



DYEING AND PAINTING WITH NATURE:  
THE CHEMISTRY OF COCHINEAL  
**LAKE PIGMENTS**

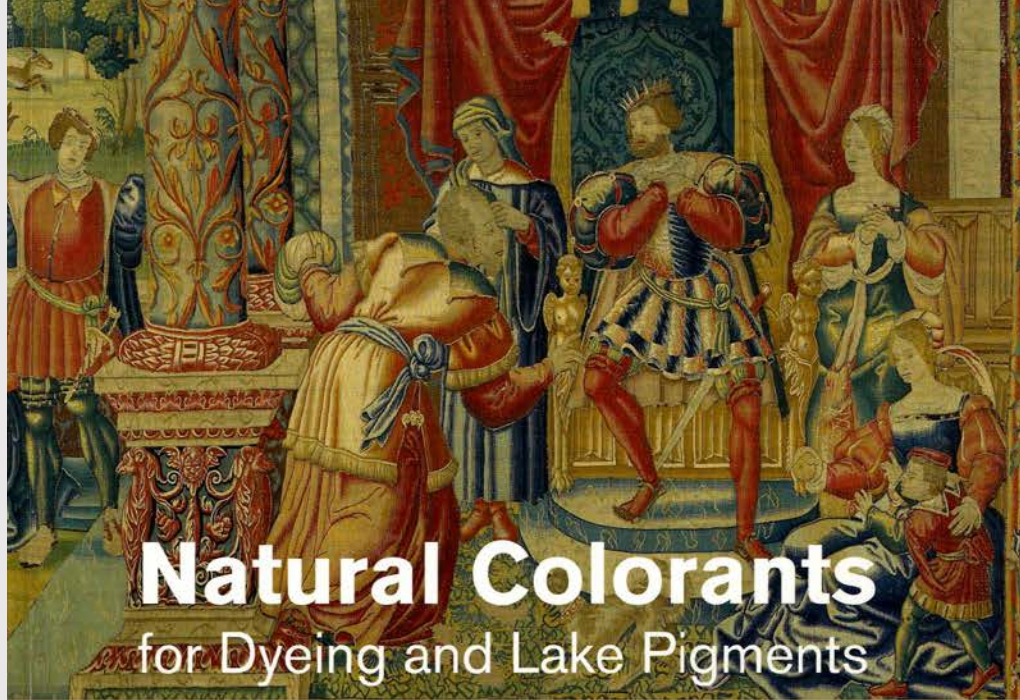
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Naomi Rosenkranz

[naomi.Rosenkranz@gmail.com](mailto:naomi.Rosenkranz@gmail.com)

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# Natural Colorants for Dyeing and Lake Pigments

PRACTICAL RECIPES AND THEIR HISTORICAL SOURCES



Avery-LC  
TT  
854.3  
.K57  
2014g

Jo Kirby, Maarten van Bommel and André Verhecken



# Pigment

- An insoluble, dry solid that is pulverized to a fine powder then mixed with a binder to form a paint, ink or crayon.



# Pigment

- Examples of inorganic pigments:
  - earth colors (ocher, sienna, umber, green earth);
  - metallic oxide (ferric oxide, titanium dioxide, zinc white; viridian);
  - metallic carbonates (lead white, calcite, malachite);
  - metallic chromates (lead chromate; barium chromate);
  - carbon black (bone black, lampblack, graphite)
- Examples of some organic pigments are:
  - animal (melanin, cochineal, Indian yellow)
  - vegetable (madder, indigo, gamboge)
  - synthetic (verdigris, phthalocyanine, lakes, para red)



806 GOLD  
308 P. RED  
310 P. ROSE

804 SILVER  
306 SCARLET  
312 ROSE  
MADDER

808 COPPER  
304 VERMILION  
314 CARMINE

101 TITANIUM N  
302 ORANGE  
316 SPEAR  
ROSE

802 PEARL W  
208 BRIGHT Y  
318 COLD  
PINK

702 FRENCH G  
210 NAPLES Y  
402 P. VIOLET

706 IVORY B  
206 INDIAN Y  
404 VIOLET

202 CITRON Y  
204 P. YELLOW  
406 CYAN



506 VIRIDIAN  
508 HOOKERS  
620 V. DYKE  
BROWN

504 Phtalo  
510 CAD G. LIGHT  
618 B. UMBER

502 MALACHITE  
512 LEON G.  
614 R. BROWN

414 P. LIGHT B  
514 Y. GREEN  
612 L. RED  
OCHRE

412 PRUSSIAN B  
512 OLIVE G  
610 R. SIENNA

704 INDIGO  
514 Y. GREEN  
608 B. SIENNA

410 ULTRA  
520 G. GREY  
606 OLIVE B

408 COBALT B  
602 Y. OCHRE  
604 R. UMBER



# Reds mineral



BURGUNDY RED OCHRE DEEP, FRANCE (KREMER PIGMENTS 11577)



RED IRON OXIDE, NATURAL, HEMATITE (KREMER PIGMENTS 48600)



SPANISH RED OCHRE, CASTILLE (KREMER PIGMENTS 11584)



RED BOILE, NATURAL RED EARTH FROM GERMANY (KREMER PIGMENTS 40503)

## RED OCHRE

Red iron oxide  
Indian red  
Venetian red  
Spanish red  
Red chalk  
Bole

## RED OCHRE

## RED OCHRE

## RED BOLE

Bole  
Bolus  
Armenian bole

# Reds mineral



RED LEAD, MINIUM (KREMER PIGMENTS 42500)



