



DYEING AND PAINTING WITH NATURE:  
THE CHEMISTRY OF COCHINEAL  
**DYE CHEMISTRY**

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Naomi Rosenkranz

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

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# 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)

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

## DYESTUFFS

The raw organic materials used to create a dye



# Natural colorants

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

They are not **COLORFAST**



# 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.



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>

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

# What creates, changes, or affects the color?

- Dyestuffs
- Textile
- Dyeing time
- Dyeing temperature
- Mordants
- Additives
- Acidity/alkalinity of dye bath



# Classification of organic dyes

# Types of dyes (by chemical class)

## Indigoids

Indigo



<http://www.saniapell.com/homemade/the-colour-of-food-homemade-fabric-dyes/>

## Anthraquinones

Cochineal



<http://www.dtcrafts.co.uk/dyesFixers/earthues/dy201.html>

## Flavonoids

Weld



<https://www.brushcreekwoolworks.com/products/weld-natural-dye>

## Carotenoids

Turmeric



<http://www.saniapell.com/homemade/the-colour-of-food-homemade-fabric-dyes/>

## Neo-flavonoids/homoisoflavonoids

Logwood



<http://www.dtcrafts.co.uk/dyesFixers/naturalDyes/ds002pic.html>

# Types of dyes (by process)

## DIRECT DYES

Colorant forms a direct bond to the textile fiber



Turmeric

<http://www.saniapell.com/homemade/the-colour-of-food-homemade-fabric-dyes/>

## MORDANT DYES

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



Cochineal

<http://www.dtcrafts.co.uk/dyesFixers/earthues/dy201.htmlw>

## VAT DYES

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



Indigo

<https://gailcreativestudies.wordpress.com/2016/06/29/indigo-in-south-east-asia-guest-blogger-penny-peters/indigo-dye-vat-near-sapa-vietnam/>



Direct Dyes

# Direct dyes

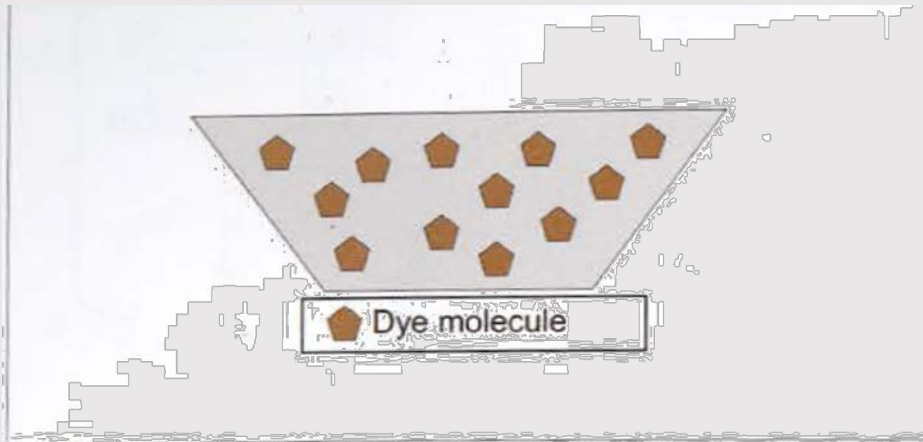
The dye binds to the textile fiber via hydrophobic interactions, hydrogen bonds and, where applicable, via ionic interactions.

Compared to the other dyeing processes, the fastness to both light and washing are poor.

