CHAPTER 13 Making carmine (lac)

Para fazeres nobre carmin

Figure 1 *Main steps in the reproduction of the process of making lac.*

'In order to make fine carmine, take a large new pot that holds four açumbres of water, and fill it with human urine. And mix it for days, and make it very clear all the while so that it gives off foam. And once it is very clear and skimmed, take a large bowl and place rye-straw over it, and above the straw a linen cloth. And on the cloth place ashes of vine branches, two parts, and a third part quicklime, and place a pot underneath. And throw on the lye the strained urine that you strained through asado [a pot with two handles] and continue straining it until the pot is full of this strained lye, in such a way that there are four açumbres of it there. And place it on the fire until only two fingers of it are left, and on the fire put another pot full of clear urine with the strained lye and heat both. And into the pot of clarified urine with the strained lye toss one pound of lac, and heat it gently, all the while stirring it with a slightly forked stick. And when the lac is melted, strain it with a linen bag, and place a basin underneath; whatever remains in the bag, place it in the pot of strained lye, which you have kept on the fire with gentle heat, until it is melted, stirring with a piece of wood. And then strain it separately with the bag containing the powder. Thus you can make carmine of two kinds, though first you must clarify the urine.' [1,2].

Reproduction

Take a beaker and fill it with 150 ml of urine and let it stand for several days (pH between 7 and 8). Keep the solution in continuous stirring during a whole day. Remove all the foam and scum formed during that period until it becomes clearer.

Afterwards, the urine is strained in a linen cloth (which can also be substituted by a paper filter) and on top of the filter make a 'bed' of a mixture of quicklime and ashes (3 to 5 g, in a 1:2 proportion). Then, the urine is filtered in that bed, at least two times, so that the pH may be above 9. The strained solution is put to stir and heated at around 90º C until it reduces a third of its volume (ca. 50 ml).

During this process, 10 g of sticklac are cleaned and finely ground in a mortar with a pestle.

The ground lac is added to the urine solution and left to stir during two hour at 60º C.

After that, the mixture is filtered over a linen cloth into a glass container. The filtered solution is then used to paint.

Rationalisation / Chemical reactions

Lac is a part of a resinous cocoon secreted by insects on twigs of branches of host trees. The dark red resinous raw material is commonly called sticklac [2,3]. Lac dye, the colouring substance, represents only 10 % of all the resin matter and its main components are laccaic acids A and B; also laccaic acids C, D and E are found in minor quantities [4,5]. When these dyes are removed, the resin gives the well-known shellac, which is a complex mixture of mono- and polyesters of hydroxyl aliphatic and sesquiterpenoid acids [6]. Erythrolaccin, also shown in Fig. 1, contributes to the yellowish orange hue that characterises the resin [5, 6-8].

Laccaic acid A, as the major component in lac dye, is the main responsible for the lac colour (it is also the one that has been most studied over time). This laccaic acid changes its colour from dark pink to dark red, by increasing the pH. According to literature, pKa values for laccaic acid A are 5.6, 7.0 and 9.8 [9,10].

The incorporation of the resin components in the final paint is essential to acquire the glassy appearance seen in Portuguese medieval illuminations (12th-13th c.).

This recipe uses urine as dye extraction solution. Human urine has in its constitution high concentrations of nitrogen (N), from the urea ($CO(NH_2)_2$), phosphorous (P), potassium (P), sodium (Na) and chloride (Cl) [11]. The pH values of fresh urine are within the normal physiological range of 5.6 and 6.8 [11,12], which indicates that the extraction solution is not alkaline. However, stale urine may develop higher pH values, due to urea hydrolysis, which may elevate pH values up to 9 [12].

Overall, by adding the quicklime and ashes extracts to the urine, the pH may increase to 9, turning the solution basic. When adding the lac to the extraction solution, the pH decreases to 6-7, making its appearance more reddish than pink.

Key aspects

pH control: There are several factors that will influence the pH along the recipe. Maintaining the extraction solution up to at least neutral conditions is important to guarantee a good lac colour. For instance, using stale urine is imperative to assure a pH ca. 7-8.

Resin extraction: It has been observed that heating around 60º C promotes more easily the incorporation of the resin in the final solution (lower than that is more difficult, since it tends only to extract the dye), as referred in the recipe: 'the lac is melted'. The use of basic extraction solutions (preferably above pH 8) tends to promote better dissolution of the resin. Furthermore, long extraction periods (at least one hour) can also contribute to the dissolution of the shellac constituents.

