COCHINEAL LAKE: HISTORY, CHEMISTRY, AND PREPARATION

HIST GU4962: Making and Knowing in Early Modern Europe: Hands-On History

Last updated 2021-05-24 by NJR

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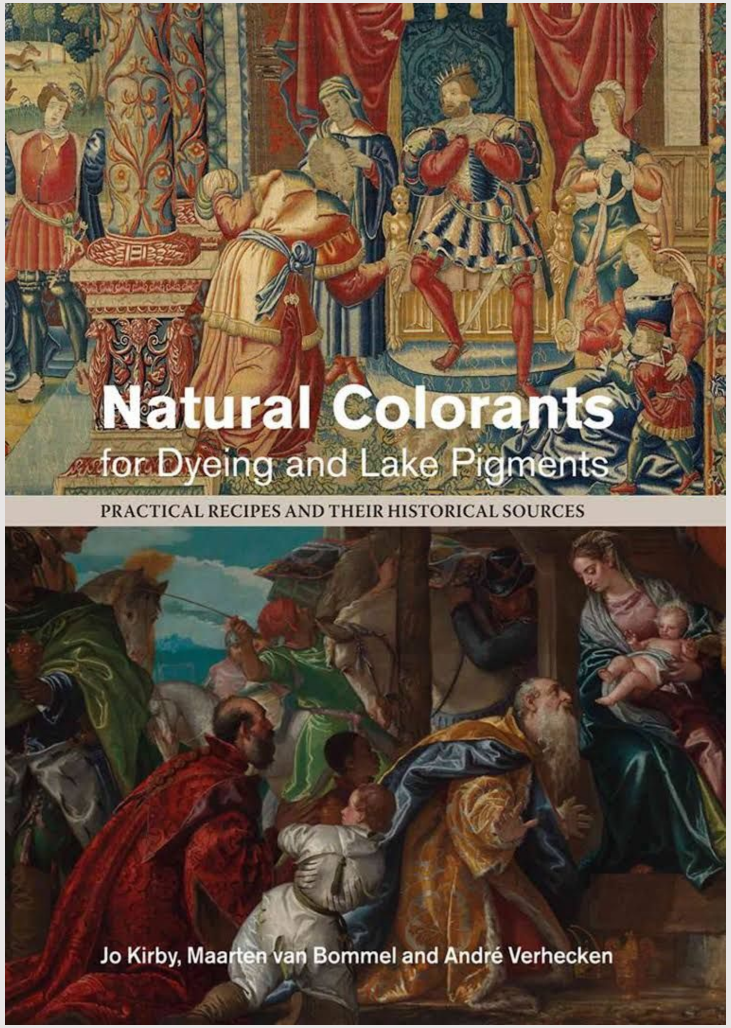
Much of this material was initially developed as part of public workshops at [Genspace Community Lab](#) (New York), made possible by the Public Outreach Grant, *Colorant Sustainability Workshops* (Naomi Rosenkranz and Sumeyye Yar), from Columbia University's [Center for Science and Society](#).

Main reference works:



Jo Kirby et al, *Natural Colorants for Dyeing and Lake Pigments: Practical Recipes and their Historical Sources* (Archetype, London, 2014).

Phipps, Elena. *Cochineal Red: the Art History of a Color*. New York (N.Y.: The Metropolitan Museum of Art, 2010. Print.) Full pdf available for free download here: https://www.metmuseum.org/art/metpublications/cochineal_red_the_art_history_of_a_color

Definitions, background and basics

http://cameo.mfa.org/wiki/Pigment

Pigment

- An insoluble, dry solid that is pulverized to a fine powder then mixed with a binder to form a paint, ink or crayon.
- See also Introduction to paints and pigments_2021

Natural pigments

- Natural colorants are obtained from natural sources:
  - **Organic materials** (such as plants)
  - **Inorganic materials** (such as minerals)
- As most organic natural colorants are soluble, they cannot be mixed directly with a binding medium and therefore cannot be used as a pigment.
- **Lake pigments**: in general, pigments prepared from soluble natural colorants, formed by precipitating (or adsorbing) the dye onto a colorless or white, insoluble, relatively inert substrate.
- Thus, to understand **lake pigments**, we must discuss **organic dyes**.

Jo Kirby et al, *Natural Colorants for Dyeing and Lake Pigments: Practical Recipes and their Historical Sources* (Archetype, London, 2014)

http://cameo.mfa.org/wiki/Dye

Dye definition and sources

A **DYE** is a compound that absorbs into and colors another material, and is generally a complex organic material.

Natural dyes have historically been extracted from:

- **PLANTS**
  - Such as alkanet, annatto, archil, brazilwood, buckthorn berries, cudbear, cutch, fustic, madder, indigo, litmus, logwood, morinda, quercitron, safflower, saffron, sassafras, sumac, turmeric, turnsole, walnut, weld, and woad
- **INSECTS**
  - Such as kermes, lac dye, cochineal
- **LICHENS** (algae or fungi) and **SHELLFISH**
  - Such as archil (lichen) and Tyrian purple (extracted from mollusks)

DYESTUFFS
The raw organic materials used to create a dye

Synthetic dyes were first derived in 1856 (from coal-tar extracts to create mauve)

https://maiwa.com/pages/natural-dyes

Natural colorants

While colors can be extracted from all plants and some animal products, not all of these colorants have **good dyeing (or coloring) properties**.

They are not **COLORFAST**

pomegranate

https://www.thespruce.com

grass

https://www.123rf.com/photo_37142470_smashed-pomegranate-on-the-table.html

Light fastness tests of textiles dyed with natural colorants. Small squares of each sample were exposed to light of varying intensities and for different durations. The squares exposed to the brightest light for the longest time have faded the most.
http://www.conservationphysics.org/fading/fade.pdf

Color fastness

FASTNESS

The resistance of color to fading.

A colorfast dye will maintain its color when exposed to light, steam, high temperatures, soap, salts, and other environmental conditions.

LIGHT FASTNESS

How resistant a color is to fading when it is exposed to light, especially sunlight.

http://cameo.mfa.org/wiki/Fastness

Classification of organic dyes

Types of dyes (by chemical class)

Indigoids

Anthraquinones

Flavonoids

Carotenoids

Neo-flavonoids/homoisoflavonoids

Types of dyes (by process)

DIRECT DYES

Colorant forms a direct bond to the textile fiber

MORDANT DYES

Colorant needs to bind to a coordination metal as a bridge between the dye and textile fiber

VAT DYES

A chemical reaction (reduction) in the dye vat is needed to bind the dye to the textile

Turmeric

Cochineal

Indigo

Common red colorants in Early Modern Europe (1400-1700)

Safflower or bastard saffron

Botanical name: *Carthamus tinctorius* L.

Chemical class: carthamin (C-glucosylquinochalcone)

Region: Mediterranean, spread to southern and central Europe

Dye type: Direct

Petals contain a water-soluble yellow dye that is discarded in the process of obtaining an alkali-soluble red. Textile is dyed by placing in red alkaline solution and adding an acid like lemon juice.

http://www.tropicos.org/Name/2700365

http://collections.vam.ac.uk/item/O485844/fukusa-gift-cover-unknown/

Japanese (ca. 1868-1912), silk

Henna

Botanical name: *Lawsonia inermis* L

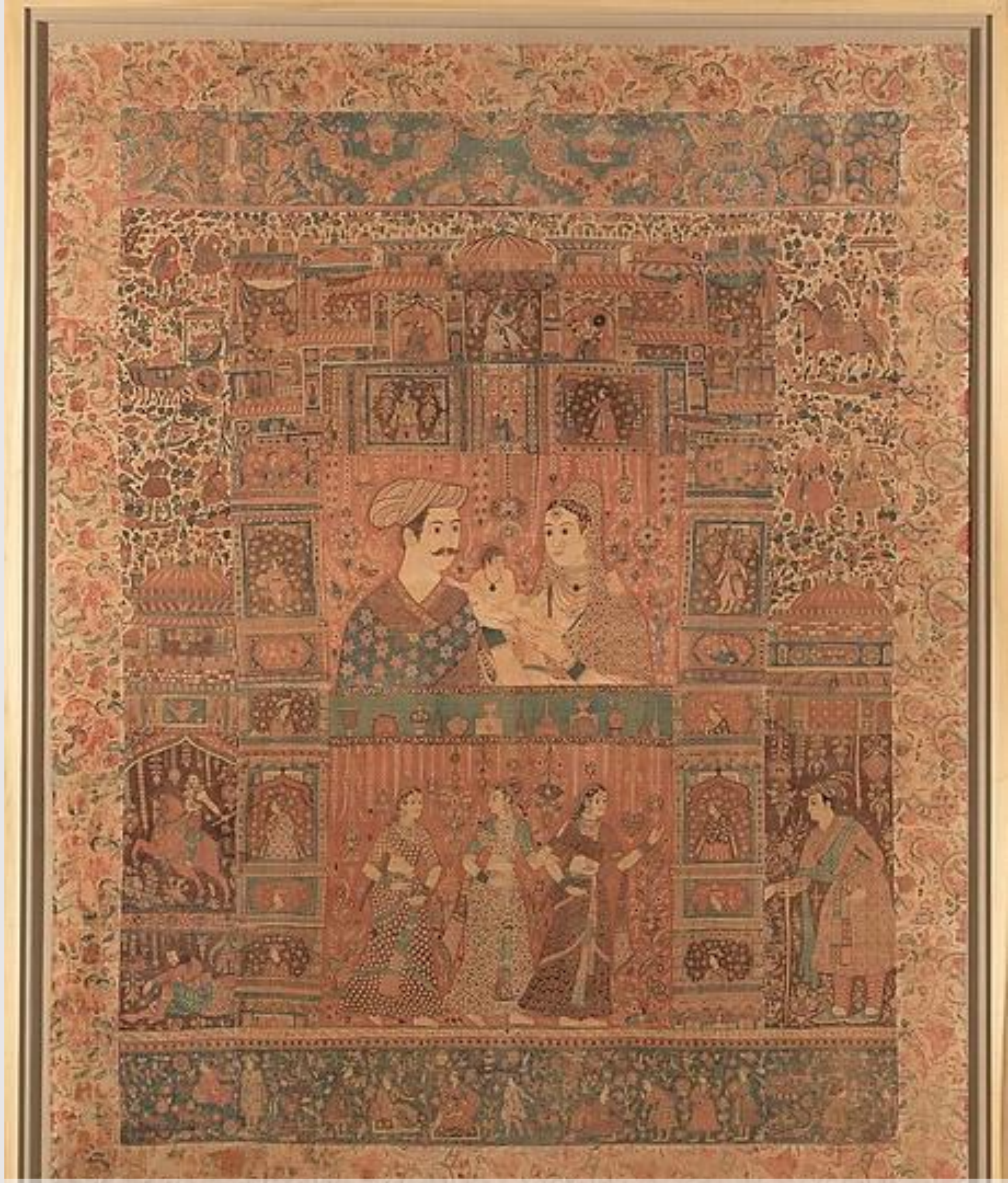
Chemical class: lawsone or isojuglone (naphthoquinone)

Region: India, tropical and subtropical regions, spread to Mediterranean, Spain, and Sicily

Dye type: Direct or mordant dye.

Leaves are used to obtain orange-red to brown colors.

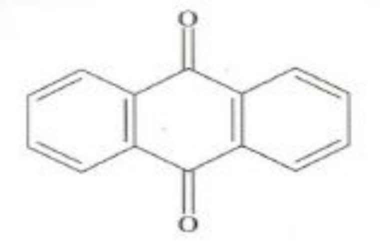
http://www.tropicos.org/Name/19200244



https://www.metmuseum.org/art/collection/search/447118

Indian (ca. 1640-50), cotton

Lac



Species name: *Kerria lacca*, *Kerria chinensis*

Chemical class: laccaic acid and erythrilaccin among other similar constituents (anthraquinone)

Region: Southeast Asia. Spread to Mediterranean and then Europe.

Dye type: Mordant dye.

Scale insect parasitic on several tree species including bastard teak *(Butea monosperma* (Lam.)