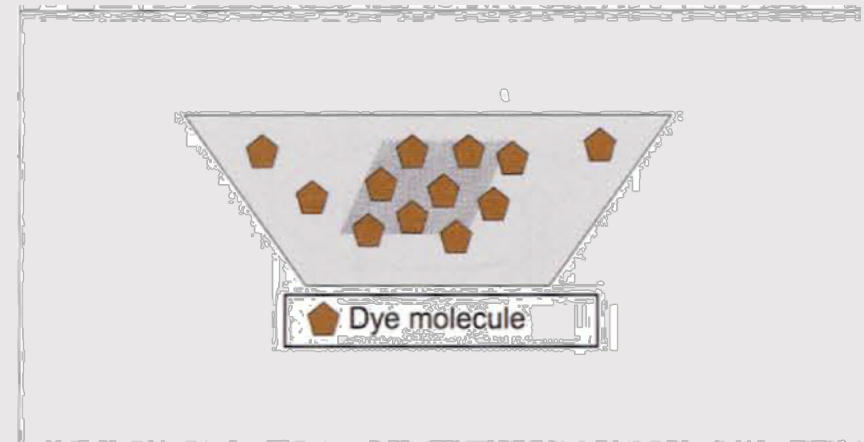


# Direct dye process

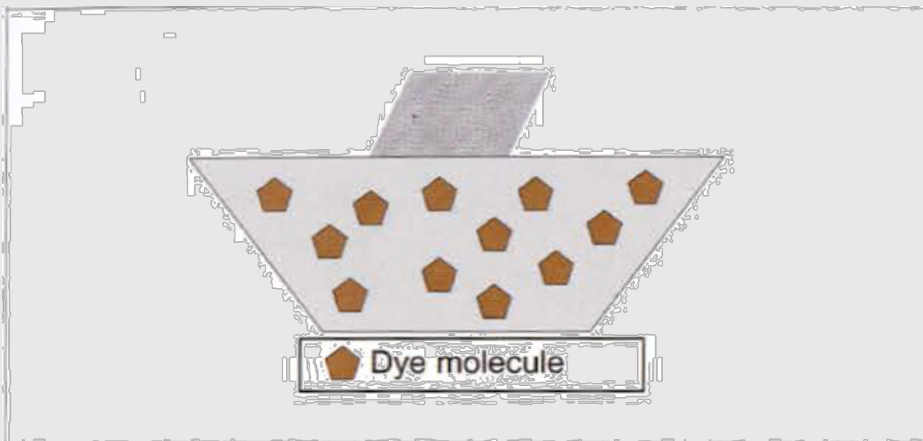
(1) Dye extracted from dye plant



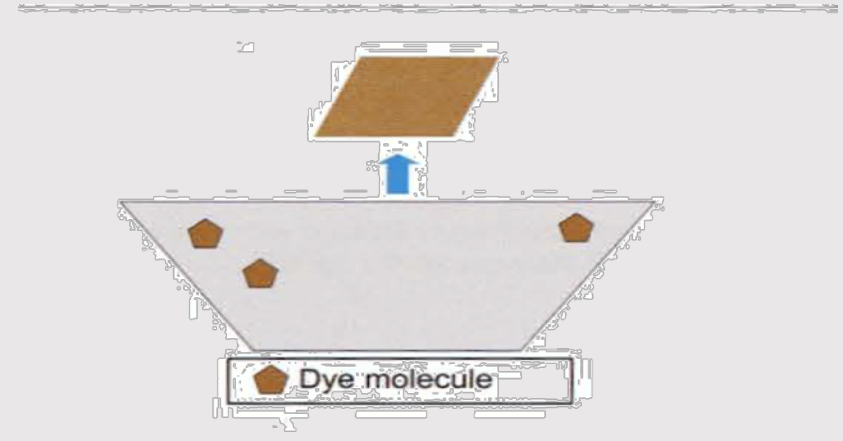
3) Dye molecules absorbed by textile



(2) Textile is added to dye bath



(4) Textile is removed



Vat Dyes

# Vat dyes - indigoids

These dyes are not soluble in water as such but must be converted into a water-soluble form. This conversion, actually a reduction, can be achieved with reducing agents such as sodium dithionite, but historically this was done by fermentation.



The fermentation vat could take hours or even days to develop in such a way that the insoluble dyes were converted into their soluble *leuco-form* needed for the dyeing process.

# Mordant Dyes

# Mordant dyes

Mordants are the largest natural dye class.



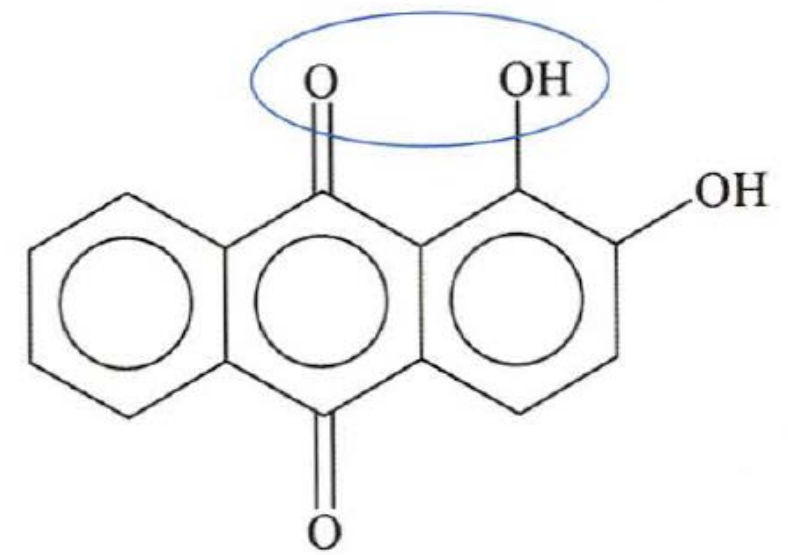
The word “mordant” is derived from the Latin *mordere*, “to bite”, as historically it was thought that the mordant would allow the dye to bite onto the fiber to create a colorfast textile.