CINNABAR, MONTE AMIATA, ITALY (KREMER PIGMENTS 10610)



CINNABAR FINE, CHINA (KREMER PIGMENTS 10625)



## MINIUM

Red lead  
Orange lead  
Lead oxide red  
Saturn red  
Lead tetroxide

## CINNABAR

Mercuric sulfide  
Vermilion (synthetic)  
English Vermilion

## CINNABAR

# Reds organic



KREMER PIGMENTS 36040 (INSECTS)



KREMER PIGMENTS 36040 (GROUND)

## COCHINEAL INSECTS

Coccus cacti



CLOTHLET RECIPE C-1



CLOTHLET RECIPE C-3



## COCHINEAL

Carmine  
Crimson lake  
Grana  
Scarlet lake  
Purple lake

## DRAGON'S BLOOD

Sanguis draconis



DRAGON'S BLOOD, RESINA DRACAENA, SUMATRA (KREMER PIGMENTS 37000)



# Reds organic



KREMER PIGMENTS 37199 (PIECES)



KREMER PIGMENTS 37201 (GROUND)

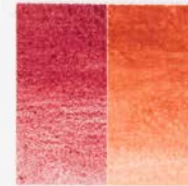
## MADDER ROOT



KREMER PIGMENTS 37202



RECIPE M-1



37202 M-1

## MADDER LAKE

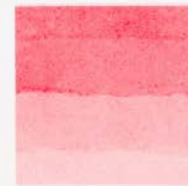
Rubia tinctorum  
Rose madder  
Garancine  
Dyer's root



KREMER PIGMENTS 36150 (PIECES)



CLOTHLET RECIPE B-1



## BRAZILWOOD

Bresilwood  
Bresill  
Pernambucco wood  
Verzino



RECIPE B-2



RECIPE B-3



B-2 B-3

## BRAZILWOOD LAKE



# Pigment

- Any relatively insoluble organic, inorganic, natural or artificial substance that imparts a color to another substance or mixture and always appears as the same specific color when viewed in white light.
- It is the constituent of paint or ink that provides the color.
- Distinguished from a dye, which is soluble in the vehicle, a pigment is insoluble in the vehicle, but instead is held in a suspension.





# Paint

- Any dispersion of pigment in a liquid binder. Paint is applied with a brush, roller, sprayer, or by dipping and dries to form a decorative or protective film.

[http://www.getty.edu/vow/AATFullDisplay?find=paint&logic=AND&note=&english=N&prev\\_page=2&subjectid=300015029](http://www.getty.edu/vow/AATFullDisplay?find=paint&logic=AND&note=&english=N&prev_page=2&subjectid=300015029)



- A liquid mixture composed of a colorant dispersed in a binder. Paint dries to form a decorative or protective film. It can be applied with a brush, roller, sprayer, or by dipping.

<http://cameo.mfa.org/wiki/Paint>



Pigment

+

Binding media



=



Paint



Lake pigments

# Lake

- **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.



# 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."

# Reds organic



KREMER PIGMENTS 36040 (INSECTS)



KREMER PIGMENTS 36040 (GROUND)

## COCHINEAL INSECTS

Coccus cacti



CLOTHLET RECIPE C-1



CLOTHLET RECIPE C-3



## COCHINEAL

Carmine  
Crimson lake  
Grana  
Scarlet lake  
Purple lake

## DRAGON'S BLOOD

Sanguis draconis



DRAGON'S BLOOD, RESINA DRACAENA, SUMATRA (KREMER PIGMENTS 37000)



# Reds organic



KREMER PIGMENTS 37199 (PIECES)



KREMER PIGMENTS 37201 (GROUND)

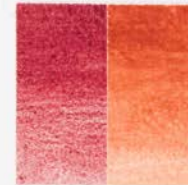
## MADDER ROOT



KREMER PIGMENTS 37202



RECIPE M-1



37202 M-1

## MADDER LAKE

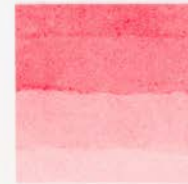
Rubia tinctorum  
Rose madder  
Garancine  
Dyer's root



KREMER PIGMENTS 36150 (PIECES)



CLOTHLET RECIPE B-1



## BRAZILWOOD

Bresilwood  
Bresill  
Pernambucco wood  
Verzino



RECIPE B-2



RECIPE B-3



B-2 B-3

## BRAZILWOOD LAKE

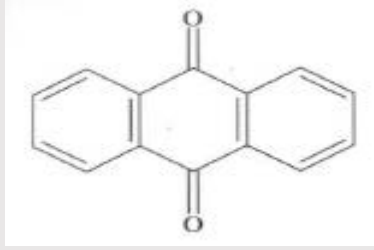


# Natural colorants - Lakes

- **As most natural colorants are soluble, they cannot be mixed directly with a binding medium and therefore cannot be used as a pigment.**
- In general, pigments prepared from soluble natural colorants, known as lakes, are formed by precipitating (or adsorbing) the dye onto a colourless or white, insoluble, relatively inert substrate. This is traditionally a form of amorphous hydrated alumina, which can bind the colorant through complexation with aluminium, a process analogous to mordant dyeing of textiles.
- 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 colour, 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.

# 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.



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.