Secretes a protective coating that encloses itself in a sticky brown mass similar to resin, known as sticklac. When purified, this is known as shellac which was less economically important than the dye unlike today.

https://www.researchgate.net/figure/Some-lac-insects-known-from-the-New-World-a-Kerria-lacca-on-Albizzia-sp-Peradeniya_fig1_51254451

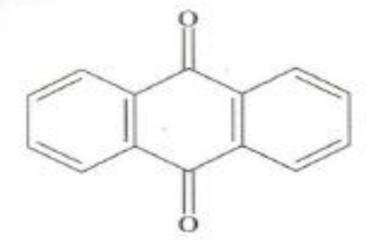
http://collections.vam.ac.uk/item/O61099/hanging-unknown/
Indian (ca. 1700), cotton and silk

15. Fragment of a caftan or robe with deer in a pearl roundel. Eastern Iran or Sogdiana, 8th–9th century. Compound twill weave silk (*samit*), the bright pink dyed with lac; 13⅜ x 17⅜ in. (34 x 44 cm). The Metropolitan Museum of Art, Purchase, Rogers Fund, by exchange, 2006 (2006.472)

“Lake” etymology (Oxford English Dictionary)

- The term derives from the Latin word *lacca*, used in the Middle Ages to denote both lake pigments and the Lac dye.
- **Origin:** Of multiple origins. Partly a borrowing from French. Partly a borrowing from Latin. **Etymons:** French *lac*, *laque*; Latin *lac*.
- **Etymology:** < (i) Anglo-Norman *lac*, *lak*, *lacca* and Middle French, French *laque*, †*lacque* natural lac (13th cent. in Old French as *lache*), coloured paint or varnish (mid 16th cent.), lacquerwork (1659 in the passage translated in quot. 1662 at sense 4),
- and its etymon (ii) post-classical Latin *lac* (12th cent. in a British source), *lacca* (from 13th cent. in British and continental sources), both denoting natural lac

Madder



Botanical name: *Rubia tinclorum* L.

Chemical class: alizarin (anthraquinone)

Region: Native to Middle East and east Mediterranean, then spread to Europe.

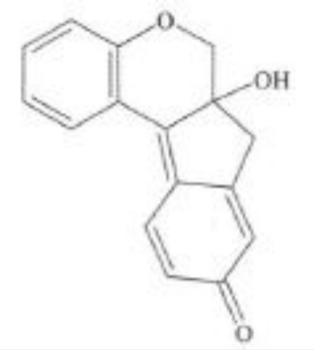
Dye type: Mordant dye.

Range of red-orange-brown dyes obtained from the roots of a bedstraw.

https://www.metmuseum.org/art/collection/search/445750
Egyptian (5th-8th century), linen and wool

http://collections.vam.ac.uk/item/O146101/jacket-unknown/
Iranian (ca. 1800-1870), cotton and silk

Redwoods
(sappanwood, brazilwood)



Chemical class: Brazilin, colorless until oxidized by air becoming orange-red brazileín (homoisoflavonoid)

Dye type: Mordant dye.

Extracted from orange-red wood, inner bark of trees, such as **sappanwood** *(Caesalpinia sappan* L.) - region: Central and southern India, Burma, Thailand, Indochina, southern China, Malaysia. Imported into Europe in early Middle Ages; **brazilwood** (*Caesalpinia brasiliensis*) and **pernambuco wood** (*Caesalpinia echinata Lamarck)* - region: Brazil and Caribbean Islands, then imported into Europe; **peachwood** *(Haematoxylum brasiletto* Karsten) - region: Central America, then imported into Europe.

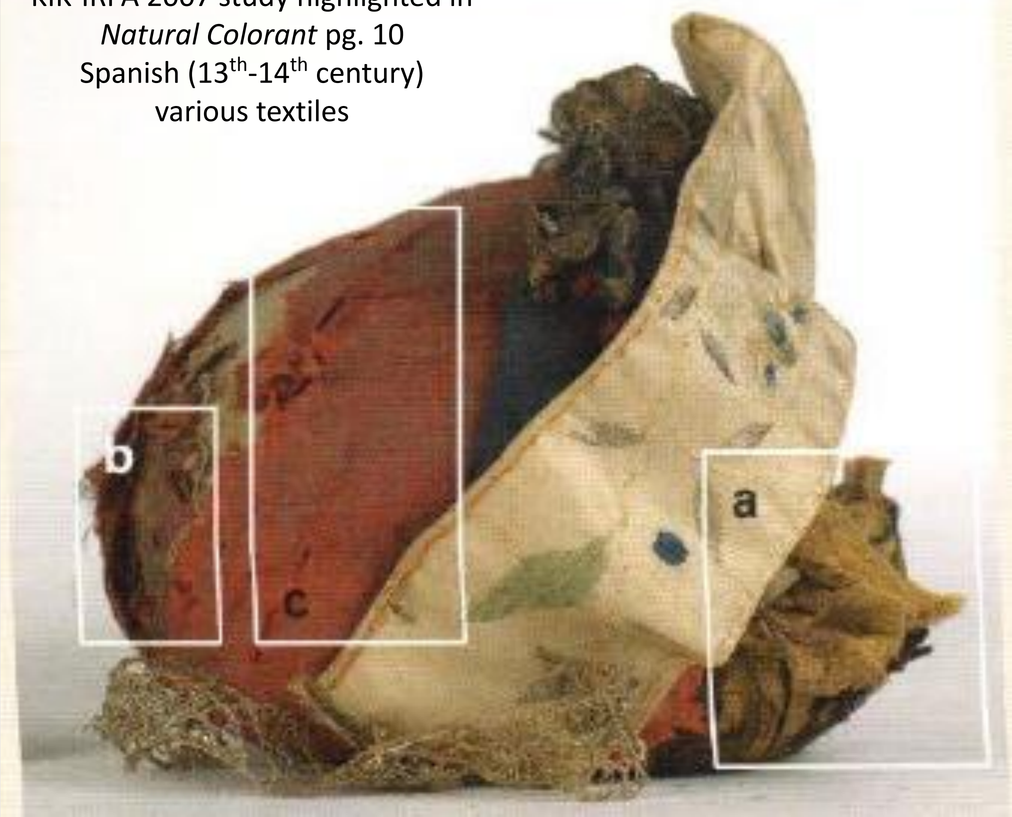
Brazilwood

Logwood

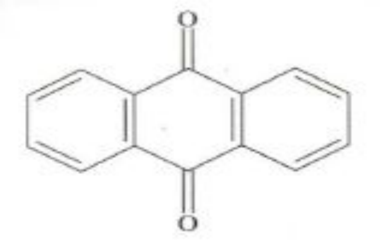
Sappanwood

http://www.tropicos.org/Image/62816

KIK-IRPA 2007 study highlighted in *Natural Colorant* pg. 10
Spanish (13th-14th century)
various textiles



Kermes



Species name: *Kermes vermilio*

Chemical class: kermesic acid (anthraquinone)

Region: Limestone coastal regions around the Mediterranean in Spain, southern France, North Africa, and the eastern Mediterranean.

Dye type: Mordant dye.

http://www.projectnoah.org/spottings/255006061

Scale insect parasitic to an evergreen oak (*Quercus coccifera* L.).
Scarlet red color used to dye the highest quality fabrics.
Used extensively throughout Europe until the arrival of cochineal from the New World in 16^{th} century.

Dye is contained in the unhatched eggs of insect, and so can be extracted from females with unhatched eggs (more common) or from the eggs directly.

http://shop.kremerpigments.com/en/dyes-und-vegetable-color-paints/natural-organic-dyes-und-vegetable-color-paints/4920/kermes-lice

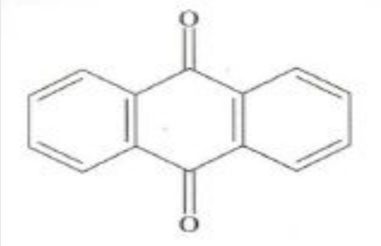
Kermes

http://collections.vam.ac.uk/item/O264602/woven-silk-unknown/
Spanish (ca. 15th century), silk damask

http://collections.vam.ac.uk/item/O261109/woven-silk-unknown/
Spanish (ca. 14th century, woven silk and satin

Cochineal

Cochineal



Species name: *Dactylopius coccus*

Chemical class: carminic acid (anthraquinone)

Region: Cultivated in Mexico and Peruvian Andes, before Spain brought to Europe in 1523 where it spread rapidly.

Dye type: Mordant dye.

http://www.projectnoah.org/spottings/1136866002

Scale insect found on prickly pear or Barbary fig cactus *(Opuntia ficusindica* (L.)).

Led to decline of use of kermes as it is almost **20% by weight more potent than kermes**. Dye is extracted from females with unhatched eggs.

Cochineal in the Americas

32. Coca bag. Peru, Moche, 5th–6th century. Tapestry-weave cotton and camelid hair, the red dyed with cochineal; 5 x 6 in. (12.7 x 15.2 cm). The Metropolitan Museum of Art, Bequest of Arthur M. Bullowa, 1993 (1994.35.88)

Cochineal red was known as a dye in Mexico and South America at least as early as the second century B.C. and was used profusely by Precolumbian peoples.

It colored special ritual and ceremonial textiles worn by rulers in both Mexico and Peru and was an important tribute item in the medieval economies of Latin America.

Habitats and areas of cultivation of cochineal in the Americas, from the 16th to the 19th century

While known and used throughout the Americas, cochineal was first brought to Europe in 1523 by the Spanish.

This new world dye revolutionized red colorants in Europe. Cochineal was ten times more powerful than any other “old world” red.

The Cultivation and Mystery

While other colorants that had been imported into Europe also eventually saw the import of the cultivation of the colorants in Europe, cochineal's production stayed a mystery to the majority of Europe for centuries.

There are three main reasons for this long-standing mystery:

1. The delicate environment and careful cultivation required to encourage insect growth and harvest them for use
2. The widespread confusion about what cochineal actually was
3. The monopoly maintained by the Spanish over cochineal cultivation

1) Environment and Cultivation

- Cochineal survive almost exclusively on the nopal (prickly pear) cactus native to Central and South America.
- As young insects, cochineal attach themselves to the cactus with straw-like mouthpieces where they feed on the nectar for the rest of their lives.
- The cacti require specific levels of atmospheric temperature, humidity, rainfall, pest control, and soil conditions, which can make their cultivation outside of certain parts of the Americas (and the Mediterranean with similar climates today) quite difficult.
- When the cochineal have reached a certain maturity and size, they must be delicately removed from the cactus by hand. For example, Aztec documents mention tools like turkey feathers or deer tails to gently brush the insects off before leaving them in the sun to dry.
- Many attempts to bring the insects or even the cacti back to Europe failed just because of environmental conditions.

Furthermore, the type of cochineal that produce the most potent red color had been carefully cultivated and bred by Mexican peasants for centuries to become larger and more potent dye producers. Even if Europeans found wild cochineal in other parts of the Americas, they were the small, wild variety with poor dyeing properties.