# Mordant dyes

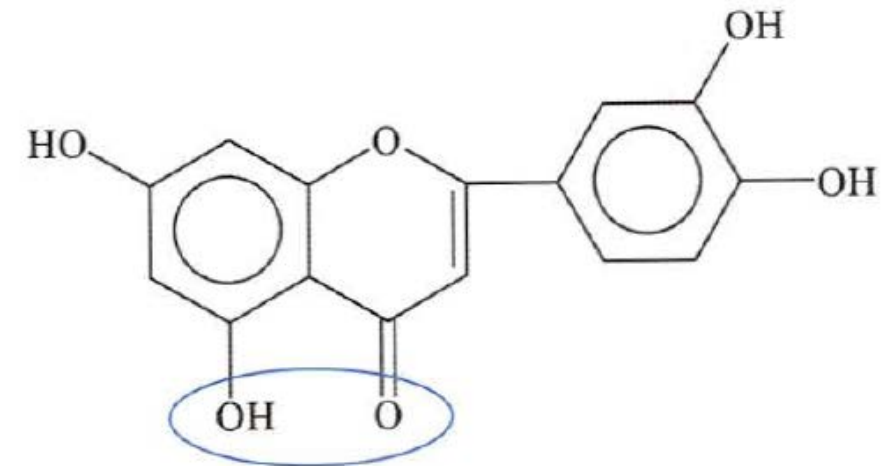
Mordants are commonly metal salts or other coordination metals that form a bridge between the textile fiber and the dye, resulting in a dye-metal-textile complex. The mordant attaches via neighboring C=O and C-OH groups in the dye.

Due to this complexation, mordant dyes have very good fastness to washing and better light fastness.

It is important to be aware that mordant dyes will also dye directly to give a (pale) color to unmordanted wool. This means that, in the case of a mordanted textile, part of the dye attached to the textile fiber may be bound directly to it, while another part is bound via the mordant. The part that is dyed directly will show poor fastness to light and washing.



**Figure 2** Probable position for coordination with aluminium ions taking alizarin as an example (Sanyova 2000/1: 66–78).

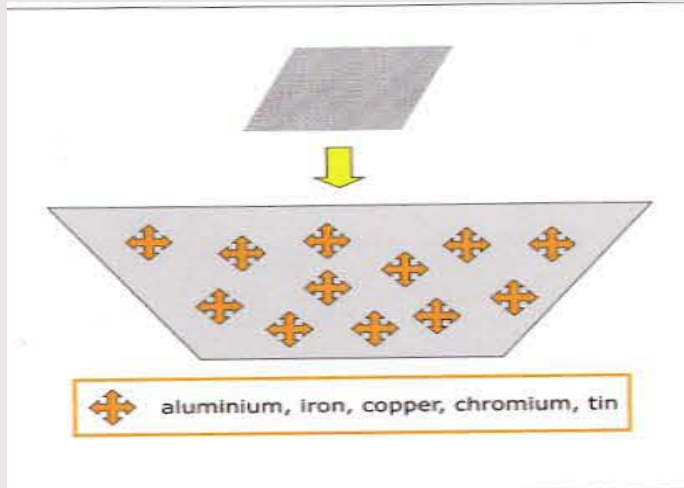


**Figure 3** Probable position for coordination with aluminium ions taking luteolin as an example (Amat *et al.* 2010).

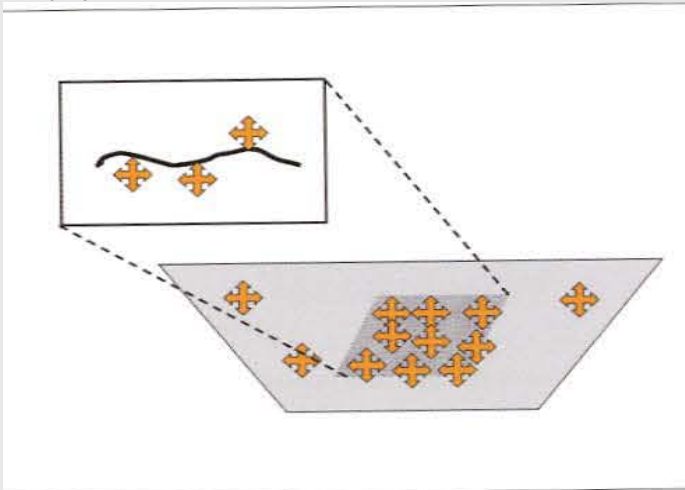


# Mordant dye process

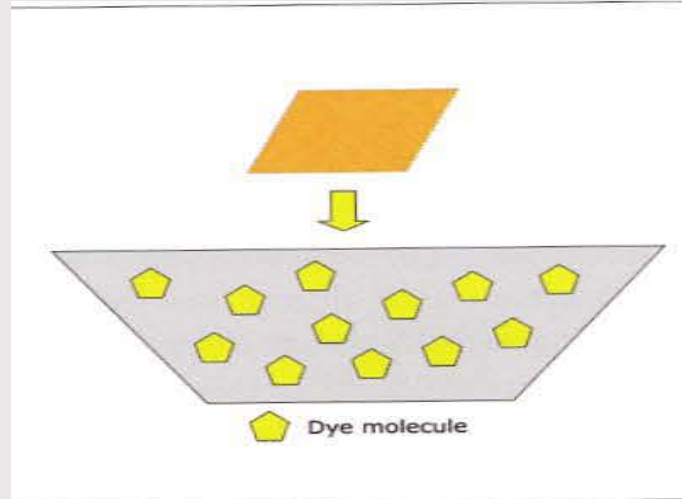
(1) Mordant bath is prepared by dissolving metal salts in water. Textile is then added