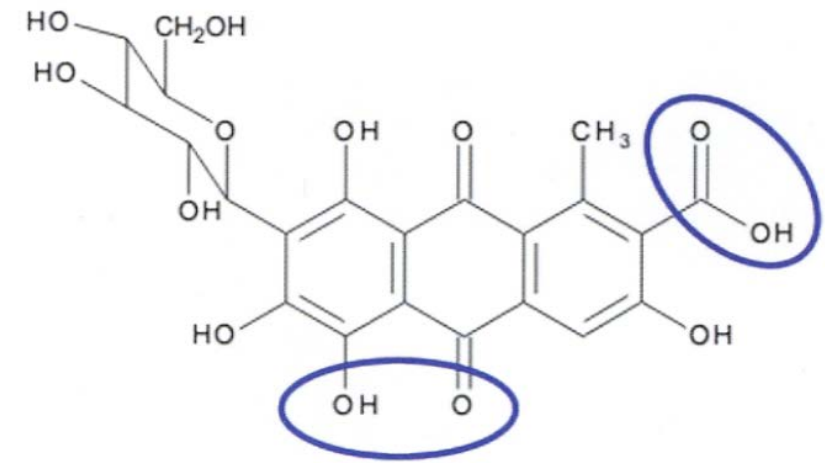
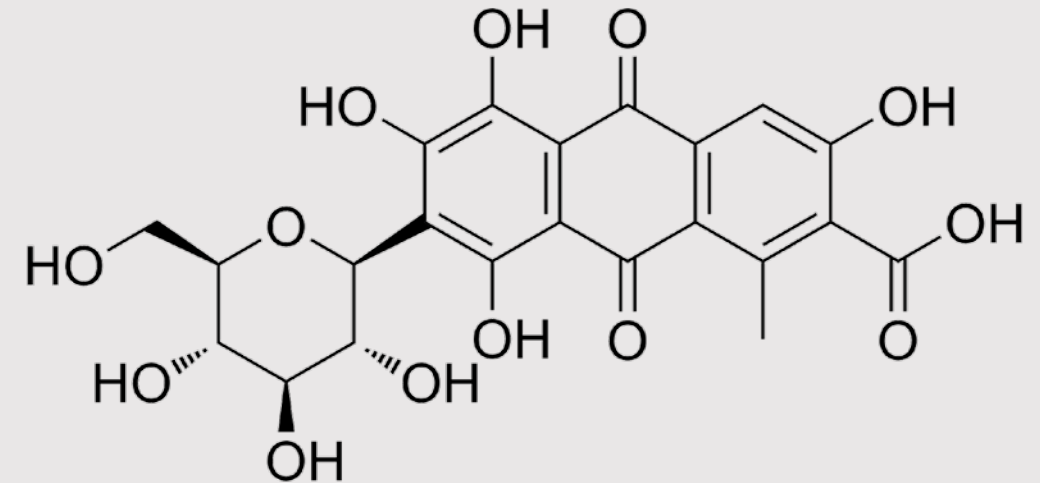


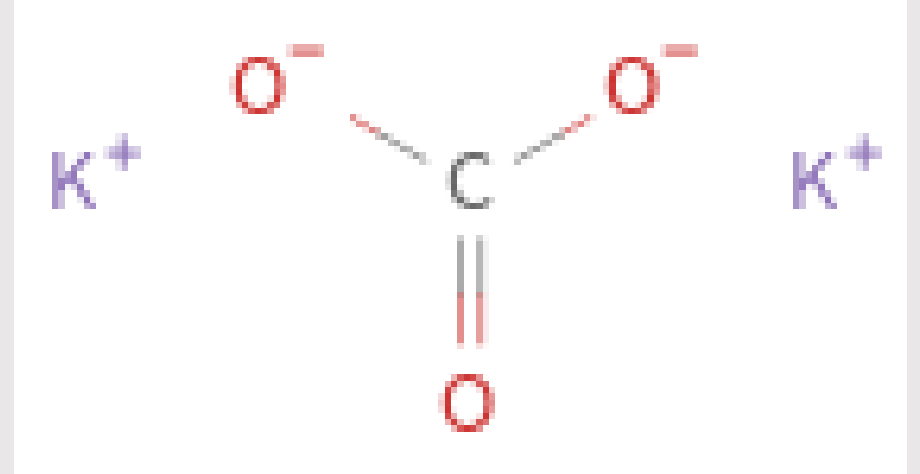
Figure 9 Possible positions for coordination with aluminium ions in the formation of aluminium-containing carmine.