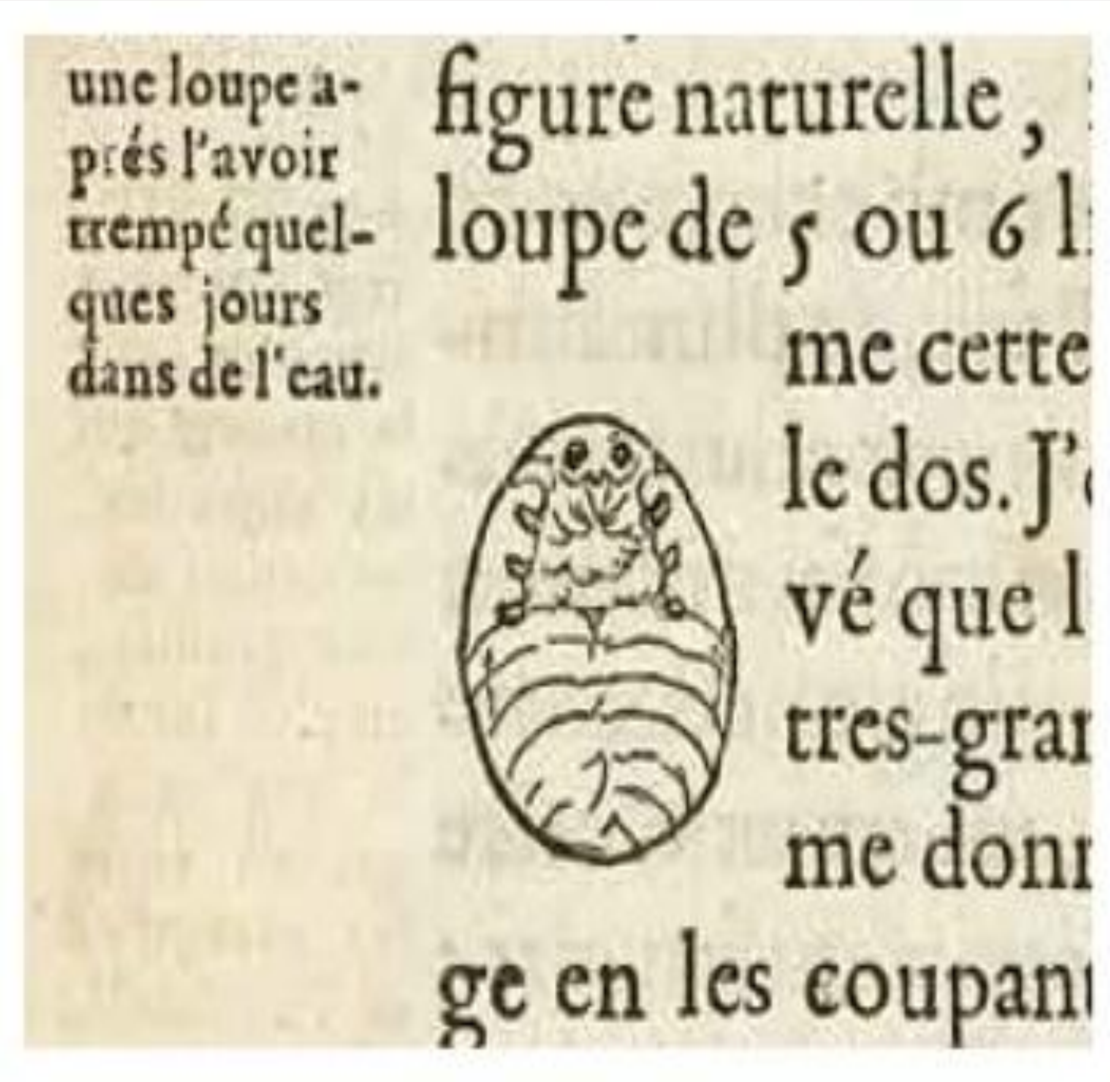
When Europeans did get hold of true Mexican cochineal, any attempts to bring them back to Europe failed, as the insects could not survive in the change of environment, often dying on the way back to Europe or perishing in Europe without access to nopal cacti.

2) Europe: What is Cochineal?

- Dried cochineal don’t really look like insects. What the little silver-purple grains are just by looking at them is still hard to distinguish.
- Many different theories developed throughout Europe:
  - Richard Hakluyt, and English collector and editor of volumes of travel tales, wrote (1589–1600): "The Cochinilla is not a worme, or a flye, as some say it is, but a berrie that groweth upon certaine bushes in the wilde fielde.“
  - French explorer Samuel de Champlain wrote(1599–1602) : "It comes from a fruit the size of a walnut which is full of seed within . . . and is esteemed as gold and silver.“
  - Some of the confusion also came from theories about Kermes. Pliny (AD 23-79) described kermes, or coccus, as a berry that turns into a worm, a belief that was held about cochineal throughout the Renaissance

2) Europe: What is Cochineal?

- Cochineal was not accurately described until it was examined under a microscope by **Nicolaas Hartsoeker in 1694** and then, in even greater detail, by **Antoni van Leeuwenhoek in 1704**.
- Leeuwenhoek, backed by **Robert Boyle** and the British Royal Society, surprisingly first described cochineal as seeds in 1685.
- Only after Boyle heard that cochineal may be parts of a fly, he asked Leeuwenhoek to examine the samples again to look for insects.
- During this second investigation, Leeuwenhoek concluded instead that “each tiny grain is a part of a little animal”. The cochineal bits were really "females whose body is full of eggs“.
- While these advances in lens-making technology and investigations into the true identity of cochineal should have cleared up the mystery, the mystery persisted throughout most of the eighteenth century. Faulty communication and skepticism led to doubts for centuries.

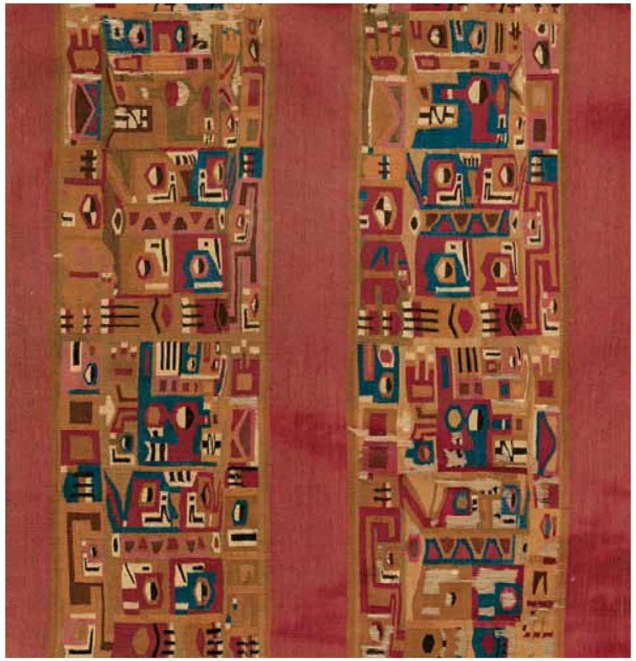


Nicolaas Hartsoeker’s representation and description of cochineal under a microscope. *Essay de Dioptrique* (Paris, 1694), sect. I, p. 52

3) Spanish monopoly

- With such a powerful and profitable new colorant, the Spanish were determined to keep their stronghold on cochineal.
- They also prohibited the export of live cochineal from Mexico, censored information about it, and forbade foreigners from traveling to their colonies.
- For three centuries, the English, French, and Dutch resorted to espionage, piracy, bribery, and theft to learn the secret of this fabulous dye and break Spain's monopoly, to no avail.
- The Spanish also encouraged the confusion about what cochineal was and did not spread information about the delicate environment required to cultivate them.

33. Tunic. Peru, Moche-Wari, 7th–9th century. Cotton and camelid hair colored with cochineal red and other dyes, in interlocking warps and wefts, with tapestry and openwork border; 34¼ x 58 in. (87 x 147.3 cm). The Metropolitan Museum of Art, Bequest of Jane Costello Goldberg, from the Collection of Arnold I. Goldberg, 1986 (1987.394.706)



34. Tunic fragment (detail). Peru, Wari, 7th–9th century. Tapestry-weave cotton and cochineal-dyed camelid hair, 22½ x 80 in. (57.2 x 203.2 cm). The Metropolitan Museum of Art, Gift of George D. Pratt, 1930 (30.16.1)

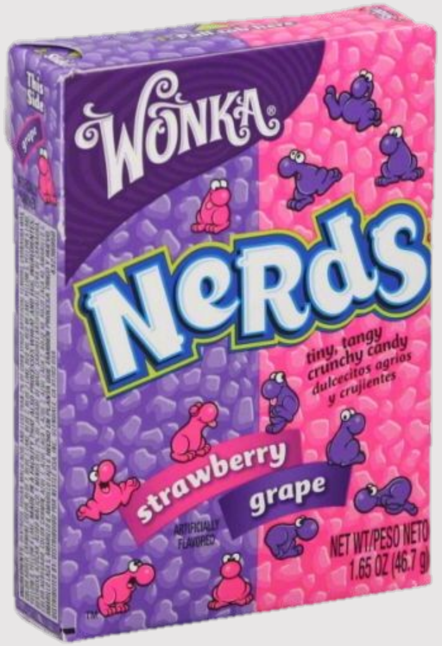
20

Cochineal industry today

- “Carmine” (natural red #3), as cochineal colorant is known to consumers, is present in numerous foods, candies, and cosmetics: grapefruit juice, strawberry yogurt, lipstick, blush, paint, and decorative home items.
- The ancient industry has seen a recent economic revival in South and Central America where cochineal insects are native. Today, Peru exports the most of the dye; the country produces close to 200 tons of it each year.
- Nearly 70,000 insects are used to make one pound of dye.
- Cochineal is the only natural red food coloring authorized by the FDA.

Azithromycin
https://www.drugs.com/imprints/93-7169-13643.html

http://lorealparisusa.com



Cochineal industry today

- Cochineal insects thrive on the prickly pear cactus.
- Rather than going into the field each day to harvest cochineal insects, workers simply collect the cactus leaves they live on.
- They then store the leaves inside a greenhouse, where the bugs can continue to thrive.
- The insects burrow into the cactus where they feed for life.
- Workers use tough brushes to scrape the insects off the cacti leaves – just like in the 16th century.

Brodwin, Erin. “These Crazy Pictures Show How Companies Use Bugs To Make Red Dye For Food And Cosmetics.” *Business Insider*, Business Insider, 27 Oct. 2014, www.businessinsider.com/how-farmers-make-red-dye-from-bugs-2014-10
Baranyovits, F.l.c. “Cochineal Carmine: an Ancient Dye with a Modern Role.” *Endeavour*, vol. 2, no. 2, 1978, pp. 85–92., doi:10.1016/0160-9327(78)90061-3.

Memorial de Don Gonfalo Gomez de Cervantes def modo de vivir que tienen los indos, y def henejicio de las minas de la plata, y de la cochinella./Relaci6n de [lo] que toca la grana cochinilla (Mexico, 1599), Anonymous Pictorial Manuscript, pp. 98 verso 1-2. British Museum, London (Add. Ms. 13964 [Am2006,Drg.210])

Cochineal

https://www.metmuseum.org/art/collection/search/91678
British (1750-75), silk and wool(uniform for redcoats)

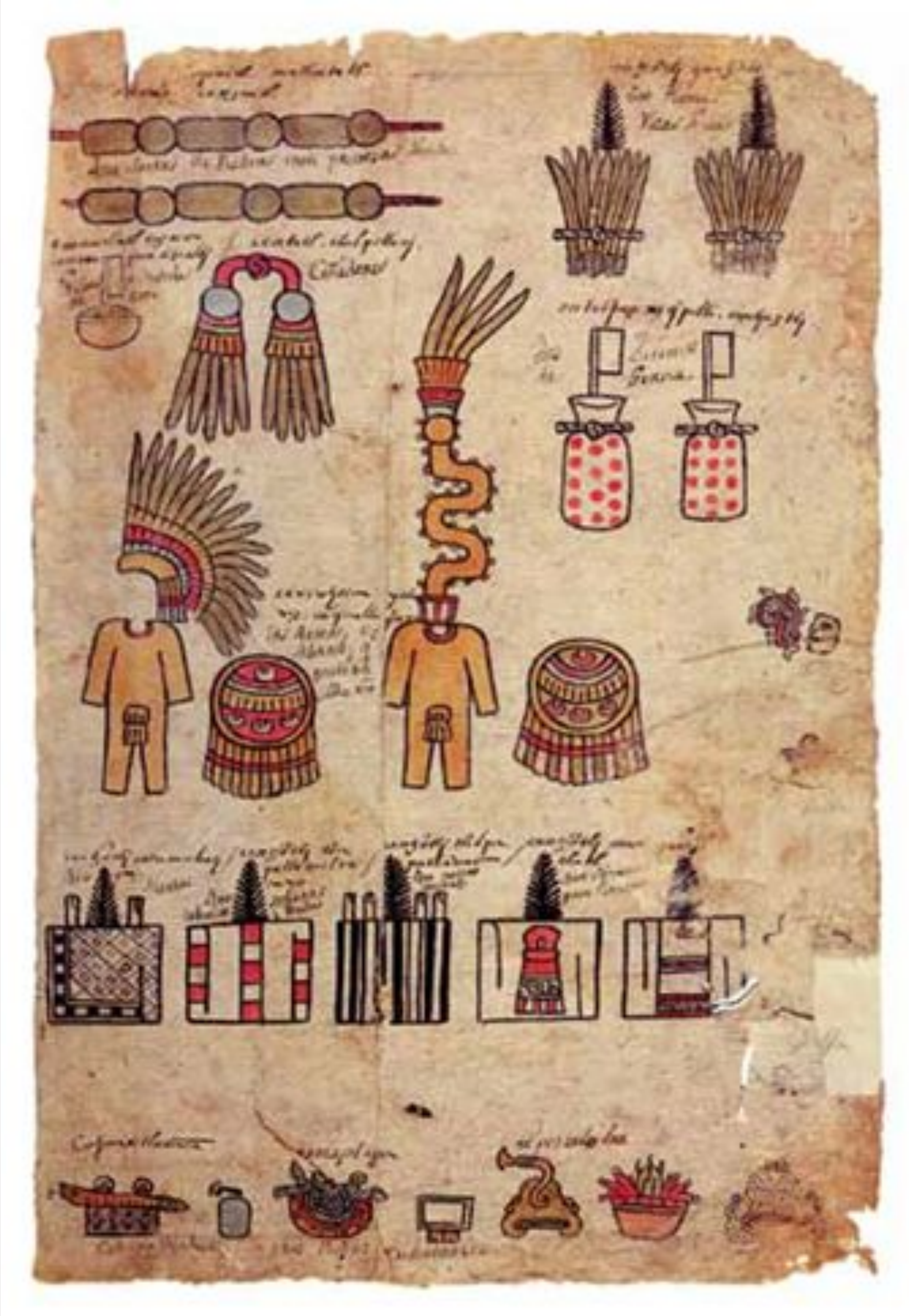
20. Samples of silk cloth dyed with cochineal, showing the many different hues that can be achieved by adding mordants and other modifiers to the dyebath