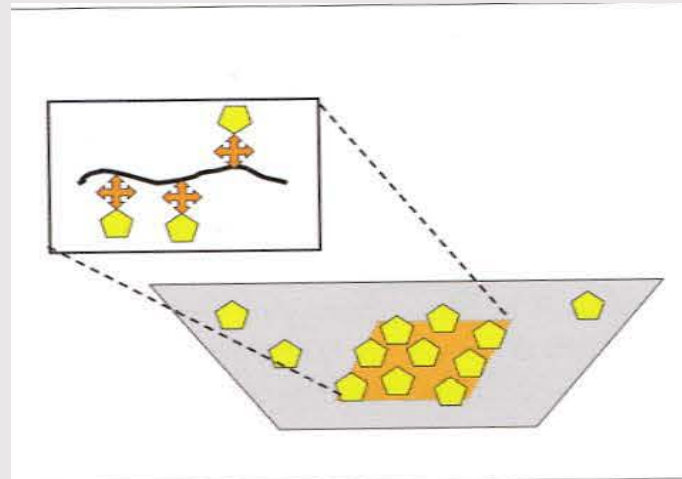
(2) Metal is bound to the textile



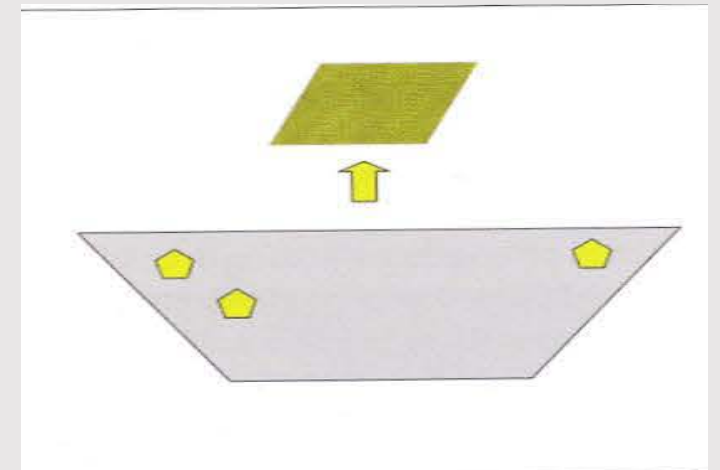
(3) Mordanted textile is added to dye bath



(4) Dye molecules bind to coordination metals of mordanted textiles



(5) Dyed textile is removed

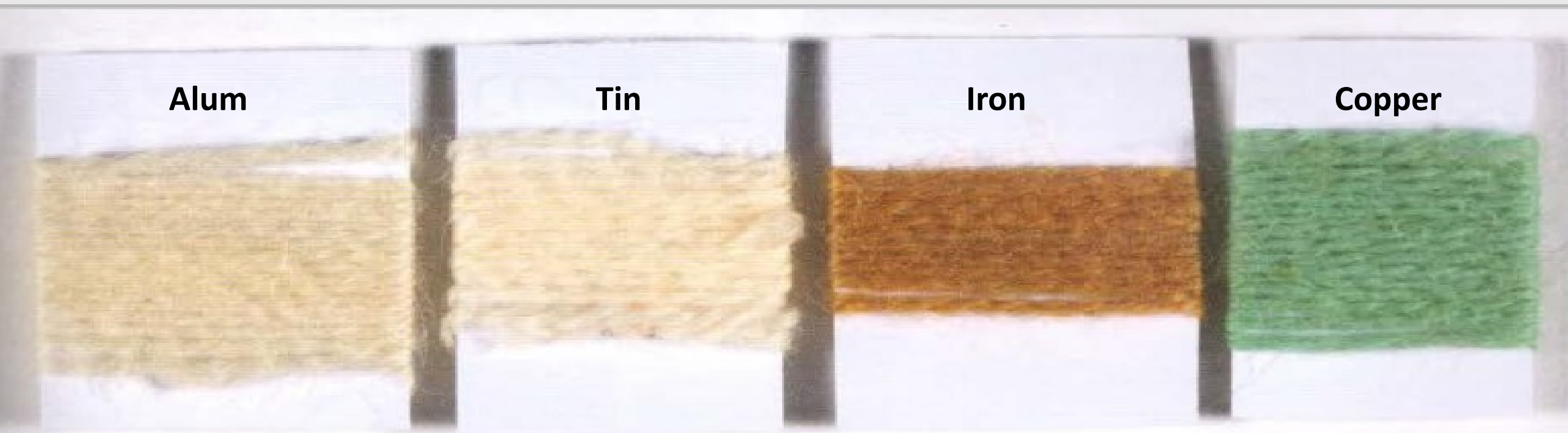


Mordants

# Mordants

Metal salts, including those of aluminum, tin, iron, copper, and chromium.

Mordants help form a dye-metal-textile complex to create a colored textile that is more color and light fast (or in some cases, completely facilitating the coloring of the textile).



# Mordant: Aluminum

Used since antiquity.

Aluminum is the most important and most vastly used mordant.



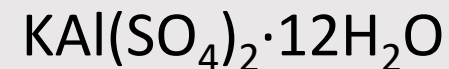
<http://www.chem.uiuc.edu/chem103/aluminum/AlIndex.htm>



[https://en.wikipedia.org/wiki/Potassium\\_alum#/media/File:Potassium\\_alum\\_octahedral\\_like\\_crystal.jpg](https://en.wikipedia.org/wiki/Potassium_alum#/media/File:Potassium_alum_octahedral_like_crystal.jpg)

Most commonly extracted from alum (also known as potash alum or potassium alum).