# Potash = Potassium carbonate $K_2CO_3$

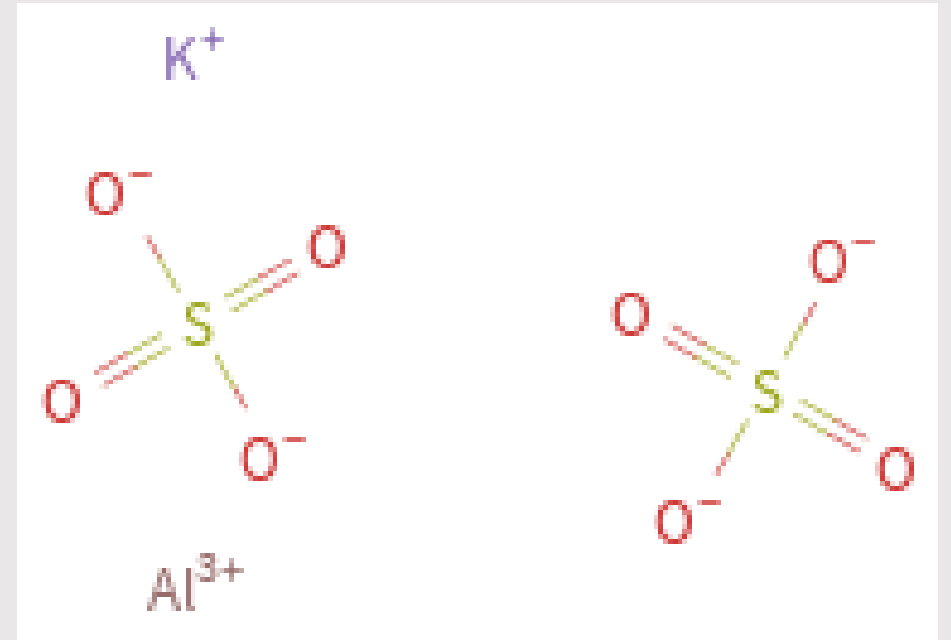
White deliquescent powder. **Potassium carbonate is used in the manufacture of glass, ceramics, smalt, and soap. It is also used in printing inks, process engraving, and lithography and in tanning and finishing leather.** In a closed environment, a saturated solution of potassium carbonate will form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



BASE  
pH = 12

# Alum = Aluminum potassium sulfate $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

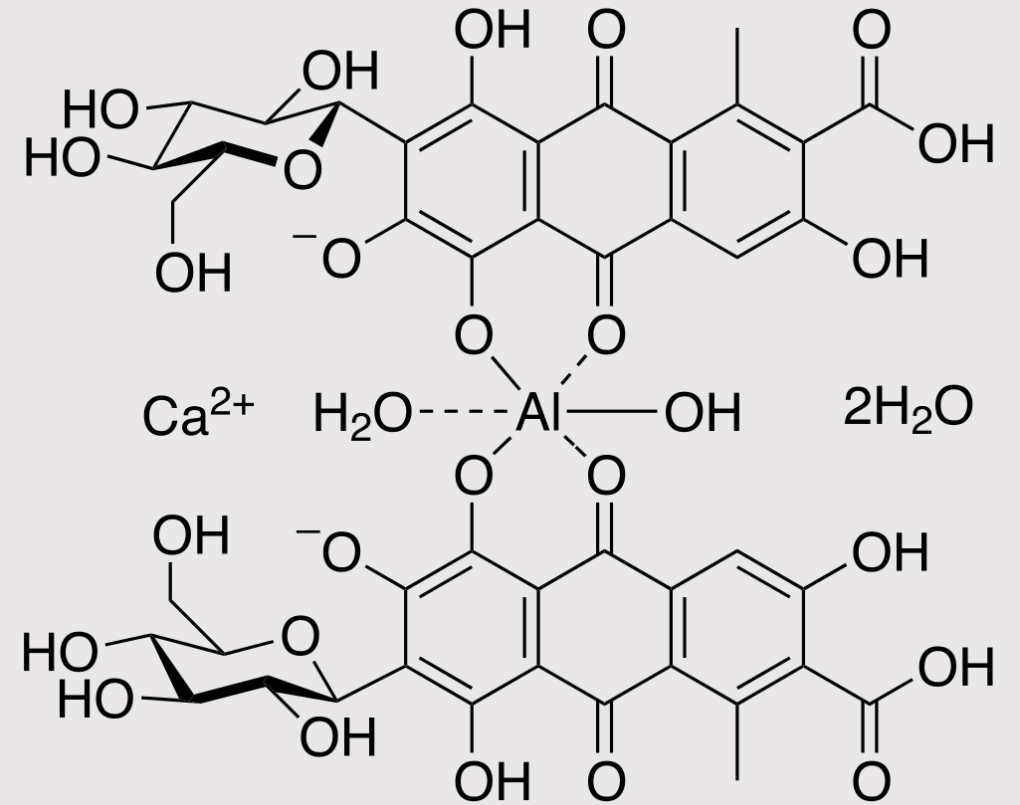
A white odorless powder with transparent crystals. Aluminum potassium sulfate occurs naturally in the minerals alunite and leucite. **It has been used since ancient times as a mordant in dyeing textiles and for tawing skins.** Aluminum potassium sulfate, or potash alum, is also used as a filler in paper, 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.**