https://www.metmuseum.org/art/collection/search/320804
Peruvian (ca. 16th-17th century), camelid hair and cotton

https://www.metmuseum.org/art/collection/search/452823
Turkish (ca. 1819-20), silk, metal wrapped thread

Cochineal

The Virgin and Child with a Pomegranate, ~1480-1500
https://www.nationalgallery.org.uk/paintings/workshop-of-sandro-botticelli-the-virgin-and-child-with-a-pomegranate



Matricula de tributos, early 16th-century, Mexico codex
Biblioteca Nacional de Antropologia y Historia (Codex 35-52)

Shoes, 1888, Vincent van Gogh
https://www.metmuseum.org/art/collection/search/436533

Two Tax-Gatherers, 1540s
https://www.nationalgallery.org.uk/paintings/workshop-of-marinus-van-reymerswale-two-tax-gatherers

Lake pigments

https://travelingscriptorium.library.yale.edu/inks-and-pigments/

Natural colorants - Lakes

- **Lake pigments**: in general, pigments prepared from soluble natural colorants, formed by precipitating (or adsorbing) the dye onto a colorless or white, insoluble, relatively inert substrate.
- This is traditionally a form of amorphous hydrated alumina, which can bind the colorant through complexation with aluminum, a process analogous to mordant dyeing of textiles.
- As most natural colorants are soluble, they cannot be mixed directly with a binding medium and therefore cannot be used as a pigment.
- The red colorants most commonly used for lake pigments are the plant dyes madder, brazilwood and sap pan wood, and the insect dyes lac, kermes, and cochineal.
- However, the final color, and the composition of the substrate, can vary depending on the recipe, which will also influence the physical characteristics of the pigment such as transparency or working properties.

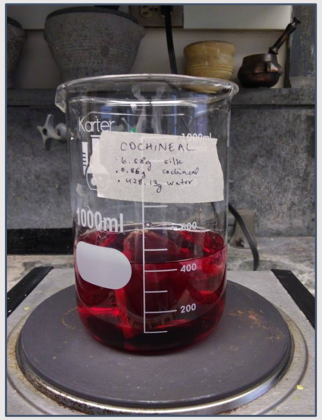
Jo Kirby et al, *Natural Colorants for Dyeing and Lake Pigments: Practical Recipes and their Historical Sources* (Archetype, London, 2014)

Lake – a few other helpful definitions

- **An organic pigment prepared by precipitation of a dye on a powdered, inorganic substrate. Because of its transparency, alumina trihydrate, is the most commonly used substrate or carrier.** Baryte (barium sulfate), produces an opaque lake pigment. Other compounds used as carriers are: chalk, clay, gypsum, zinc oxide, white earth, and green earth. Often a mordant, such as tannic acid, lactic acid, or sodium phosphate, is used to fix the dye to the substrate. Many natural dyes were made into lake pigments, such as cochineal, kermes, madder, and lac for use in oil painting. Some modern synthetic dyes, such as aniline dyes, are also prepared in this manner for use as paint pigments. Lake pigments are used in painting, printing inks, plastic colorants, and coated fabrics. –http://cameo.mfa.org/wiki/Lake
- General term for numerous oil-soluble **organic pigments that are prepared by the precipitation of a dye on an absorptive powdered, inorganic substrate**; alumina trihydrate is most often used as the substrate because of its transparency. All pigments invented in relatively early periods and made in this way are still called "lakes." – http://www.getty.edu/vow/AATFullDisplay?find=lake&logic=AND&note=&english=N&prev_page=1&subjectid=300014015

Preparing and Using Organic Pigments

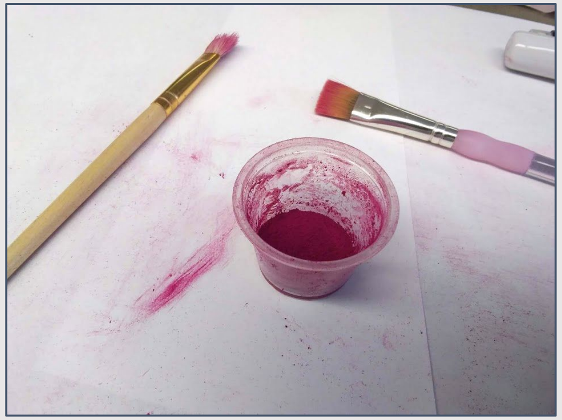
Crush dried cochineal



Extract

Precipitate

Filter and wash



Pigment

Paint

Recipe Example: Making Pigment from Cochineal

Another sort of fine lake. Take 12 grains of powdered cochineal or fine grana, add to it 2oz of ley; leave the infusion for about 2 hours; strain it through a linen cloth and put it over hot cinders; When it boils add to it pulverized roche alum of the size of 2 peas then the ley will make a thick red scum; as soon as this happens throw it all onto a stretched linen cloth, when the clear ley will pass through leaving the coagulum on the cloth, which coagulum must afterwards be dried and made into tablets.

"Paduan Manuscript," (anonymous, Venice, late 16th-17th century)

Mary P. Merrifield, *Medieval and Renaissance Treatises on the Arts of Painting: Original Texts with English Translations* (1849, Dover Publications, 1969), p. 702.

Recipe Example: Making Pigment from Cochineal

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Recipe Example: Making Pigment from Cochineal

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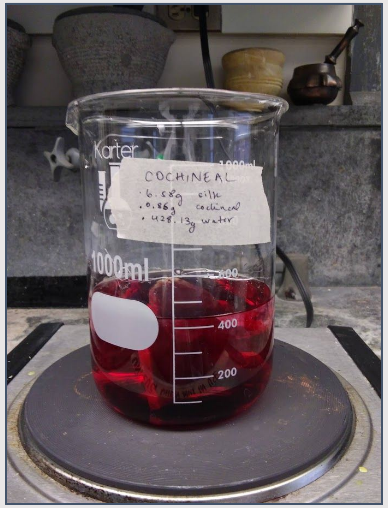

“Paduan Manuscript,” (anonymous, Venice, late 16th-17th century)
Mary P. Merrifield, *Medieval and Renaissance Treatises on the Arts of Painting: Original Texts with English Translations* (1849, Dover Publications, 1969), p. 702.

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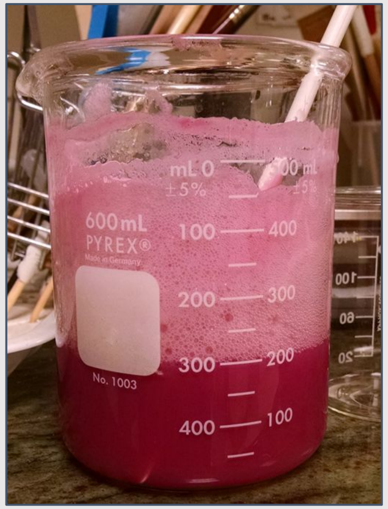

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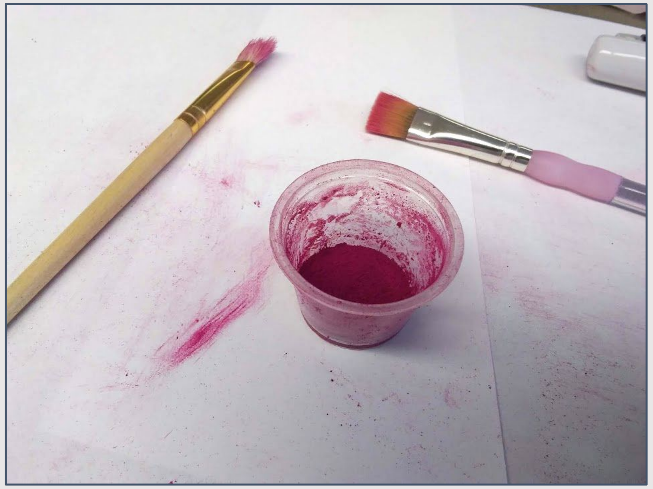

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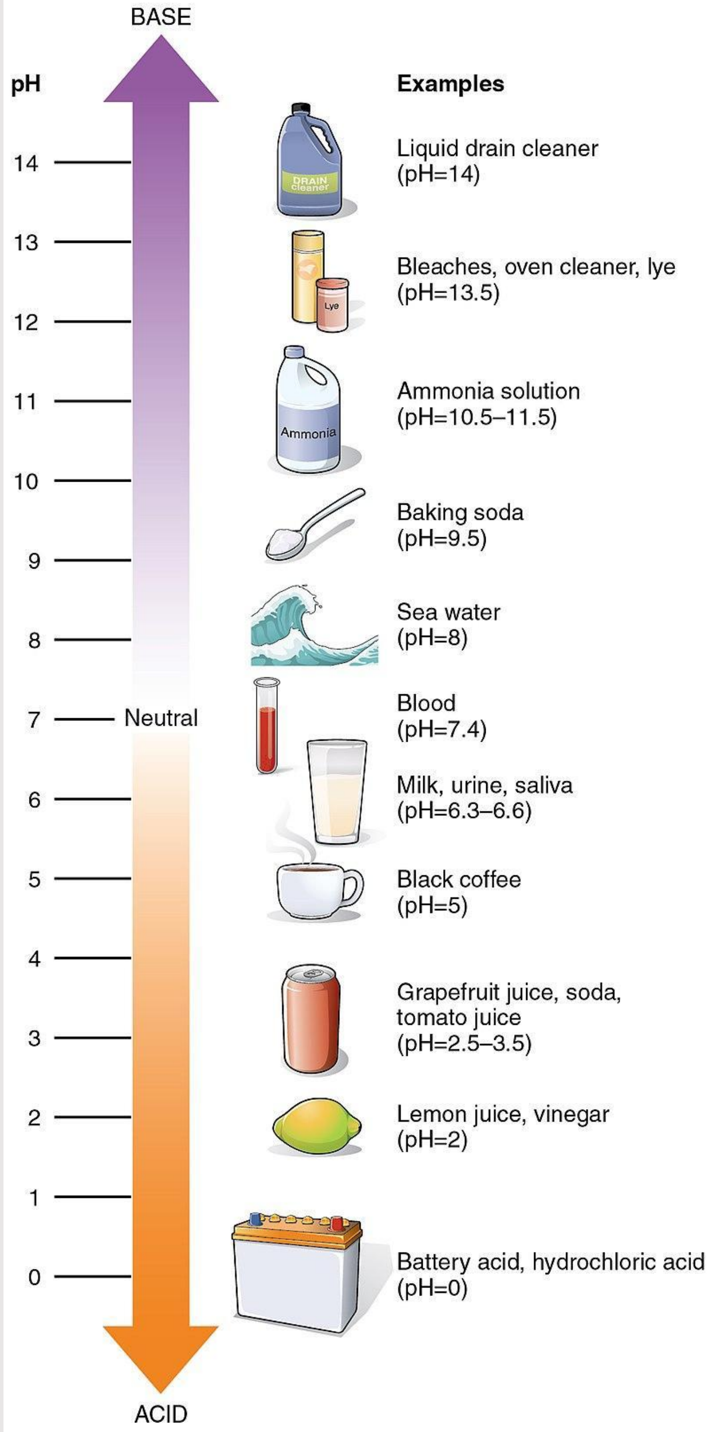
Chemistry