**Aluminum potassium sulfate,**



- Acidic – pH of 3

# Mordants: other metals used since antiquity

## Iron

- Usually in the form of iron(II) sulfate (also known as ferrous sulfate, vitriol, green vitriol, copperas)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
- Sometimes iron acetate  $\text{C}_{14}\text{H}_{27}\text{Fe}_3\text{O}_{18}$



## Copper

- Usually copper(II) sulfate (also known as cupric sulfate, blue vitriol, Roman vitriol)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
- Sometimes copper acetate  $\text{Cu}(\text{CH}_3\text{COO})_2$



# Mordant: Plant-based used since antiquity, Tannin

Tannins, in the form of oak galls, bark, wood, and leaves of certain tree families like oak, sumac

- Tannic acid  $C_{76}H_{52}O_{46}$



Oak galls formed on *Quercus infectoria*



Sumac

# Mordants: used more recently

Since 17<sup>th</sup> century

- Tin, usually as tin(II) chloride (also known as stannous chloride)  $\text{SnCl}_2$

Since 19<sup>th</sup> century

- Chromium usually as chromate  $\text{CrO}_4^{2-}$  or dichromate  $\text{Cr}_2\text{O}_7^{2-}$

Potassium chromate



Potassium dichromate



Stannous chloride



# Additive: Potash

Potassium carbonate  $K_2CO_3$

- Alkaline – pH of 12

Addition of potash to dye baths is 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)

## Effect on dye color

- Anthraquinone dyes, particularly **kermes** and **cochineal** become much paler while **madder** becomes dull or pale
- In historical recipes, it is much more common to find preparation of these dyes in “sour water” aka acidic conditions.





Textiles

# Textiles

The chemical interaction between the dye and the textile fiber is dependent on the dye itself and the type of fiber to be dyed.

There are two main textile groups: those with proteinaceous fibers - primarily wool and silk - and those such as cotton or linen that have cellulosic fibers.

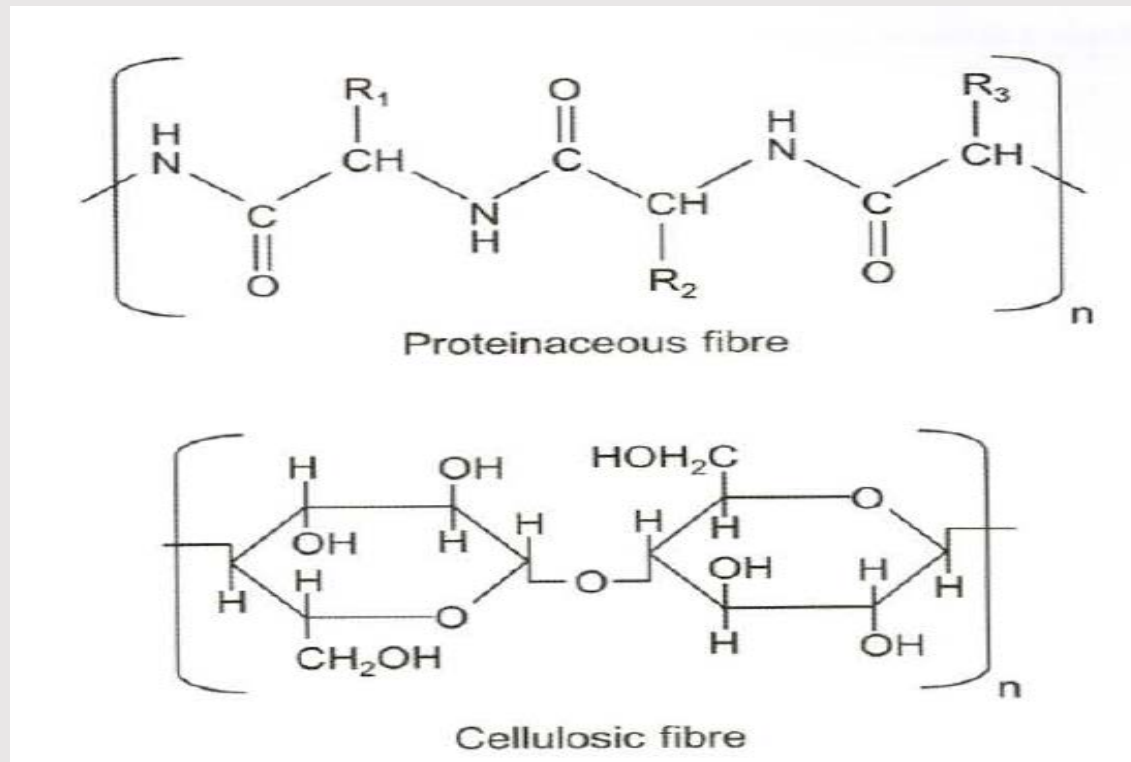


Figure 1 The basic structure of proteinaceous and cellulosic fibres.



