identified by their retention times and compared with known standards.

The mobile phase of the sample analysed in gas chromatography is injected into the stationary phase and is vapourised into a gas. The stationary phase is silicone oil or waxes either adhered to the surface of tiny particles of solid or as a coating on the inside of a very long (100m) thin glass or silica capillary tube. This tube is often coated on the outside with a polymer to give it strength. The components of the sample dissolve into and therefore absorbed by the stationary phase to form intermolecular bonds. These components are eluted through the stationary phase by a supply of an inert gas such as helium, argon or nitrogen. The component substances are separated both by polarity and volatility into bands or zones along the column. Those compounds that favour the mobile phase are carried along more quickly and the most volatile compounds usually emerge first.

GC-MS (Gas Chromatography- Mass Spectrometry) is considered to be a more powerful tool than GC alone for the analysis of organic materials. With GC-MS, a mass spectrometer is attached to the end of the gas chromatography column where energy in the form of a stream of electrons is applied to the vapourised compound which becomes ionised. This molecular ion is usually unstable and undergoes partial breakdown into pattern into a pattern of fragment ions which, separated according to their masses and measured in intensity, form the mass spectrum. The resultant mass spectrum gives valuable clues to the structure of an unknown compound and can be also be used as a fingerprint for the identification of a compound whose spectra are already known. However their may be uncertainty in results which should always be considered. Experimental error may occur during hydrolysis and derivitisation and the natural variation in fatty acid content of drying oils may alter results.
Refer to the practical manual for treatment of results and chromatograms.
• The azelate to palmitate ratio is calculated by taking the azelate ratio percentage and dividing it by the percentage palmitate ratio. In this case 100 ÷ 68.122 = 1.46. A ratio above indicates the presence of a drying oil in comparison to egg tempera which has a ratio of approximately 0.1.

• The palmitate to sterate ratio is 1.2 (68.122 ÷ 52.823). This ratio indicates that it falls between the ratios known for linseed oil of 1.4 to 1.9.

• The azelate/ suberate ratio (Az/Sub) is 1.85 and the azelate/ decandioate ratio (Az/Dec) ratio is 6.14. If the Az/Dec ratio is around 4 and theAz/Sub around two then this may indicate that the oil has been et bodied. In this case the Az/Sub ratio matches that of a heat bodied oil but the Az/Dec ratio is a little higher than 4 although this may still indicate a heat bodied oil which were commonly used in the nineteenth century.
The mass spectrums for paint sample BS7a (as seen above) show high base peaks. Scan 1824 shows the compound sample giving a base peak of 239 at 27.302 minutes which appears to relate to a database compound called methyl-7-oxohydroabietate M314. Scan 2129 shows base peaks of 253 at 30.213 minutes. This seems to relate to methyl oxohydroabietate M328. In conclusion both these base peaks show that a coniferous resin is present.

The brown paint sample therefore may be a heat bodied linseed oil mixed with a resinous material.

The description of the sample appears to correspond to the pigment vermilion. As mentioned before the colourless particles could be clay. The EDX spectra shows the presence of Mercury and Sulphur from vermilion which is mercuric sulphide. Calcium, sulphur and oxygen could confirm the presence of gypsum \((\text{Ca SO}_4 \cdot \text{2H}_2\text{O})\). Again, the presence of aluminium and silicon confirms the presence of clay.
High performance liquid chromatography employs phenyl isothiocyanate as a derivitising agent for the amino acids obtained by hydrolysis of the media samples. It has been suggested that HPLC has an advantage over GC as a chromatographic method for the analysis of proteins because the amino acid ratios obtained are not affected by the volatility of the derivatives. However its disadvantage is that sample sizes need to be slightly larger than those for media analysis.

For the particular components used refer to the practical manual.

Experiments with standard samples of typical proteins found in paint media or conservation adhesives show the following typical results. As expected for a collagen, rabbit skin glue contained hydroxyproline and glycine peaks in a 1:3 ratio. Proteins in animal connective tissues contain approximately 30 percent glycine and 10 percent hydroxyproline. The identifying feature of animal and fish glues is the presence of hydroxyproline in considerable quantity. Hence we are not surprised to find that this amino acid in gelatine and isinglass. As expected only trace quantities of hydroxyproline are detected in egg-white or egg-yolk, the strongest peaks in the chromatogram for the former being due to proline and serine. In contrast, egg-yolk shows a smaller proline:serine ratio and higher ratios for alanine:serine and glutamic acid:serine than egg-white. Gluten is the protein present in wheat and therefore in flour paste, an oadhesive often used in conservation. Analysis of gluten also shows only trace quantities of hydroxyproline and while the serine:glycine ratio is similar to that found in egg-yolk, the most distinguishing feature of the chromatogram is the much larger glutamic acid:serine and glutamic acid:glycine ratios as well as the smaller relative quantity of alanine.