Overview of pH

pH is a numerical scale from 0 to 14 that describes the relative acidity or alkalinity of a solution

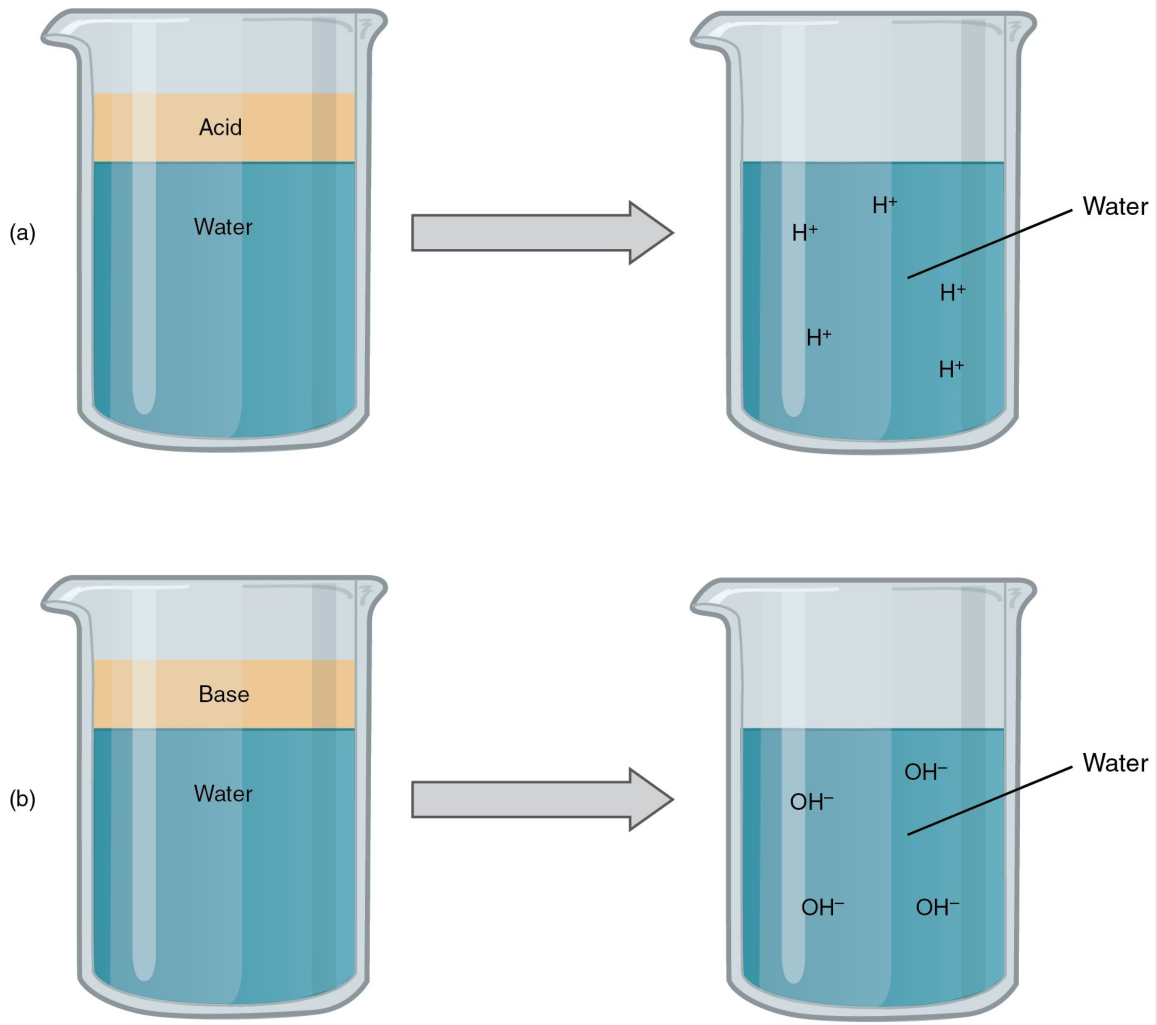
ACID

Donates a hydron (proton or hydrogen ion H^+)

BASE/ALKALI

Releases hydroxide (OH^-) ions.

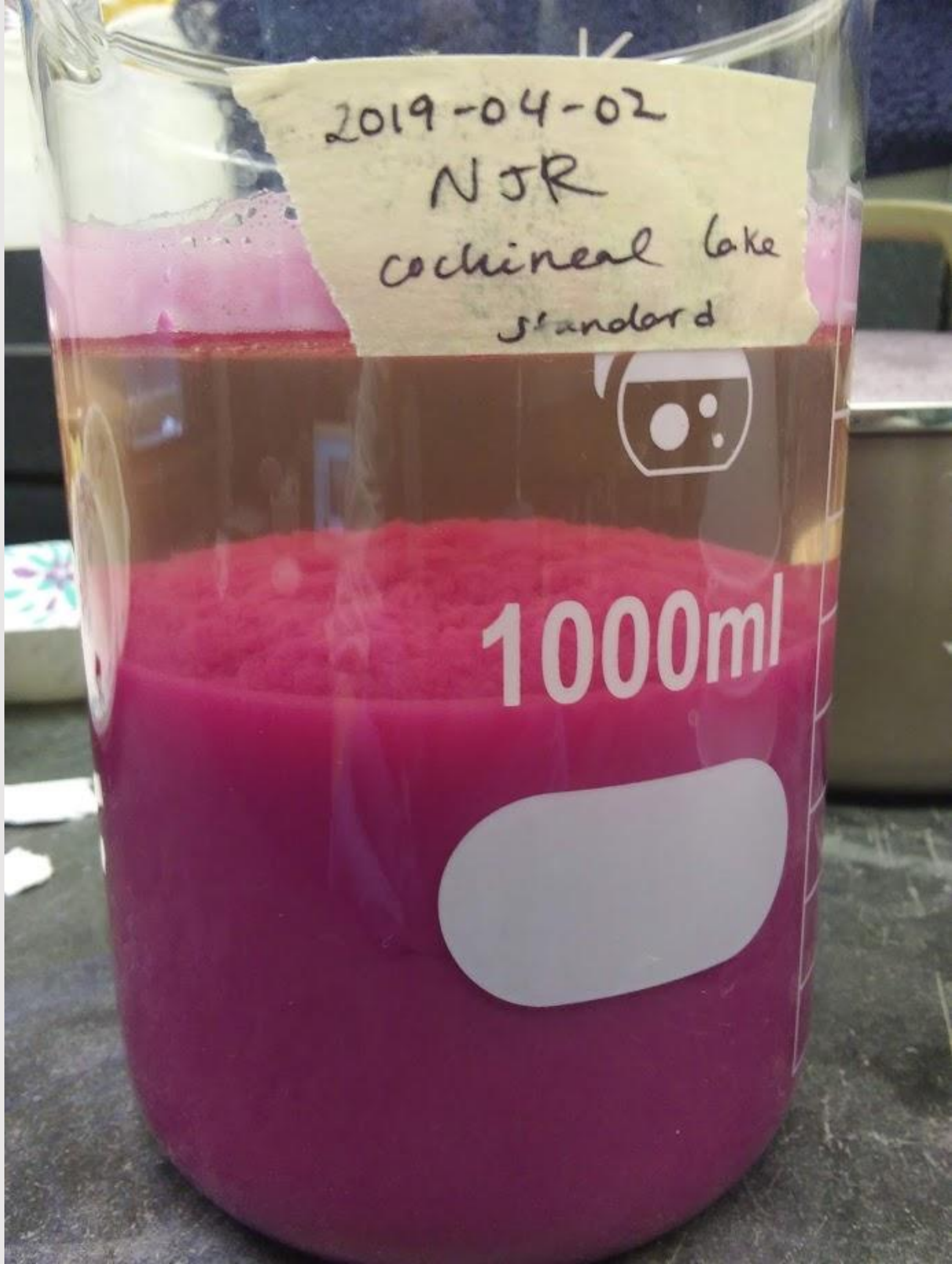
Many times the terms "base" and "alkali" (or basic and alkaline) are used interchangeably.
More precisely, an alkali is a base that can be dissolved in water.



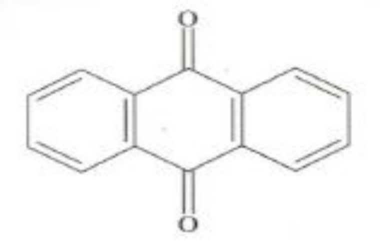
https://cnx.org/contents/FPtK1zmh@6.27:5ORVCb_A@3/Inorganic-Compounds-Essential-

Lake – Process 1

- Earlier recipes, used for most lakes at least until the beginning of the eighteenth century.
- **The dye is extracted into an alkaline solution, usually potash** (while heating).
- The dye solution is then filtered to remove any remnants of the dyestuff source. **Alum is added to the dyestuff solution**.
- It reacts with the alkali to **produce an amorphous hydrated alumina substrate** which precipitates together with the dyestuff, forming the pigment.
- The sulphate remains in solution as the potassium salt, and the pigment is retrieved by filtering.



Cochineal



Species name: *Dactylopius coccus*

Chemical class: carminic acid (anthraquinone)

Region: Cultivated in Mexico and Peruvian Andes, before Spain brought to Europe in 1523 where it spread rapidly.

Dye type: Mordant dye.

http://www.projectnoah.org/spottings/1136866002

Scale insect found on prickly pear or Barbary fig cactus *(Opuntia ficusindica* (L.)).

Dye is extracted from females with unhatched eggs.

Carminic acid $C_{22}H_{20}O_{13}$

A bright red or dark purple brown powder. **Carminic acid is the primary colorant in cochineal dyestuff. It is a tricyclic compound that is extracted from the dried insects Coccus cacti with water.** Carminic acid changes colors with acidity. It is a bright red in neutral solutions, below pH 4.8, it is yellow and above 6.2, it is a deep violet color. Carminic acid is used as a lake pigment for oil colors, as a red dye for photography and as a textile colorant.

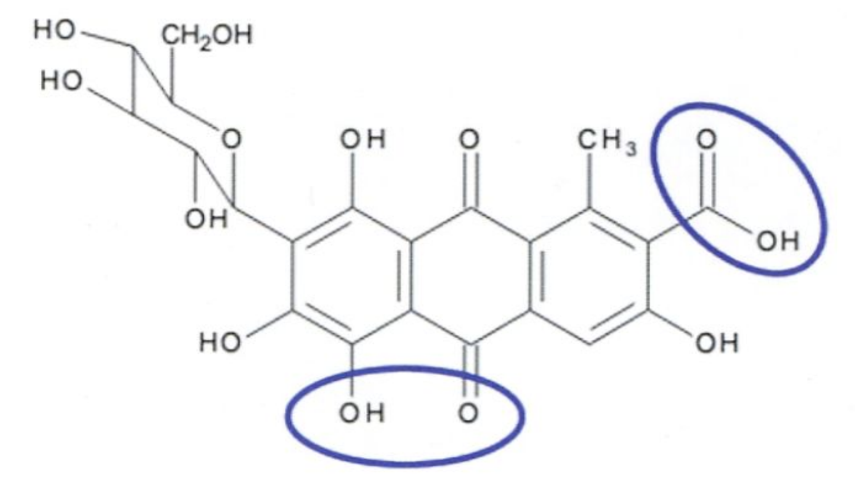
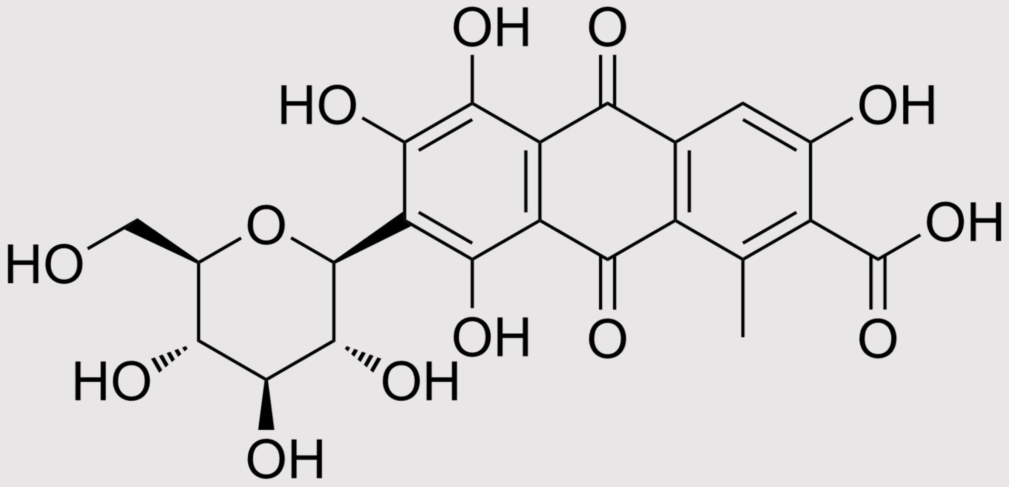


Figure 9 Possible positions for coordination with aluminium ions in the formation of aluminium-containing carmine.