Filtration: The filtration step is also important to assure the neutral to basic extraction. Although the recipe does not give quantities, it refers proportions: 'place ashes of vine branches, two parts, and a third part quicklime' (2:1).

Missing / Obscure indications

asado: This word was only proposed recently by Débora Matos [2], which is associated to a Galician word for a pot with two handles. This type of pot is still found in Portugal, particularly in rural areas. Prior to that, Strolovitch transliterated the Portuguese word 'assado' as 'fried meat' [1]. We believe the recently proposed version is probably more accurate, since we did not find any rational reason for the use of 'fried meat'.

Rye-straw: The rye-straw could have been used as a bed just to give additional support to the linen cloth during the filtration.

The **other 'pot of strained lye'** is normally left out of the recipe, since its purpose is to produce another type of carmine ('make carmine of two kinds'), less concentrated. The instructions suggest putting two equal solutions of urine (previously filtered in the quicklime and ashes bed) in the heat. On the first

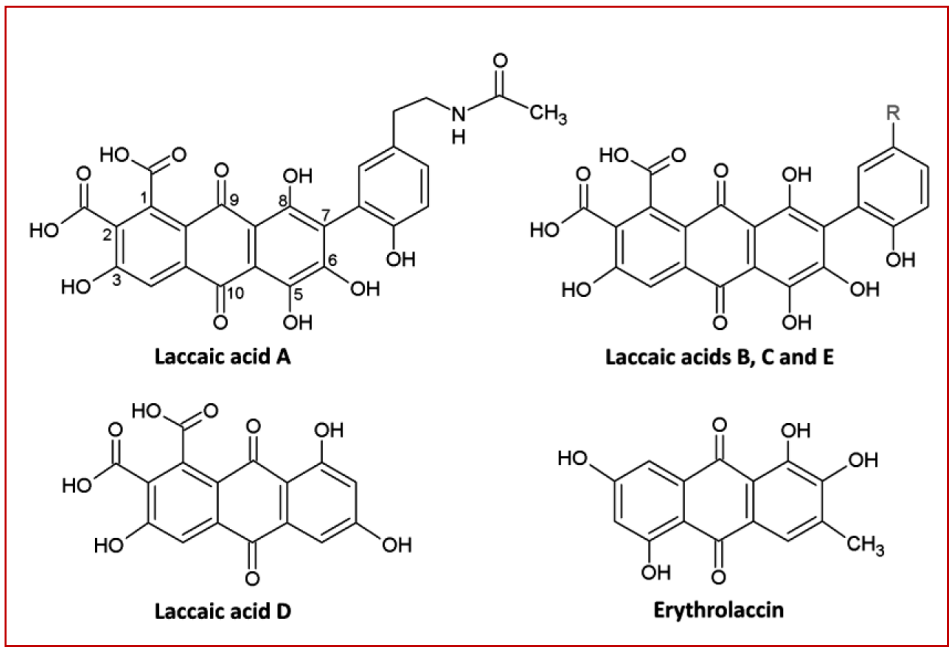

Figure 3 Chemical structures of laccaic acid A, laccaic acids B, C and E (B, R=CH_2CH_2OH; C, R=CH_2CHNH_2COOH; E, R=$CH_2CH_2NH_2$), laccaic acid D and erythrolaccin.

Figure 3 Above, De Avibus *(Lv.5, f.4) from Lorvão monastery,* Legendarium *(ALC 419, f.98) from Alcobaça monastery and Hagiographies (20, f.128v) from Santa Cruz monastery; Bellow, several examples of lac paints from the three monasteries.*

pot, the lac is added. Then, the second pot, is only used after the other pot with the lac mixture has been filtered. In other words, after straining the first lac solution, the remaining in the bag/filter is added to the second pot ('whatever remains in the bag, place it in the pot of strained lye, which you have kept on the fire with gentle heat') and after melting that second pot is finally filtered. In this manner, new carmine is obtained (with a much less intense colour), as seen in Fig. 4.