<table>
<thead>
<tr>
<th>amino acid</th>
<th>sample % of FMOC derivs. by peak area</th>
<th>animal glue</th>
<th>casein</th>
<th>gluten (wheat flour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>gly</td>
<td>26.2</td>
<td>24.7</td>
<td>1.7</td>
<td>4.0</td>
</tr>
<tr>
<td>ala</td>
<td>9.8</td>
<td>10.1</td>
<td>2.7</td>
<td>2.1</td>
</tr>
<tr>
<td>val</td>
<td>2.3</td>
<td>2.2</td>
<td>7.2</td>
<td>2.7</td>
</tr>
<tr>
<td>leu</td>
<td>3.5</td>
<td>3.7</td>
<td>9.0</td>
<td>?</td>
</tr>
<tr>
<td>iso leu</td>
<td>1.5</td>
<td>1.2</td>
<td>6.0</td>
<td>11.9</td>
</tr>
<tr>
<td>pro</td>
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<tr>
<td>phen</td>
<td>2.0</td>
<td>1.6</td>
<td>5.1</td>
<td>6.4</td>
</tr>
<tr>
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<td>3.7</td>
<td>4.0</td>
<td>4.0</td>
<td>4.9</td>
</tr>
<tr>
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<td>1.3</td>
</tr>
<tr>
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<td>20.2</td>
<td>45.7</td>
</tr>
<tr>
<td>hypro</td>
<td>7.5</td>
<td>7.4</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The sample appears to correlate most closely to an animal glue.
Glossary of Terms

Abaca - Another name for manilla hemp (*Musa textilis*), a leaf fiber commonly cultivated in the Phillipines.

Alkaline - Alkaline substances also known as bases are those which have a pH value above 5 (6-11) on the pH scale. Chemically defined they are those substance which have a reduced amount of hydrogen ions...... Examples of common alkalis include caustic soda, lye, sodium carbonate, which is known as soda or washing soda in crystalline form. Baking soda (sodium bicarbonate) and trisodium phosphate are less alkaline as also is borax (sodium tetraborate) and gypsum.

Alkaline reserve - An alkaline paper additive such as calcium carbonate. Also called 'buffer'.

Anisotropy - The opposite of isotropy; Particles are said to be 'anisotropic' when they are visible against the black background obtained in the field of view when the analyzer on the microscope is pushed in. Azurite, cobalt blue, chalk white and lead white particles, for example, appeared light against the black background; these pigments can therefore be described as anisotropic.

Base - An inert compound, an alkaline or alkaline forming substance.

Bast Fiber - The inner bark or phloem of woody plants (dicotoleydons) which occur in the outer ring of vascular tissue. Bast fibers transplant aqueous solution from the leaves. The term is also used to refer to the fibers found in the cortex and pericycle rings of herbaceous plants. Mitsumata, kozo, gampi, hemp, flax and jute are all considered bast fibers.

Becke Test- A method of determining the refractive index of a particle through observing the direction on which the Becke line moves. A particle fiber mounted in a medium will exhibit a halo of light around its circumference when observed under reflected light on an normal incident light microscope. The halo will always move to the higher refractive index medium when the focus is raised (increased). The halo will go into the lower refractive index medium when the microscope is focused downward. (See Appendices for a more detailed description.)

Conchoidal Fracture - A type of fracture seen when a mineral or other substance, such as glass, breaks to give irregularly curved and usually striated surfaces.

Covering Power - The extent of area covered satisfactorily by a pigment, paint or varnish across a given area. The term is often expressed in square feet and is often confused with the term 'hiding power'.

Dichroism - The ability of a substance/ pigment to appear two different colours when viewed under different circumstances or , for instance, different lights. For example alizarin crimson can appear deep maroon in water colour but ruby-red in thin layers of paint and when viewed by transmitted light.