ACID  
pH = 3

# 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.**

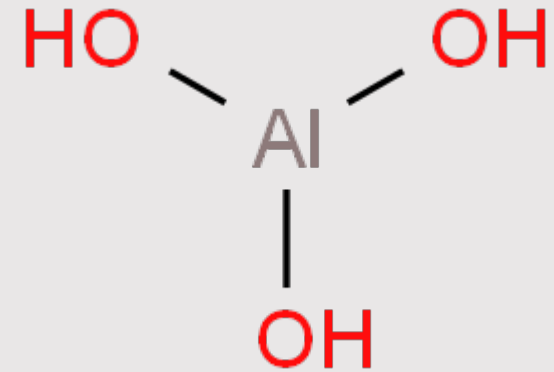




# Aluminum hydroxide (or alumina trihydrate) $\text{Al}(\text{OH})_3$

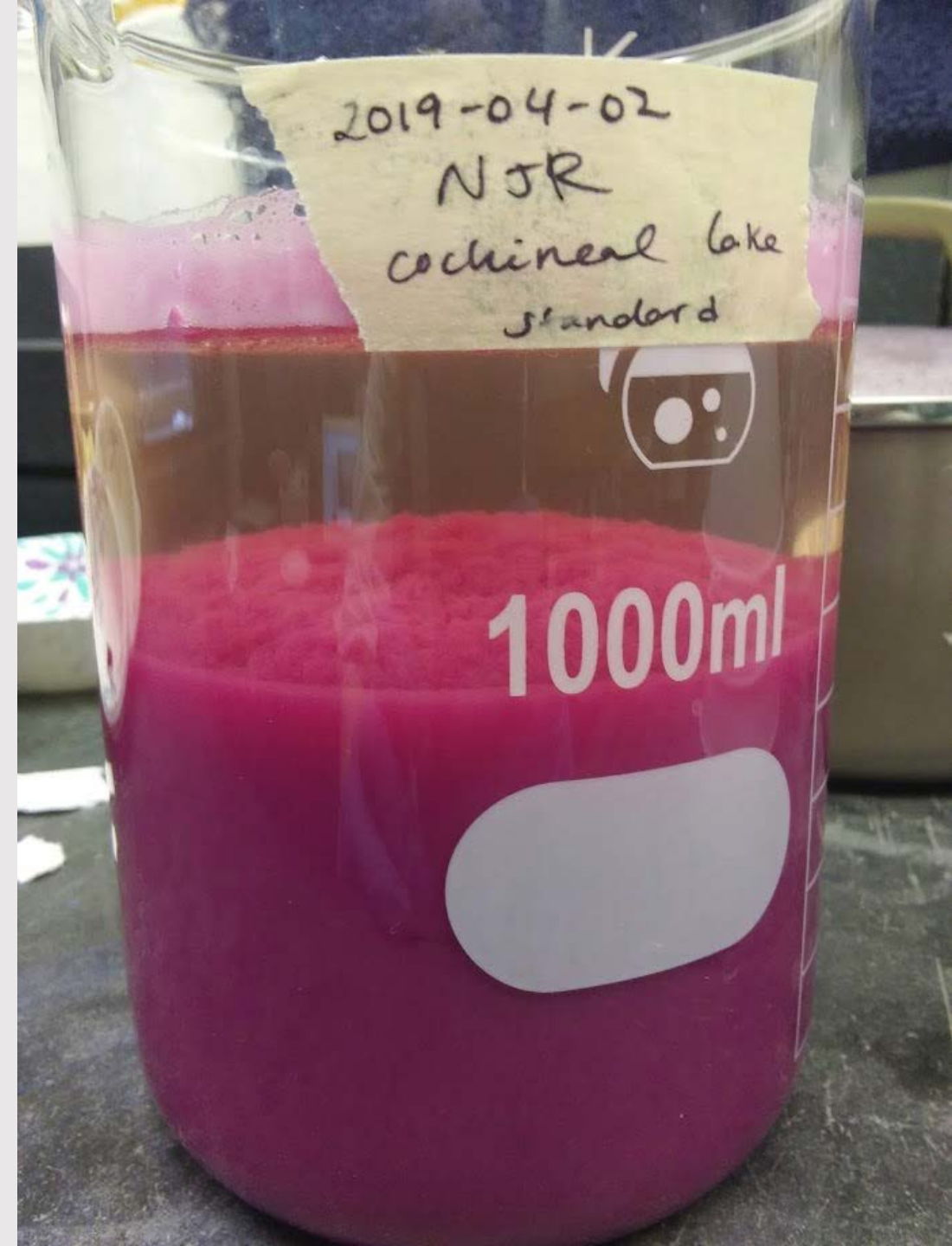
A white, translucent powder that is also called aluminum hydroxide. Alumina trihydrate is obtained from bauxite. When it is strongly heated, alumina trihydrate will convert to aluminum oxide with the release of water. **Alumina trihydrate is used as a base in the preparation of transparent lake pigments. 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 repellent, and as a filler in glass, ceramics, inks, detergents, cosmetics, and plastics.



# 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** (while heating).
- The dye solution is then filtered to remove any remnants of the dyestuff source. **Potash 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.