Additional info

# Historical Recipe Examples

# *Neueroffneter curioser Schatz-Kasten* (Anon. 1706: 556, translated)

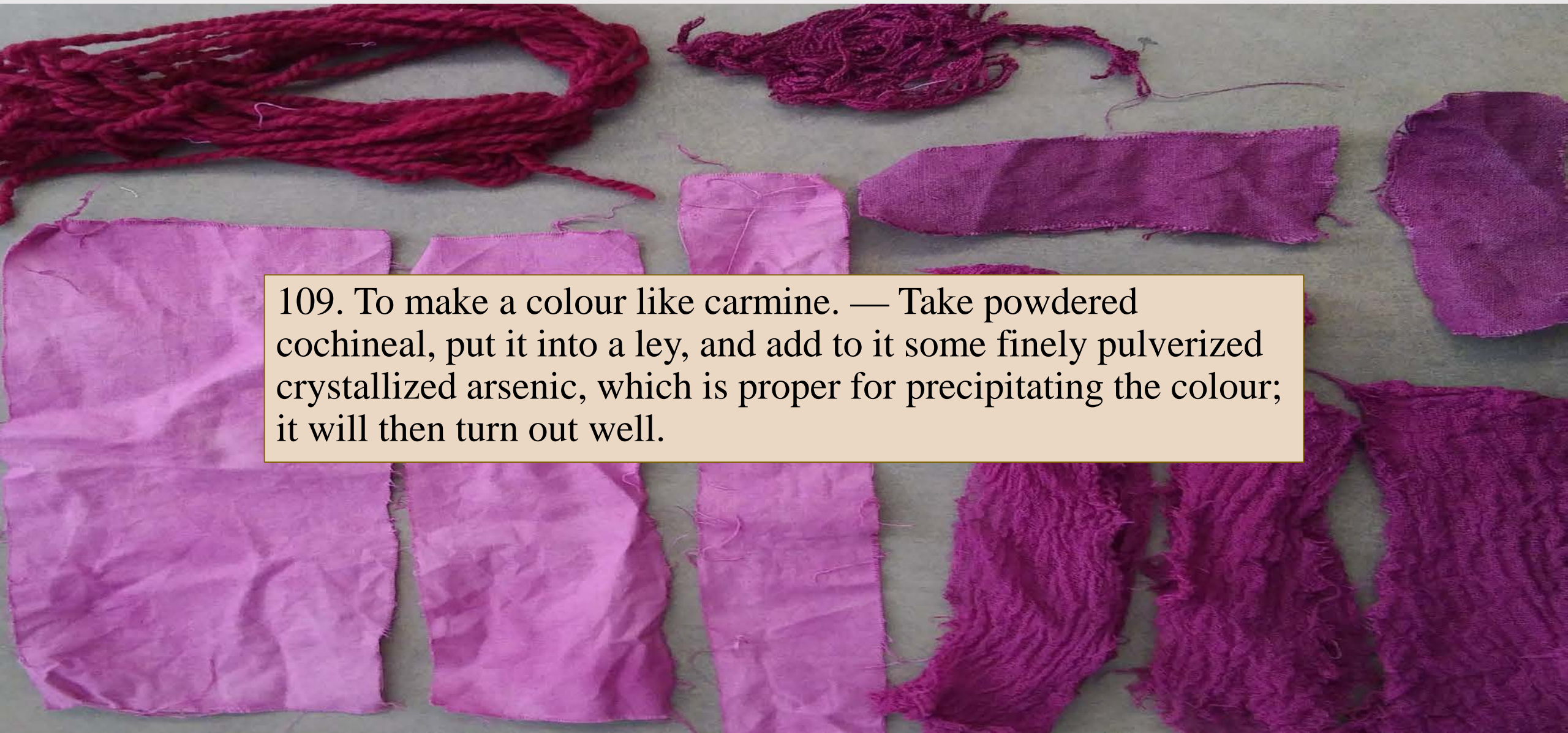
As quoted in Kirby, et. al. *Natural Colorants*



To dye nice carmine-coloured cloth. One has to take for 8 pounds of woollen cloth 2 *Loth* of cochineal, 2 quarters of wheat flour, or *Gaitz* [?]; the bran must be soaked in water for 8 days so that the water gets really acid. When one wants to dye then, the water must be poured off from the bran into the kettle. But the cochineal must be soaked before in warm water overnight. When one now dyes, a good fire must be made under it to warm the [bran) water. Then take a little of it [the warmed bran water], stir it with some dye and put it in the kettle as long as one still has some dye. When now it starts to boil, and one wants to give it an after-treatment [*meistem*], one must take lye extracted three times, or one takes 1.5 or 2 quarters of ashes of pressed wine-grapes, pours it into lukewarm water, and passes the dyed cloth through it until the shade is to your liking.

# Paduan Manuscript (pg. 698)

*Original Treatises, Dating from the XIIIth 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* by Mary P. Merrifield (1804)



109. To make a colour like carmine. — Take powdered cochineal, put it into a ley, and add to it some finely pulverized crystallized arsenic, which is proper for precipitating the colour; it will then turn out well.