Extinction - Oblique; If the vibration directions are oblique to the long direction of the crystal. Parallel; If the vibration directions are parallel or perpendicular to the long direction of the crystal. Symmetrical; If the vibration directions bisect a prominent angle. (See Appendices for a diagram explanation!)

Fibrils- Microscopic raised strands which protrude from the cell walls of cellulose and other fibers during beating. Their diameter depends upon how much mechanical treatment they have undergone.
Gouache;

An opaque watercolour made by grinding pigments in the same medium as is used for watercolours but with a larger percentage of vehicle than is used in watercolour; and by adding various amounts of inert pigments such as chalk or blanc-fixe (to improve colour and textural effects). Gouache colours sold in tubes, contain the same ingredients as transparent watercolours, but chalks added to some of the dullest pigments to brighten them. Gouache, watercolour, pastel, and India ink are frequently combined in painting.

Gouache was occasionally used in Medieval manuscript illumination, and for miniature painting in the 16th - 18th Centuries, although toward the end of this period its use was confined to emphasising highlights. In the 18th Century, it was popular with Italian and Swiss watercolourists. It has a potential to dull and is, as a result, more difficult to add gouache to watercolour successfully than it is to add transparent watercolour to a painting done predominantly in gouache.

Hemicellulose - Cell wall polysaccharides. They form a non-crystalline matrix which absorbs water, which helps swell the fibrils and when drying tends to harden, due to its adhesive nature, as fibers and fibrils shrink.

Hydrolysis - A chemical reaction of a substance caused by the presence of water resulting in formation of a new substance and a salt.

Herzberg Stain - Also known as the zinc chloride stain needs to be used within a month of preparation.

Colour result;

Blue, blue-grey or purple - chemically treated wood, straw, grass, jute or similar fibers.
Brownish-red - Cotton, linen, ramie, hemp, paper mulberry, manilla and other similar fibers. Sometimes wood fibers which have undergone partial chemical and partial physical treatment.
Yellow, brownish-yellow or green - Wood fibers which have undergone mechanical treatment alone or mechanical treatment followed by limited chemical treatment; Also straw, grass or jute fibers which have some or no chemical treatment.

Ink;

A coloured liquid used for writing or printing. There are three categories: water insoluble inks, water soluble and printers inks. Water soluble is know as India ink, prepared from carbon and resinous medium which becomes water insoluble upon drying.
Writing ink is water soluble and not regarded as absolutely permanent because it has a tendency to fade in strong sunlight. It is made of tannic acid, ferric sulphate and blue or black dyes.
Chinese inks that are solid and solid in stick form are compounds of a carbon pigment bound by a water-soluble substance.
Printing ink is oil-based; Made by grinding lamp black very fine and mixing it with oil. Less oil is used in a relief or typographic ink than an intaglio ink to make it more viscose so that it will not run into the hollows.

Isotropy - The opposite of anisotropy; Particles are said to be 'isotropic' if they disappear in the field of view, becoming dark with the black background obtained when the analyzer on the microscope is pushed inward.

Lake - A pigment made by precipitating or developing a dyestuff on an inert pigment with the assistance of chemicals and other manufacturing aids, by a process comparable to the dyeing of textiles. All older pigments made by this method are still called lakes, but a few of the synthetic or organic pigments developed in the last forty years use the name. The inert pigment in a lake is called the base, alumina hydrate is the standard base for transparent lakes and blanc fixe is the base for pigments where an opacity is desired. Clay, chalk, gypsum, white earth, and various chromatic pigments have all been used as lake bases at one time or another. All lakes made from natural dyestuffs (except madder lakes) are insufficiently permanent for artist's paints. Similarly, most of the early lakes made from synthetic organic dyes are not sufficiently non-bleeding for use in oil
colours, even though the lightfastness of some of them has increased in recent years by the molybdic and phosphotungstic processing methods.
The word lake may come from the Ancient Egyptians or Greeks, Roman recipes still survive for making paint pigments form natural dyestuffs such as kermes and Tyrian purple.
17th and 18th Century writers used the term 'lake' to mean transparent red lake, without specifying crimson lake, carmine lake or lac lake.

**Lightfast** - The ability of a pigment or substance to resist fading or decomposition to result in fading through exposure to light. Usually when applied to artists pigments it refers to pigments which are totally unaffected by the chemical process of photoxidation which affects many organic pigments readily fading them dramatically with exposure tot he sun and/or even predominantly ultraviolet rays emitted by most light bulbs.