# Lake – Process 2

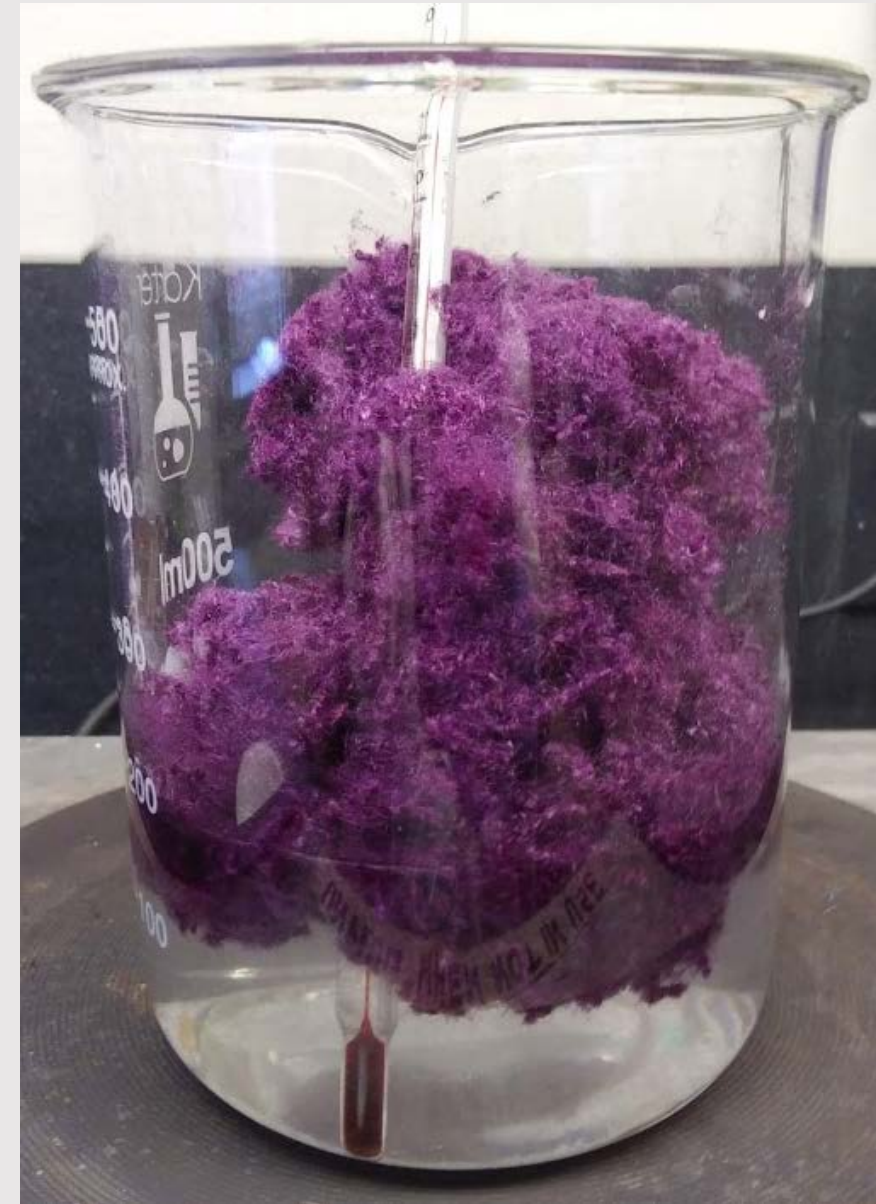
- Recipes more typical of the nineteenth century and onwards.
- **The substrate is made by the reverse sequence, adding alkali to an alum solution that contains the dyestuff.**
- The dyestuff is first extracted with water, the solution is filtered and then alum is added.
- This **forms a complex with the colorant via the neighbouring hydroxyl groups** present on the organic colorant. It is still soluble; **precipitation occurs when the acidic solution is neutralised 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

- 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.

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### 11. Ad faciendum lacham finam.-

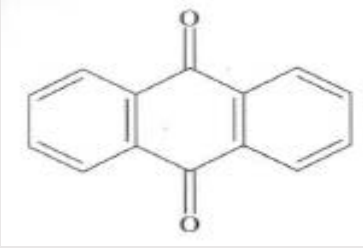
Tolle cineres ligni cerri, vel roboris, et fac lexivium, et in ipso fac bulire cimaturam scarlate fine rubeae de grana, tantum quod ex dicta cimatura extractus sit color; postea ipsum lessivum, cum dicta cimatura, colla per pannum lineum; postea accipe de alio lexivio simili superscripti quod prius accepisti, 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 lessivum 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.



# Lac



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

Chemical class: laccaic acid and erythrillaccin 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.



<http://collections.vam.ac.uk/item/O61099/hanging-unknown/>

Indian (ca. 1700), cotton and silk



[https://www.researchgate.net/figure/Some-lac-insects-known-from-the-New-World-a-Kerria-lacca-on-Albizia-sp-Peradeniya\\_fig1\\_51254451](https://www.researchgate.net/figure/Some-lac-insects-known-from-the-New-World-a-Kerria-lacca-on-Albizia-sp-Peradeniya_fig1_51254451)



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; 13 3/8 x 17 1/8 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