# Paduan Manuscript (pg. 710)

*Original Treatises, Dating from the XIIIth 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* by Mary P. Merrifield (1804)

139. To make super-excellent carmine. —Take an egg, make a hole in it so that the white will run out, then take mercury and fill the egg with it, stop up the hole and lute it according to the best of your ability; then bury it two feet deep in horsedung which is very much exposed to the sun, and do this in the dog days. Leave it in this situation for 40 days, then take it out, with great care, lest it should break ; then break it, and you will find in it a living animal; let the animal die, and preserve it, it will fall to powder; use this powder, which will be a most splendid carmine, for painting and miniatures, but you must beware of the smell at the beginning.

2018-04-18 Fleece  
Mordant: None  
Dye: Cochineal

## Paduan Manuscript (pg. 660)

*Original Treatises, Dating from the XIIIth 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* by Mary P. Merrifield (1804)

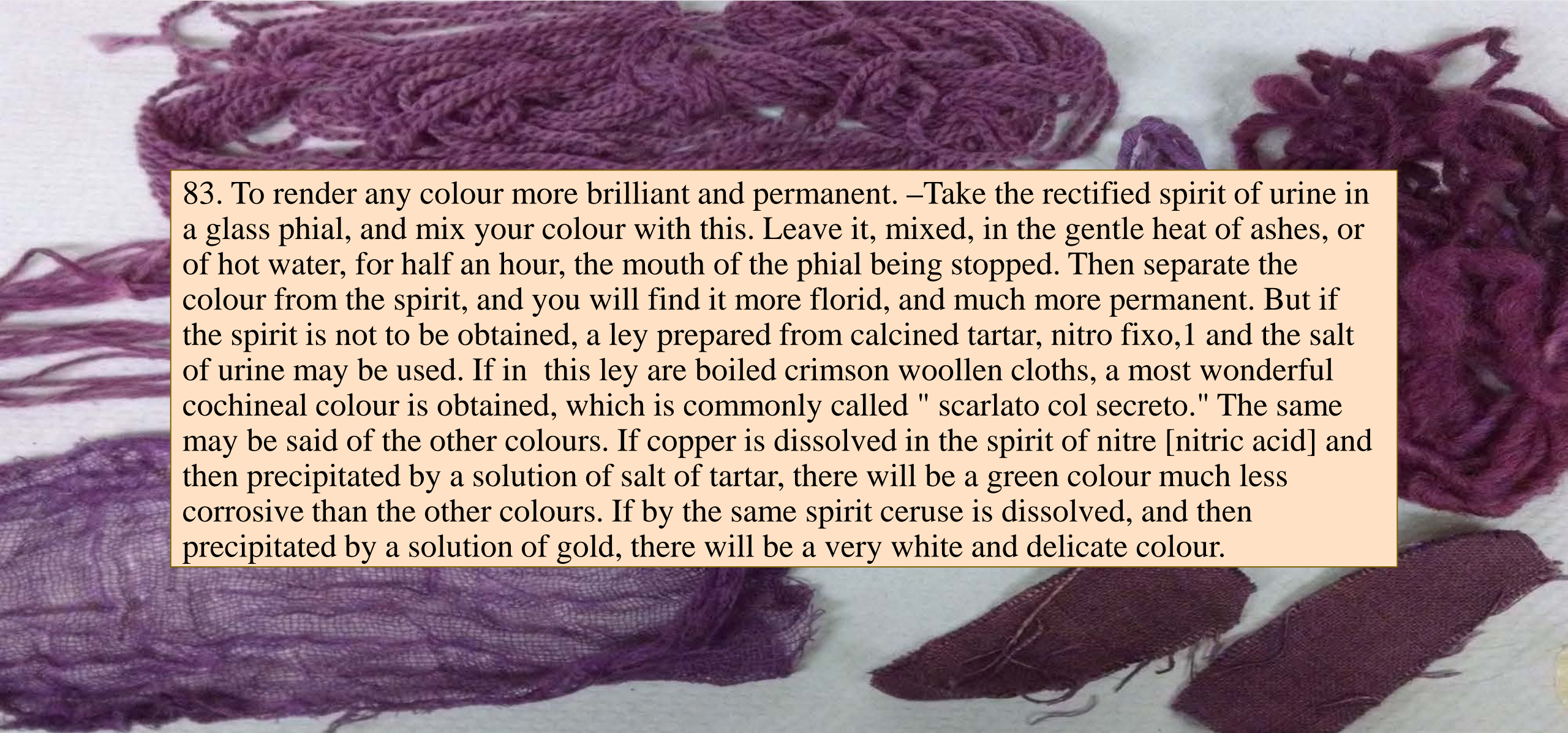


22. How to prepare cochineal. —Boil it with lemon juice, garlic juice, and burnt alum.



# Paduan Manuscript (pg. 682-684)

*Original Treatises, Dating from the XIIIth 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* by Mary P. Merrifield (1804)



83. To render any colour more brilliant and permanent. –Take the rectified spirit of urine in a glass phial, and mix your colour with this. Leave it, mixed, in the gentle heat of ashes, or of hot water, for half an hour, the mouth of the phial being stopped. Then separate the colour from the spirit, and you will find it more florid, and much more permanent. But if the spirit is not to be obtained, a ley prepared from calcined tartar, nitro fixo,<sup>1</sup> and the salt of urine may be used. If in this ley are boiled crimson woollen cloths, a most wonderful cochineal colour is obtained, which is commonly called " scarlato col secreto." The same may be said of the other colours. If copper is dissolved in the spirit of nitre [nitric acid] and then precipitated by a solution of salt of tartar, there will be a green colour much less corrosive than the other colours. If by the same spirit ceruse is dissolved, and then precipitated by a solution of gold, there will be a very white and delicate colour.