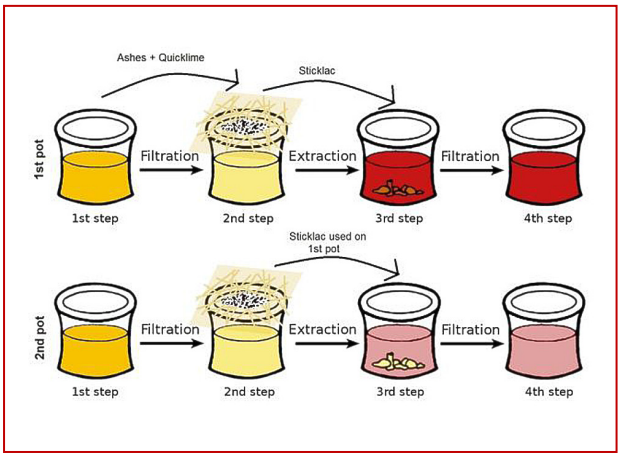

Figure 4 Scheme for the reproduction of the recipe.

Comments

This recipe allows a satisfactory extraction of the colourant on the first pot; however we still find some dye and most of the resin in the filter at the end. On the second pot, when using the remains from the first one, the extraction is much less efficient and the final colour is less intense. Therefore, we could be obtaining better yields, but this indication behind the two types of carmine could mean that this was the desired extraction. Whether this was the purpose of this recipe we cannot be certain, but in order to increase the efficiency of the first pot, we could try to increase the pH of the extraction solution (which under the proposed conditions tends to be around 8), increase the temperature (never above 90ºC) and leave the sticklac in the solution for a longer period.

The part of the recipe that describes the other pot is actually important since it says from where you should take the lac paint. For a while there was this idea that the final product should be taken from the filter, but by re-utilizing the same bag/filter for another pot/ another carmine suggests that the final product is the filtered solution and not the solid part (which is mostly composed of resin) remained in the linen.

In the infrared analysis the main fingerprint comes from the shellac (the resinous part of the lac) and occasionally, calcium carbonate appears as well as characteristic bands from urea. This confirms at least that the first extraction is effective in extracting a part of the resin.

Lac dye in Portuguese medieval illuminations

Lac dye has been identified in Portuguese medieval illuminations (12th-13th c.) [13,14]; it was used both

to paint small initials as well as illuminations, displaying in general a good conservation condition.

The dark reds, carmine or pink colours found in the manuscript illuminations were applied as a single colour or as a matiz; the pink colour was admixed with white lead or with white lead and vermilion (found particularly in Alcobaça manuscripts [15]); dark red could be admixed with vermilion (more characteristic in Santa Cruz manuscripts) [16]. All of these paints were applied with a proteinaceous binder, such as parchment glue or egg white [17], which may also have an influence in the glassy appearance. In some samples, the dye is indirectly detected by the shellac resin, particularly by the C-H stretching absorption bands seen in the infrared spectra. The use of chalk or gypsum as fillers was characteristic of Alcobaça, but was also found in some paints from Santa Cruz.

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Further reading

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Appendix

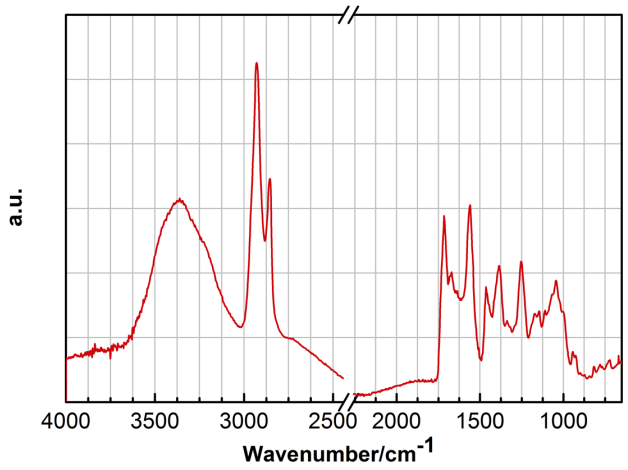
Lac dye characterisation: synthesised following 'The book on how to make colours', Chapter 13

Colour

Table 1 *Colour coordinates, Lab*, for lac dye paint reconstructions using two different binders (arabic gum and parchment glue) applied over filter paper and parchment.*

Support	Binder	L	a*	b*
Filter paper	Parchment glue	45.66	14.52	4.88
	Arabic gum	42.09	13.97	5.50
Parchment	Parchment glue	26.1	26.7	25.3
	Arabic gum	28.54	13.77	5.74

Spectroscopic characterisation



Infrared spectrum acquired with a Nicolet Nexus spectrophotometer coupled to a Continuμm microscope with a MCT-A detector. Spectra was obtained in transmission mode, with a resolution of 4 cm^{-1} and 128 scans. The dye was previously compressed using a Thermo diamond anvil compression cell.