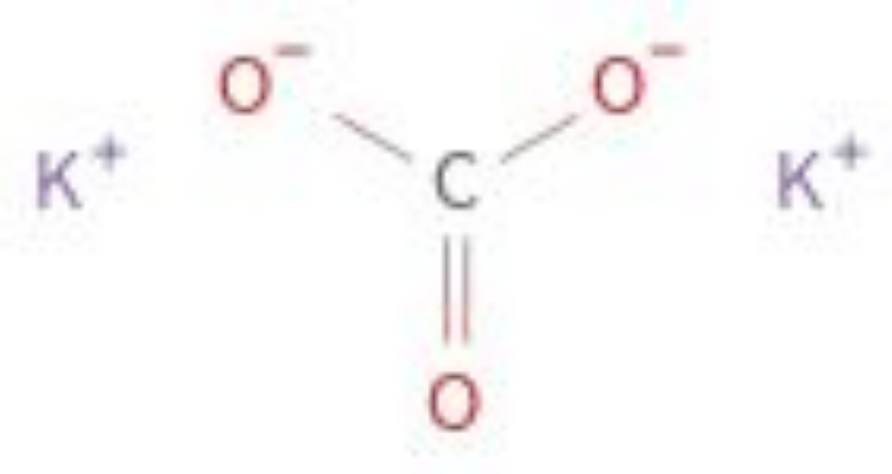


http://cameo.mfa.org/wiki/Carminic_acid

Potash = Potassium carbonate K_2CO_3

BASE
pH = 12

White deliquescent powder. **Potassium carbonate is used in the manufacture of glass, ceramics, smalt, and soap. It is also used in printing inks, process engraving, and lithography and in tanning and finishing leather.** In a closed environment, a saturated solution of potassium carbonate will form an equilibrium at a relative humidity of about 44% (20C).



Addition of potash to dye baths in based on historical examples. It can result in:

- Greater solubility of the dyestuff
- A different hue due to a reversible pH change of the dye
- Perhaps a conversion of the dye glycosides (sugars) to the corresponding free dye molecule
- Perhaps conserve the glycosides in the dyestuffs (seen in weld which becomes brighter)

http://cameo.mfa.org/wiki/Potassium_carbonate

Jo Kirby et al, *Natural Colorants for Dyeing and Lake Pigments: Practical Recipes and their Historical Sources* (Archetype, London, 2014)

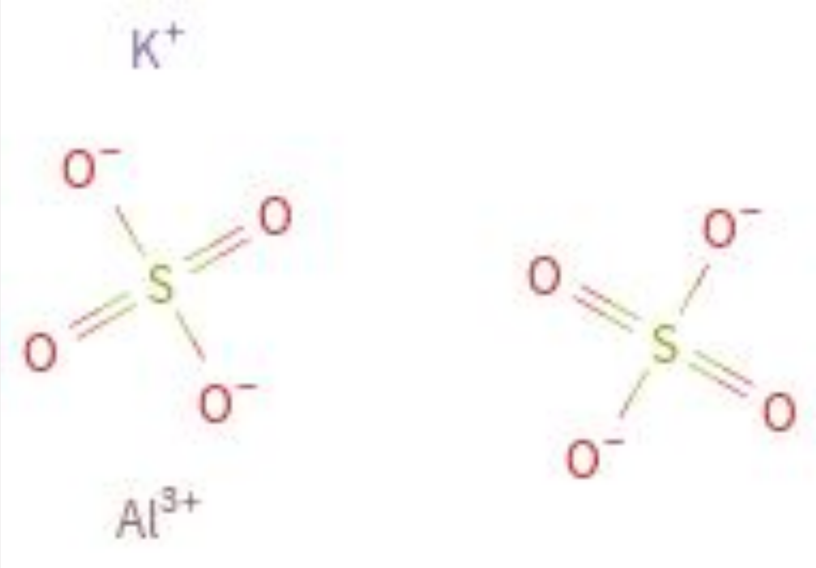
Alum = Aluminum potassium sulfate

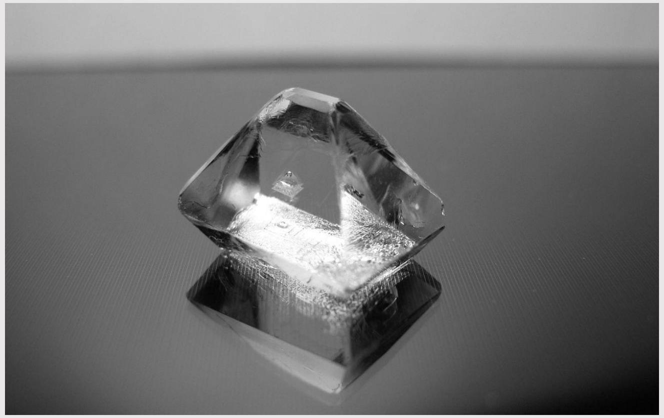
$KAl(SO_4)_2 \cdot 12H_2O$

ACID
pH = 3

Also often called "potash alum"
(NOT to be confused with "potash")

A white odorless powder with transparent crystals. Aluminum potassium sulfate occurs naturally in the minerals alunite and leucite. **It has been used since ancient times as a mordant in dyeing textiles and for tawing skins.** Aluminum potassium sulfate, or potash alum, is also used as a filler in paper, cement, and paints. It is used to harden gelatin, plaster, and cement. **Potash alum has also been used as a substrate in the preparation of lake pigments.**

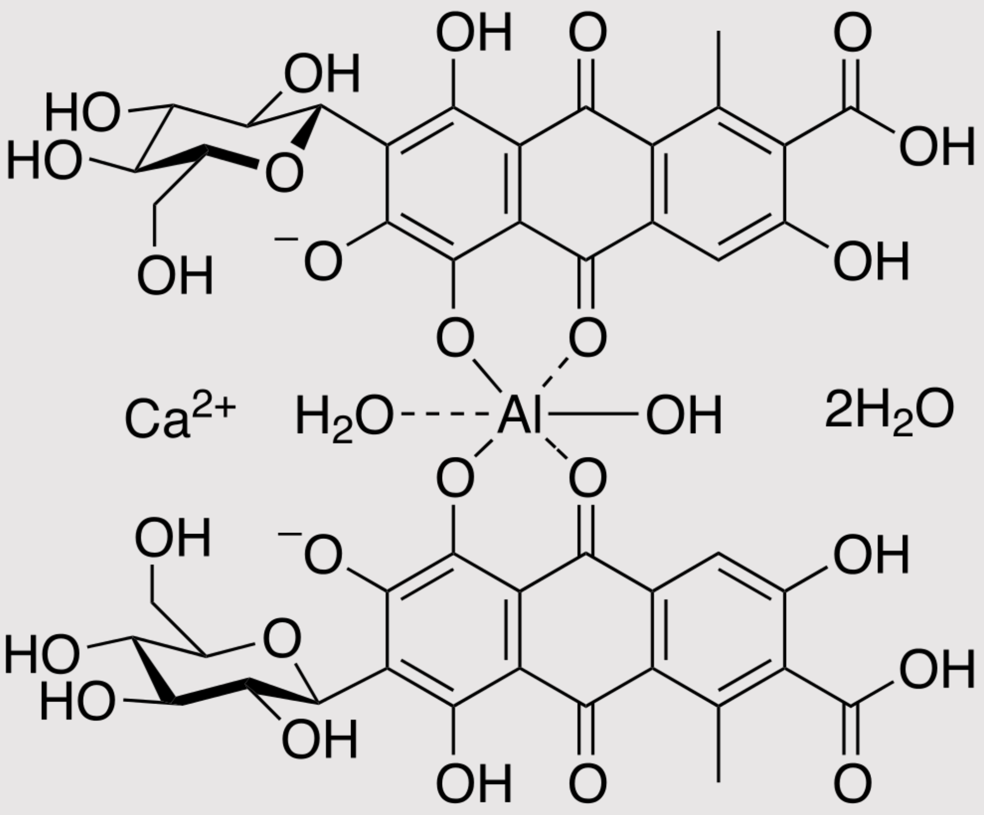




http://cameo.mfa.org/wiki/Aluminum_potassium_sulfate

Carmine

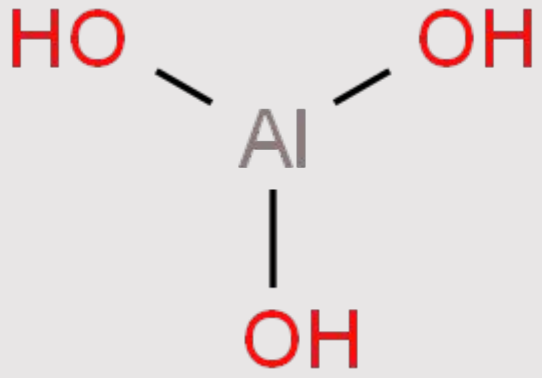
A generic name for two closely related organic red lakes that are obtained from scale insects, cochineal and kermes. Carmine lake first referred to kermes, one of the oldest organic colorant, which is rarely encountered today. Kermesic acid is extracted with alkali from the kermes scale insect and precipitated on an iron-free alum to produce carmine. The name for a kermes lake changed to crimson lake after cochineal, found in Mexico, was brought to Europe in the late 16th century. **Carminic acid is extract from the cochineal insect (Coccus cacti) bodies with an aqueous solution of tartar then precipitated on alumina trihydrate to produce carmine lake.**



http://cameo.mfa.org/wiki/Carmine_lake

Aluminum hydroxide (or alumina trihydrate) $Al(OH)_3$

A white, translucent powder that is also called aluminum hydroxide. Alumina trihydrate is obtained from bauxite. When it is strongly heated, alumina trihydrate will convert to aluminum oxide with the release of water. **Alumina trihydrate is used as a base in the preparation of transparent lake pigments. It is also used as an inert filler in paints and tends to increase the transparency of colors when dispersed in oils.** Alumina trihydrate is used commercially as a paper coating, flame retardant, water repellant, and as a filler in glass, ceramics, inks, detergents, cosmetics, and plastics.