Examples of cochineal lakes in art

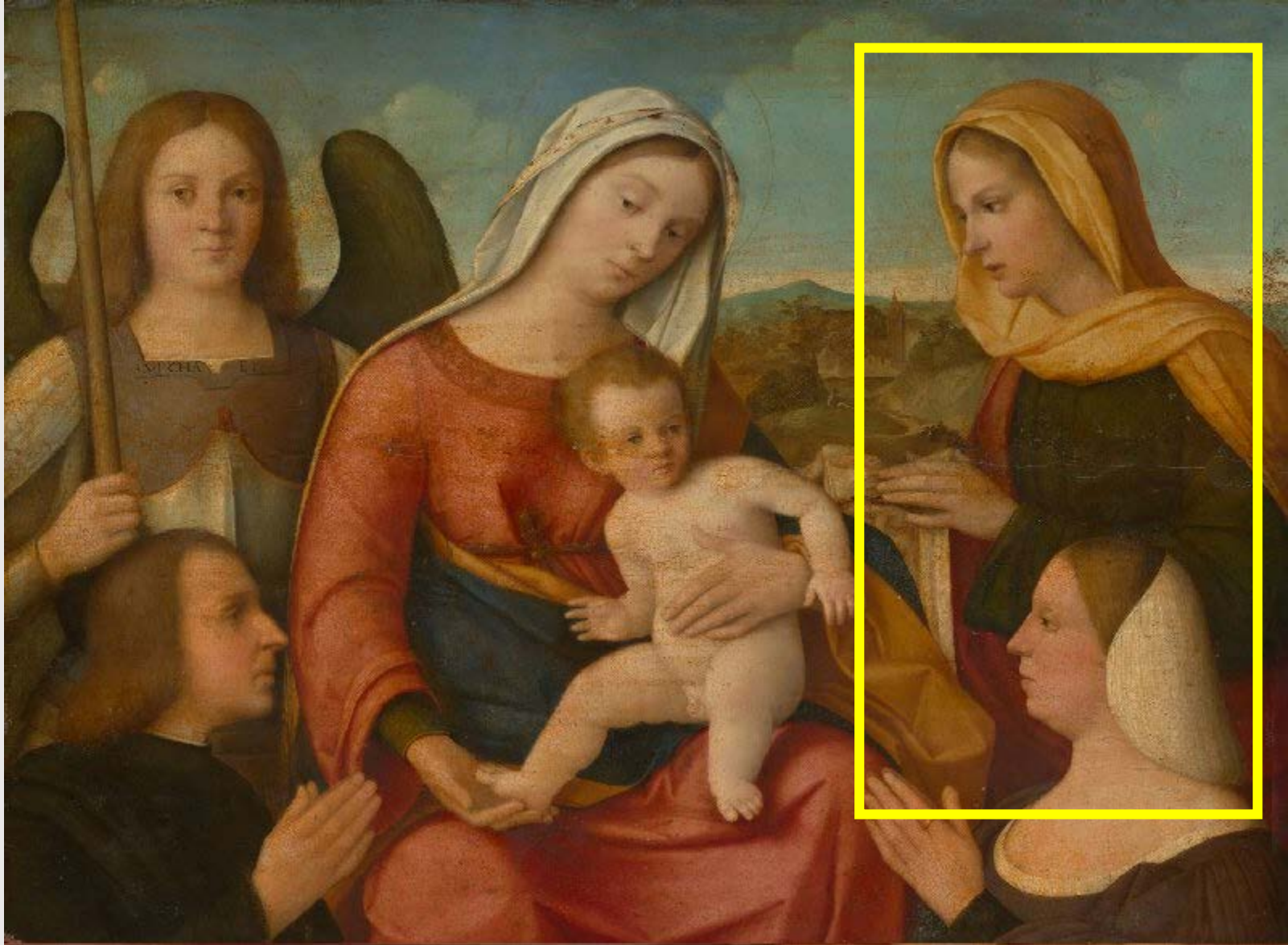
An intense cherry-red lake pigment has been used in the Virgin's red dress (plate 1). It contains the dyestuff extracted from the kermes insect, *Kermes vermilio* Planchon. In the EDX spectrum of the red lake, the largest peak is from aluminium (Al). The FTIR spectrum shows that the substrate is essentially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