**Lignin** - The non-carbohydrate portion of most plant cell walls. Lignin gives strength and structure to the plant but it is an inherently acidic material and large proportions of it in paper leads to discolouration. It has also been suggested (Barret,T 'Japanese Papermaking') that lignin interferes 'with hydrogen bonding of fibers during papermaking leading to weakness in the paper.'

**Neri** - Term given to the viscous liquid binder added to the pulp vat. The word originating from the verb nebaru 'to become sticky or viscous'.

**Oxidation** - The chemical reaction of a substance with oxygen to form an oxide.

**Photomicrograph** - A photograph of a small area as viewed under a microscope. The extent of magnification depends upon the lens being used.

**Pigment** - A Natural or synthetic colouring matter which is mixed with a medium to form a paint. Natural pigments can be found in plants, minerals and clays whereas synthetics are man-made and usually formed though chemical reaction.

A solid material which, following grinding and being reduced to a powder, can be used with a binder as a paint or ink. A pigment is soluble whereas a dye is not. Many pigments are inorganic compounds such as ochres, sienns or umbers, iron oxieds, chrome yellow, ultramarine and lamp black. (Lake colours are white pigments carrying precipitated organic dystuff.) Pigments are solids which by definition do not dissolve when mixed with a vehicle. A dye, on the other hand, will generally stain a vehicle. Pigments which are chemically identical are grouped together under a Colour Index Generic name, even though they are different colours, e.g. raw sienna and burnt sienna. The lightfastness of a pigment is dependant upon the amount and quality of light; length of exposure, extent of mixing with other colours etc. Lightfastness of specific pigments in specific conditions is rated on the Blue Wool Scale (British Standard 1006) by numbers 1-8, 8 being most lightfast.

**Pleochroism** - The term for a subtle colour change seen in some particles under the microscope as they are rotated on the stand when illuminated by transmitted plane polarised light. It may be necessary to focus on a number of particles as a few only may change colour.

**Polarized Light** - Light rays with one single propagation direction and a single vibrational direction. The vibrational direction is always perpendicular to the propagation direction. It is produced from ordinary light by reflection, by double refraction in a suitable crystal or by absorption with a suitable pleochroic substance. (See 'Polarized Light and Crossed Polars' in section on How to Use a Microscope.)
**Raw Fiber** - Harvested, dried black, white or green bark from the tree or plant in the case of Eastern papers and flax cotton etc freshly cut prior to papermaking in terms of Western fibers.

**Refractive Index (n)** - The ratio of the velocity of light in a vacuum to the velocity of light in some medium. Refractive index generally increases with the atomic number of the constituent atoms. A higher density or high atomic number elements usually results in a high refractive index.

**Translucent** - Transmission of light so that the image-forming rays are irregularly refracted and reflected.

**Transparent** - Transmits visible light appearing clear such as glass.

**Washi** - Japanese term for paper where 'wa' means Japan and 'shi' means paper. The term is used today to refer to any Japanese paper, hand or machine-made, traditionally produced or not.

**Watercolour** - Pigment bound in a water-soluble medium
The technique of painting with pigments in a gum arabic solution, a work so produced; also, the paint used in this technique.
The gum acts as a binder, but the other ingredients in watercolour paint included a plasticizer such as hydromel or sugar water, a glycerin to keep the paint moist, a wetting agent to obtain a uniform flow or paint on surfaces, and a preservative such as phenol.
Watercolours are characterised by a luminous transparency, although gouache is sometimes considered an opaque watercolour technique.
At the modern technique of transparent watercolour painting was developed in the late 18th and early 19th Century's
Watercolour paints were being made commercially by the late 1700s. They were at first hard, dry cakes embossed with the maker's trademark. Moist watercolours, obtained by adding glycerine and sold in pan's, were introduced around 1835.

**White bark** - The inner bark used to make paper in Japanese papermaking yielding the best fibers and producing a naturally off-white soft cream paper. Lesser quality papers will combine inner and outer, 'black', bark in papermaking.

**Woodpulp** - Mechanically/chemically and combined soft and hardwood fibers used in papermaking. Fiber length, hemicellulose and lignin content can vary dramatically as can the additives such as fillers, coating bleaches and whiteners that are often added into the pulp.