http://cameo.mfa.org/wiki/Alumina_trihydrate

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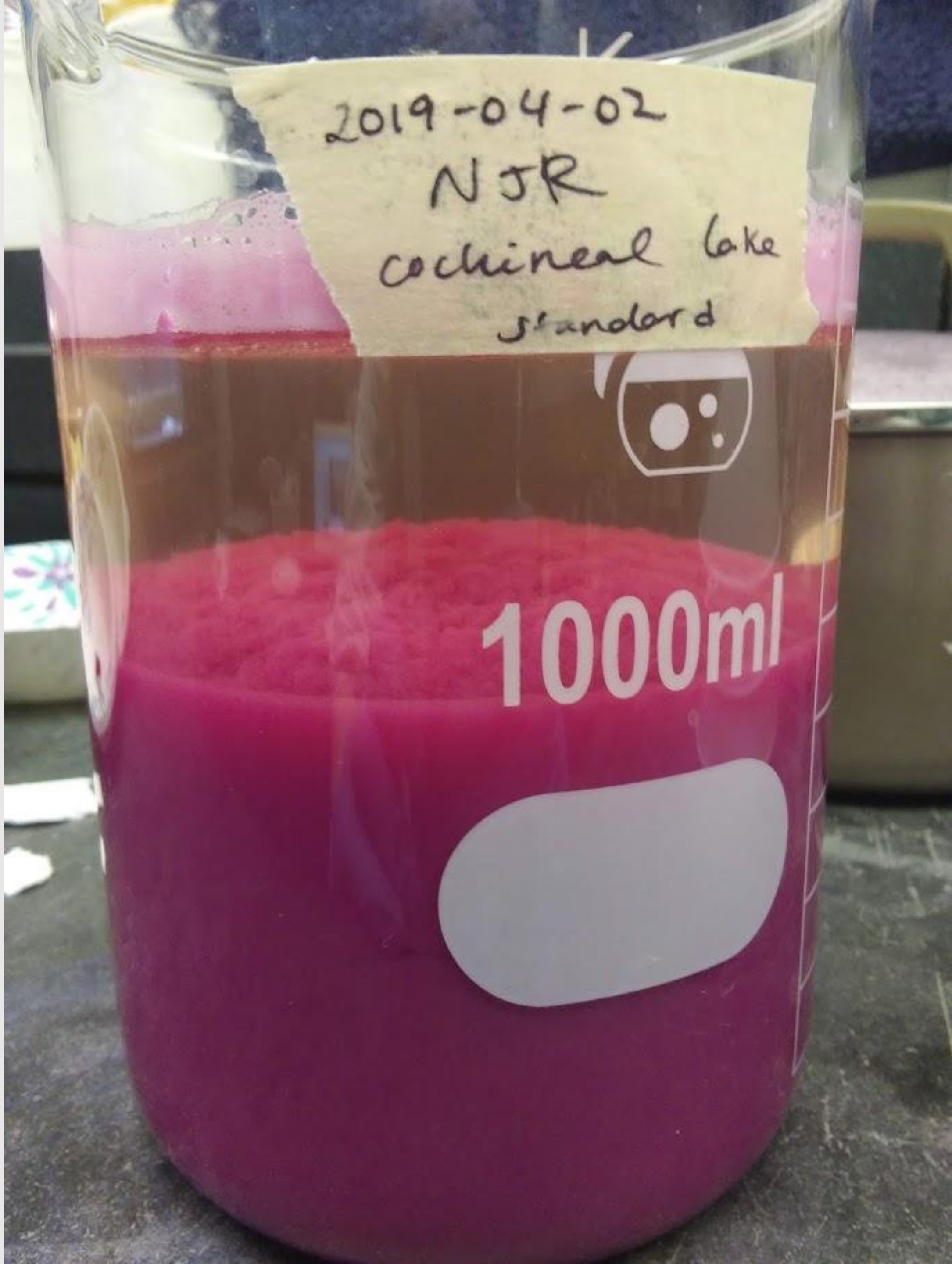
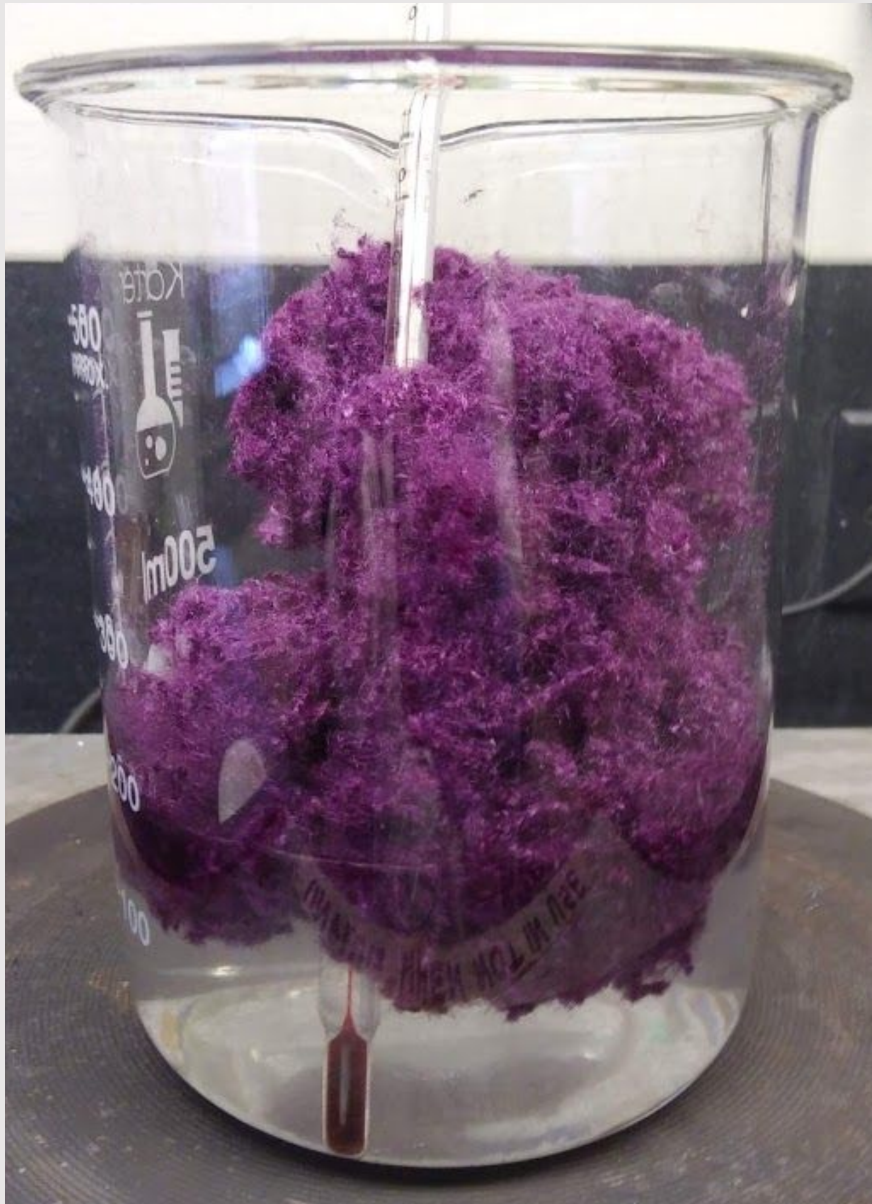


Lake – Process 2

- Recipes more typical of the nineteenth century and onwards.
- **The substrate is made by the reverse sequence, adding alkali to an alum solution that contains the dyestuff.**
- The dyestuff is first extracted with water, the solution is filtered and then alum is added.
- This **forms a complex with the colorant via the neighbouring hydroxyl groups** present on the organic colorant. It is still soluble; **precipitation occurs when the acidic solution is neutralized by means of the slow addition of an alkali or base**, which again might be potassium carbonate solution.
- The composition of this pigment is slightly different to the first type. It is similar to **the 'light alumina hydrate'** described in modern paint technology literature, with the most evident difference being that sulphate anions become incorporated into the substrate as it precipitates

Lake from raw material vs. dyed cloth - Thoughts about why?

- For kermes, cochineal and madder lakes, the recipes and analyses of pigments in paintings suggest that **from the fourteenth to the seventeenth century**, at least in Europe, **the dyestuff source was usually shearings of dyed textile**. Kermes or cochineal shearings were generally silk, from which the dye was easily extracted into solution.
- **From the seventeenth century onwards, recipes began to appear for cochineal lake prepared directly from the insect**, and also for cochineal carmine. For this pigment, the aim was to precipitate the dyestuff, predominantly carminic acid (present as a potassium compound in the insect), in the form of a metal salt or complex, with little or no substrate.



KERMES or COCHINEAL

11. To make fine lake.-

Take the ashes of oak, and make a ley, and boil in it clippings of fine scarlet of rubea de grana until the colour is extracted from the clippings, and then strain the ley with the colour through a linen cloth. Afterwards take some more lay, similar to what you first took, and heat it, and put into it some finely powdered roche alum, and let it stand until the alum is dissolved. Then strain it through the strainer with the liquor or ley in which the clippings were put, and immediately the ley will be coagulated, and make a lump or mass, which you must stir well. Remove it afterwards from the vase, and lay it on a new hollow brick, which will absorb the ley, and the lake will be left dry. You must afterwards take it off the brick and keep it for use.

11. Ad faciendum lacham finam.-

Tolle cineres ligni cerri, vel roboris, et fac lecivium, et in ipso fac bulire cimaturam scarlate fine rubee de grana, tantum quod ex dicta cimatura extractus sit color; postea ipsum lessivum, cum dicta cimatura, colla per pannum lineum; postea accipe de alio lexivio simili suprascripti quod prius accepisti, et calefac, et pone in ipso de alumine roche trito subtiliter, et permitte donec alumen sit fusum, postea cum dicto colatorio cola ipsum in dicta alia collatura vel lexivio, in quo stetit cymatura, et subito dictum lessivium stringetur, et faciet unam bussaturam seu massam, quam mistica bene, et postea trahe ipsam de vase, et pone in madono concavo novo, qui bibet lessivium, et remanebit sicca dicta lacha, quam postea trahe de madone et serva usui.

This recipe was taken from *Exprimenta de Coloribus* in the Manuscripts of Jehan Le Bègue which is found in *Original treatises, dating from the XIIth to XVIIIth centuries on the arts of painting, in oil, miniature, mosaic, and on glass; of gilding, dyeing, and the preparation of colours and artificial gems; preceded by a general introduction; with translations,prefaces, and notes.* By Mrs. Merrifield. v. 1, Merrifield, Mary P. (Mary Philadelphia), London, J. Murray, 1849, p. 50.

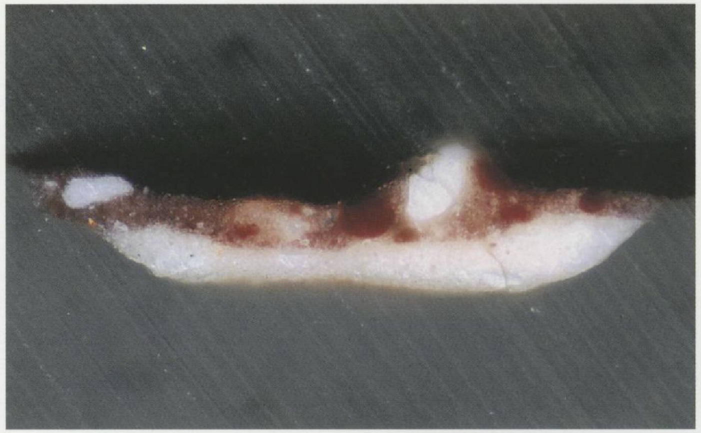
https://travelingscriptorium.files.wordpress.com/2014/06/scopa-recipes-booklet_web-june-2014.pdf