# The Plictho (pg. 145-147)

*The Plictho: instructions in the art of the dyers which teaches the dyeing of woollen cloths, linens, cottons, and silk by the great art as well as by the common by Giovanventura Rosetti (active 1530-1548)*

To dye silk in perfect crimson color.

122. First arrange the silk over the small rods that it be eight ounces of silk each. Couple them two by two so that it stays well in cooking. It needs half a bucket of water for each pound of silk. See that your work load is pocketed in manner that in the pocket it be not too tight, in fact better wide. Take eight ounces of black soap for each pound of silk to be worked and it need be boiled at a gentle boil a half hour and no more. Then take it out of the pocket, and wash it well to advantage so that in such manner that by the hand is known its scroop. To alumate it, takes ounces of alum for each pound of cooked silk and that the roche alum be fine. Note that as you dissolve the roche alum it needs be dissolved in river water that is well boiling in a cauldron. Let it cool, and when it is cool take it out and throw it into a tub and over that, as much water that in all it be one bucket for each pound of cooked silk. It makes the water biting as it must be, that is, one bucket of bath for each pound and see that you understand. When you want to use the water, divide it and make it to eight rods of about eight ounces each, and you put them in that tub where is the bath of alum. Make it stay well under the water and it must stay in the said alum fourteen hours and up to thirty. As you take out the silk from the alum, wash it well to advantage, and when you will have done this, divide it again as is said above for dyeing.

Also, the crimson needs to be soaked and it needs to soak according to the season, and especially when you work urgently. See that it be well soaked above all, and that it be well ground similarly to advantage. Then make up the bath and put in as much water as is half a bucket per pound of load. Then put bath into the cauldron and make a bright fire and see that it boil. As it begins to boil, have set up three fazi of poppo for each pound of load, and it must be well pestled and sifted. You will put the said poppo into the cauldron and stir well and then put your load inside and go turning it over as usual, with a good fire

below and that it fail not and that it be a bright fire. Make it boil thus a half hour and not more. Then take it out and have ready a tub of water and put it in immediately as you take it out of the cauldron. Wash it therein, and squeeze it well to advantage. Then you will go to wash it at the river so that the grease of the crimson comes out of the silk.

Having done this, divide it and return to give it the aluming in a tub and that it be sweeter than the first one. Put your load inside as you did the other time, and let it stay inside fifteen hours to advantage\*and then take it out and wash it well in river water. Then divide it up and make rods as above to dye the silk the second time. Then have ready first a half bucket of bath as before and make it boil and when it raises the boil see that there are made ready two fazzi of popo for each pound of silk worked. Soak it in the cauldron, pestled as I said above at first, and it needs a half fazo of indigo that has been to soak 24 hours, for each pound, and that has been soaking in a vase of glass. Throw it inside and stir well and then put in your load as you did before. Make it boil a half hour with bright fire and then take it out and it will be dyed competently. Have set up two tubs of water and first wash your load in one and then throw it into the other and then to the flowing river to advantage. And this is approved by Master Matthio of Odati from Venice.

Note this rule, with four pounds of crimson one makes good color and with five one does better, and up to six for each pound of silk. But do not pass beyond this relation to the cooked silk because it dyes perfectly and do not pass that sign.

And it needs crimson, minute and German and it will be perfect color.

When the crimson that you want to grind is soaked it is divided by eye and you take for the first time two thirds and the second the rest and manage as is said above.<sup>136</sup>

# 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](https://www.metmuseum.org/art/metpublications/cochineal_red_the_art_history_of_a_color)
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- CAMEO: Conservation & Art Materials Encyclopedia Online: [http://cameo.mfa.org/wiki/Main\\_Page](http://cameo.mfa.org/wiki/Main_Page)
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- 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](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](https://medium.com/@zip_lehnus/paint-it-red-cochineal-the-wonder-bug-51d280c41d56)
- Artist Screen-Prints Fabrics With Bacteria: <http://mentalfloss.com/article/504090/artist-screen-prints-fabrics-bacteria>
- American Society for Microbiology: Bacterial Dyes in Fashion: <https://www.asm.org/index.php/general-science-blog/item/6929-bacterial-dyes-in-fashion>

# Dye sustainability resources

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- Baliarsingh, Sasmita, et al. "Exploring Sustainable Technique on Natural Dye Extraction from Native Plants for Textile: Identification of Colourants, Colourimetric Analysis of Dyed Yarns and Their Antimicrobial Evaluation." *Journal of Cleaner Production*, vol. 37, 2012, pp. 257–264., doi:10.1016/j.jclepro.2012.07.022.
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