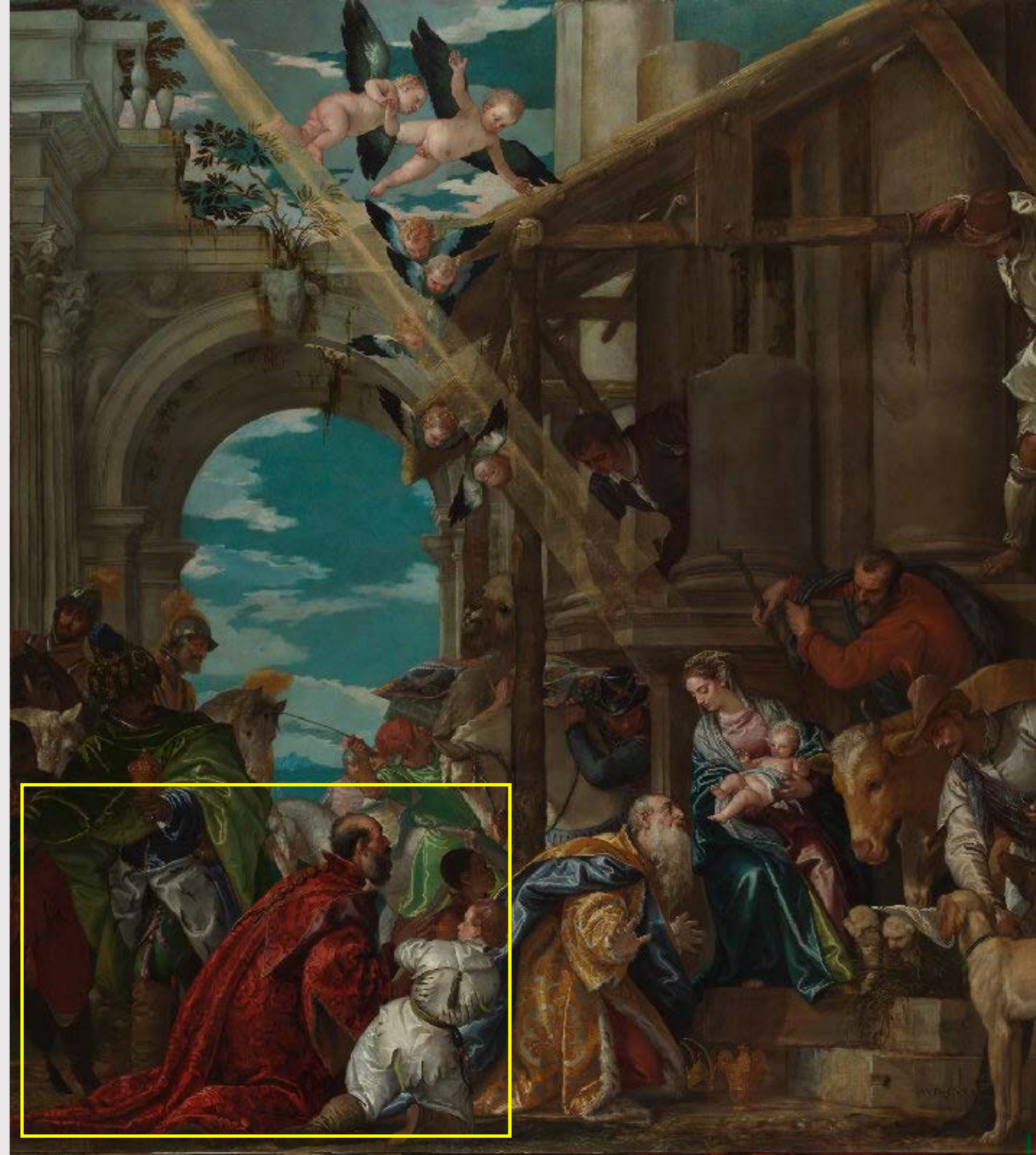


The Virgin and Child with Saints and Donors probably 1500-25, Francesco Bissolo

<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

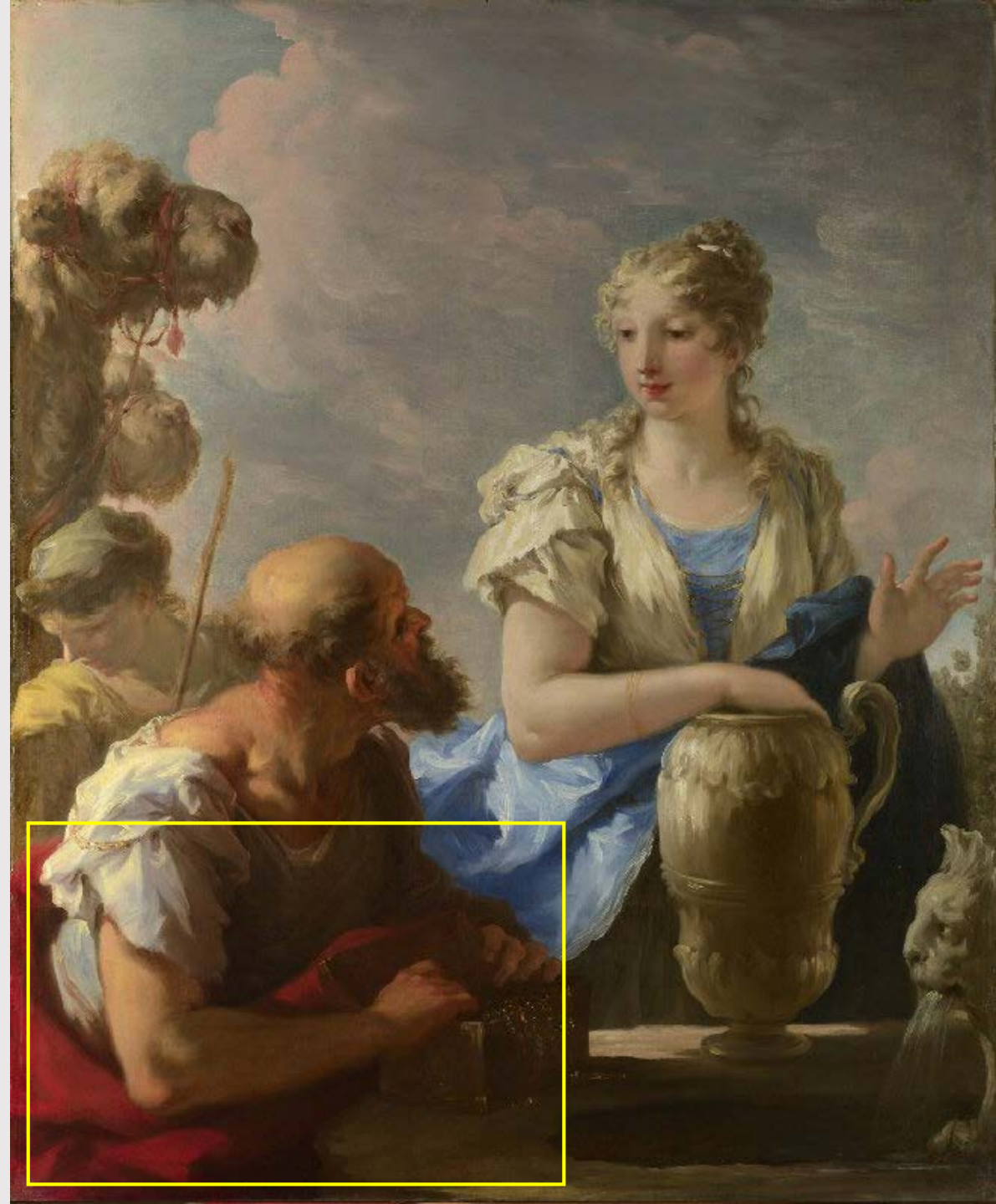
<https://www.nationalgallery.org.uk/paintings/canaletto-a-regatta-on-the-grand-canal>

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>



# References and Links

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- <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](https://travelingscriptorium.files.wordpress.com/2012/03/scopa-pigment-swatches_web.pdf)