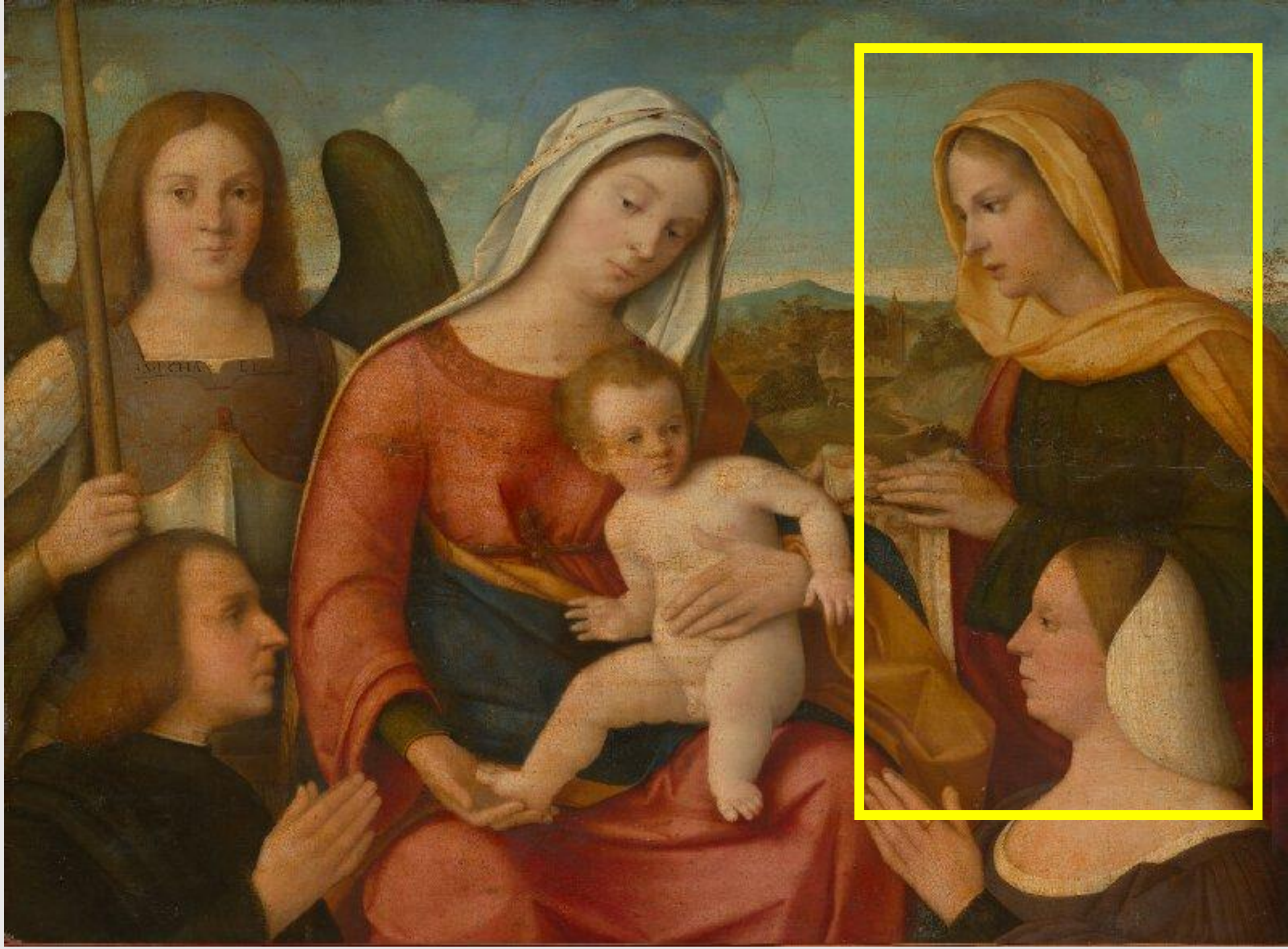
Examples of cochineal lakes in art

An intense cherry-red lake pigment has been used in the Virgin's red dress (plate 1). It contains the dyestuff extracted from the kermes insect, Kermes vermilio Planchon. In the EDX spectrum of the red lake, the largest peak is from aluminium (Al). The FTIR spectrum shows that the substrate is essentially hydrated alumina

The Virgin and Child with a Pomegranate
probably about 1480-1500, Workshop of Sandro Botticelli
https://www.nationalgallery.org.uk/paintings/workshop-of-sandro-botticelli-the-virgin-and-child-with-a-pomegranate

Kermes lake in Francesco Bissolo's Virgin and Child with Saints Michael and Veronica and Two Donors (NG 3083), dating from 1500-25 (plate 2). In a cross-section from Saint Veronica's red cloak in the latter painting.





The Virgin and Child with Saints and Donors
probably 1500-25, Francesco Bissolo
https://www.nationalgallery.org.uk/paintings/francesco-bissolo-the-virgin-and-child-with-saints-and-donors

The upper- most glaze layer of the kneeling king's red brocade cloak in Veronese's Adoration of the Kings (NG 268, 1573. The dyestuff in this case has been identified as perhaps having been extracted from Polish cochineal.

The Adoration of the Kings
1573, Paolo Veronese
https://www.nationalgallery.org.uk/paintings/paolo-veronese-the-adoration-of-the-kings

1) Red sleeve of figure, right; 2) cloth below birds, centre: Mexican cochineal

The Four Elements: Air
1570, Joachim Beuckelaer
https://www.nationalgallery.org.uk/paintings/joachim-beuckelaer-the-four-elements-air

Red of textile: cochineal
(HPLC; probably Mexican).

A Regatta on the Grand Canal
about 1740, Canaletto
https://www.nationalgallery.org.uk/paintings/canaletto-a-regatta-on-the-grand-canal

Servant's red cloak, lower left: Mexican

Rebecca at the Well
1708-13, Giovanni Antonio Pellegrini
https://www.nationalgallery.org.uk/paintings/giovanni-antonio-pellegrini-rebecca-at-the-well

Red of sleeve of left figure: underpaint contains madder lake (HPLC), upper layer contains kermes lake. Madder lake; Al, large S (slightly smaller than Al). FTIR microscopy: the red lake particles contain protein suggesting that the dyestuff has been extracted from wool. Also amorphous hydrated alumina, some calcium carbonate and calcium sulphate.

Two Tax-Gatherers
probably 1540s, Workshop of Marinus van Reymerswale
https://www.nationalgallery.org.uk/paintings/workshop-of-marinus-van-reymerswale-two-tax-gatherers

Mid-brownish red of curtain. Red lake, lead white, vermilion.
HPLC: cochineal

Mrs Siddons
1785, Thomas Gainsborough
https://www.nationalgallery.org.uk/paintings/thomas-gainsborough-mrs-siddons

Cochineal lake pigment was found in the shadow on the inside of the right shoe and on the flooring.

Shoes, 1888
Vincent van Gogh
Accession Number:1992.374
https://www.metmuseum.org/art/collection/search/436533

Resources and References

Sources of historical evidence

- Analysis of existing objects, such as surviving textiles and paintings in museum collections
  - However, it must be kept in mind that these represent only a small part of history. They are items that have been selectively collected by museums or upper class. Many were made for or bought by the elite, were luxury or just generally expensive items
- Recipe books and collections, instruction manuals
- Work orders, inventories, accounts, orders for materials, import records, and guild regulations

References and Links

- Jo Kirby et al, *Natural Colorants for Dyeing and Lake Pigments: Practical Recipes and their Historical Sources* (Archetype Publications, London, 2014)
- Phipps, Elena. *Cochineal Red: the Art History of a Color*. New York (N.Y.: The Metropolitan Museum of Art, 2010. Print.) Full pdf available for free download here: https://www.metmuseum.org/art/metpublications/cochineal_red_the_art_history_of_a_color

- Merrifield, Mary P. *Original Treatises, Dating from the XIIth to XVIIIth Centuries, on the Arts of Painting in Oil, Miniature, Mosaic, and on Glass of Gilding, Dyeing, and the Preparation of Colours and Artificial Gems; Preceded by a General Introd., with Translations, Prefaces, and Notes*. J. Murray, 1849.

- CAMEO: Conservation & Art Materials Encyclopedia Online: http://cameo.mfa.org/wiki/Main_Page
  - CAMEO is a searchable information resource developed by the Museum of Fine Arts, Boston. The MATERIALS database contains chemical, physical, visual, and analytical information on historic and contemporary materials used in the production and conservation of artistic, architectural, archaeological, and anthropological materials.

- http://shop.kremerpigments.com/en/
- https://maiwa.com/pages/natural-dyes

- Greenfield, Amy Butler. *A Perfect Red Empire, Espionage, and the Quest for the Color of Desire*. Harper Perennial, 2006.

- Padilla, Carmella. *Red like No Other - How Cochineal Colored the World*. Rizzoli International Publicat, 2015.

- Cardon, Dominique. *Natural Dyes: Sources, Tradition, Technology and Science*. Archetype, 2007.

- Gettens, Rutherford J., and George L. Stout. *Painting Materials: a Short Encyclopedia*. Dover Publications, 1966.

- Vejar, Kristine. *The Modern Natural Dyer a Comprehensive Guide to Dyeing Silk, Wool, Linen, and Cotton at Home*. Abrams, 2015.

- Short History of Cochineal Red: https://artechne.wp.hum.uu.nl/short-history-of-the-cochineal-red/

- Putting the Red in Redcoats: http://www.history.org/foundation/journal/Summer12_newformat/dye.cfm

- A short introduction (about cochineal): https://medium.com/@zip_lehnus/paint-it-red-cochineal-the-wonder-bug-51d280c41d56

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- Jo Kirby et al, *The Technology of Red Lake Pigment Manufacture: Study of the Dyestuff Substrate* (National Gallery Technical Bulletin, Vol. 26 (2005), pp. 71-87)

- Jo Kirby et al, *The Technology of Eighteenth and Nineteenth Century Red Lake Pigments* (National Gallery Technical Bulletin, Vol. 28 (2007), pp. 69-95)

- https://www.naturalpigments.com/
  - And their very helpful blog postings: https://www.naturalpigments.com/artist-materials/
  - Ancient Pigments and their Identification in Works of Art https://www.naturalpigments.com/artist-materials/cat/natural-pigments-supplies/post/ancient-historical-pigments/
  - Traditional Oil Painting: The Revival of Historical Artists' Materials https://www.naturalpigments.com/artist-materials/cat/natural-pigments-supplies/post/traditional-oil-painting-revival/

- https://travelingscriptorium.library.yale.edu/
  - See blog posts as well as resources on inks and pigments: https://travelingscriptorium.library.yale.edu/inks-and-pigments/
  - https://travelingscriptorium.files.wordpress.com/2012/03/scopa-pigment-swatches_web.pdf

Popular articles

- Yardley, Jim. “Bangladesh Pollution, Told in Colors and Smells.” *The New York Times*, The New York Times, 15 July 2013, www.nytimes.com/2013/07/15/world/asia/bangladesh-pollution-told-in-colors-and-smells.html.
- “A Monstrous Mess: Toxic Water Pollution in China.” *Greenpeace International*, www.greenpeace.org/international/story/6846/a-monstrous-mess-toxic-water-pollution-in-china/.
- “These Truly Organic Bed Sheets Are Made With Cotton, Rainwater and Wind.” *Interesting Engineering*, 10 Mar. 2018, https://interestingengineering.com/organic-bed-sheets-cotton-rainwater-and-wind.
- “Wear The Change You Want To See In The World.” *Ayo*, https://madebyayo.shop/blogs/let-s-go-ayo/wear-the-change-you-want-to-see-in-the-world.
- “Dye Industry.” *:: WorstPolluted.org : Reports*, www.worstpolluted.org/projects_reports/display/105
- www.fibre2fashion.com. “Indian Dyes & Dye Intermediates Future, Indian Dyestuff Industry, Indian Dyes Sector Growth, Indian Dyestuffs.” *Fibre2Fashion*, www.fibre2fashion.com/industry-article/5118/the-future-of-indian-dyes-and-dye-intermediates?page=1.
- “Environmental Pollution Control in Textile Industry.” *Fashion2Apparel*, http://fashion2apparel.blogspot.com/2017/08/environmental-pollution-control-textile.html.
- “The Case for Natural Dyes.” *Avani E-Store*, https://avani-earthcraft.com/blogs/blog/the-case-for-natural-dyes.
- Todd, Elliot. “Reflections on the Journey of Fashion and Sustainability.” *Centre for Sustainable Fashion*, 22 May 2018, http://sustainable-fashion.com/blog/reflections-on-the-journey-of-fashion-and-sustainability/.
- “Gujarat's Troubling Environmental Record.” *USAPP*, 6 Dec. 2016, http://blogs.lse.ac.uk/southasia/2014/04/04/gujarats-troubling-environmental-record/.
- “V&A · Fashioned from Nature.” *Introduction to 20th-Century Fashion*, Victoria and Albert Museum, Cromwell Road, South Kensington, London SW7 2RL. Telephone +44 (0)20 7942 2000. Email Vanda@Vam.ac.uk, www.vam.ac.uk/exhibitions/fashioned-from-nature.
- Kimani, Natalie. “Dye Off: Natural vs. Synthetic.” *The Designers Studio*, 19 Nov. 2016, http://tdsblog.com/dye-off-natural-vs-synthetic/.