

## Novel Natural Dyes for Eco-Friendly Leather Articles

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**Abstract:** There is a growing demand for eco-friendly and non-toxic dyes that can be used to provide color to a wide variety of materials. The present study aims to study the application of natural dyes as an alternative to the use of synthetic dyes in the leather industry. Many dyes can also cause health hazards due to possible carcinogenic effects associated with hazardous azo dyes, high heavy metals concentrations and the possible use of other restricted substances. This work analyzed the dyeing capacity of wet white leather (chrome free) with natural dyes from urucum (*Bixa orellana* L.) and cochineal carmine (*Dactylopius coccus*). The influence of the following variables in the dyes' diffusion and fixation were studied: the dye supplied (two added), the temperature during fixation and Tocopherol addition. The amount of dye absorbed by the leather was obtained from UV-VIS spectroscopy of the dyeing baths, and the quality parameters of the process were analyzed through color intensity. The tested dyes showed good surface coating of the leather, good penetration and equalization in the dyeing and good bath exhaustion. The parameters had large effects in the tests.

**Key words:** natural dyes, leather dyeing, urucum, cochineal carmine.

### 1 Introduction

The current global market for leather demands the continuous development of safer alternatives to synthetic dyes that may be harmful to humans and the environment, as well as the development of more sustainable processes. The requirements for hazardous substance control in footwear, leather articles and consumer products is growing strongly (AAFA, 2010; ECHA, 2011; Fuck *et al.* 2011).

Dyeing is one of the leather manufacturing steps that will change due to the necessity of new dyes as alternatives to synthetic dyes, the promotion of the better utilization of raw

materials and the need to achieve the best characteristics of the final product. It is estimated (Rai *et al.*, 2005) that 10 - 35% of the dye is lost in the effluent during the dyeing process. The majority of dyes used today for dyeing leather are categorized as “azo dyes”. About 70% of all leather (and textile) dyes listed in the literature have the azo chromophore group underpinning their coloring ability. In practice, more than 90% of all dyed leather is colored with azo dyes (Page, 2001). Some of these dyes have the capacity to release certain aromatic amines, which pose cancer risks. For this reason, the EU has established legislation aimed at reducing exposure to these hazardous amines. This implies that azo dyes that release the aromatic amines can no longer be used to dye textile and leather products that come in contact with the skin (CBI, 2011).

Dyes are generally synthesized organic molecules of an aromatic or heterocyclic nature and are classified by the type of basic molecule from which they are derived. The application of soluble organic dyes in an aqueous bath to wet leather leads to fixation of the dye molecules on both the surface of the tanned fiber network and inside the network. This type of coloration of leather is completely different from the finish operations performed in crust leather manufacturing, where insoluble dyes and/or pigments are applied, together with polymeric binder substances, to the surface of the dry leather (Heidemann, 1993).

The dye molecule is composed of chromophore and auxochrome groups that set the characteristic color of the dyestuff and fix the dyestuff to the leather, respectively. The colors of dyes and pigments are due to absorption of electromagnetic radiation in the range of visible light by the compounds.

Pigments are small in size, water insoluble and do not have chemical affinity for the fiber. In comparison to dyes, pigments have lower

tintorial power and greater light and high-temperature stability (Frinhani, 2003).

Natural dyes and pigments are emerging as an important alternative to the potentially harmful synthetic dyes (Sivakumar *et al.*, 2009). In Europe, the demand for the use of natural dyes in the manufacturing of textile and leather products is growing (CBI, 2011). Natural dyes are environmentally friendly and can exhibit better biodegradability and higher compatibility with the environment than synthetic dyes (Postsch, 2002; Nagia, 2007).

Suparno *et al.* (2005) state that biomimetic degradation of lignin yields simple phenolic products that may have new uses. For example, processes may be able to exploit the affinity between phenolic compounds and hides or skins, or these molecules may form the basis of synthetic organic tanning agents (syntans) for leather dyeing. The study of Velmurugan *et al.*, (2010) indicates that substances produced from fungi could be an alternative natural dye for leather dyeing. There are other sources of natural dyes, such as cacaui, *Theobroma speciosum*, cajiru, *Arrabidaea chica* verlot, cumatê - *Myrcia atramentifera* and tucumã - *Astrocaryum vulgare* (Kato, 1998; Melo, 2005).

The application of natural dyes and pigments in the dyeing of cotton, silk, wool and leather samples has been reported in several studies (Rekaby, 2008; Kamel, 2009; Velmurugan, 2010), but the process and dyes still need improvement. According to Liu (2010), the problem of the low light and heat stability provided by natural dyes can be solved with Tocopherol addition in the finishing steps.

The dye from urucum (*Bixa orellana* L.) has been used for food production, cosmetics and dyeing fabrics for many years. The dyes from urucum seeds are extracted with vegetable oil or an aqueous alkaline solution, yielding mainly bixin (fat soluble) and norbixin salts (water soluble) with a variation in shade from yellow – orange to reddish - brown (Kato, 1998; Frinhani, 2003). Bixin is a carotenoid, monomethyl ester of a dicarboxylic acid of Norbixin (Alves, 2005). According to Silva *et al.* (2008), urucum is the main source for obtaining bixin and norbixin pigments among the natural sources, followed by carmine. The dye extracted from urucum is resistant to microbiological growth, according to Barra

(1992) and Lauro (1995). Figure 1 shows the molecular structure of urucum dye.

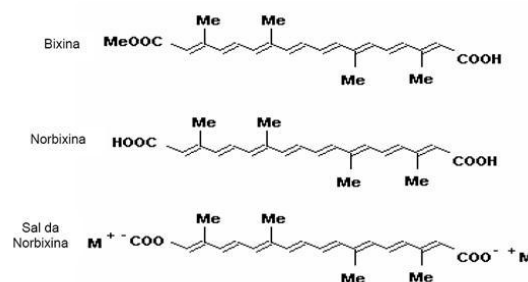


Figure 1: Molecular structure of urucum dye

The cochineal carmine dye is extracted from the cochineal insect in aqueous solutions, typically alkaline, resulting in a reddish color. According to Carvalho *et al.* (2001), varying the extraction pH can yield a bluish-red dye. The molecular structure of cochineal carmine dye is presented in Figure 2.

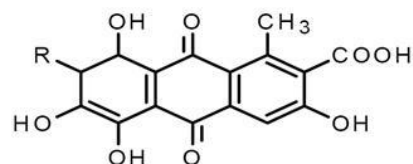


Figure 2: Molecular structure of cochineal carmine dye

In the present article, we used the urucum and cochineal carmine dyes for dyeing wet white leather and analyzed the influence of temperature and the addition of antioxidant in this process. The application of these dyes in wet blue leather also was tested.

## 2. Materials and method

The hide for the experiments was purchased from a tannery in the pickled stage, and the wet white pre-tanning (polyaldehyde base) and the retanning (sulphone base) were performed by a chemical company, which provided the formulation and the chemical products. This type of product was chosen in an attempt to produce more environmentally friendly leather. The experiments were performed for wet white leather dyeing with both dyes. Tests for the comparison of wet blue and wet white leather dyeing were performed with a cochineal carmine dye.

The solution in the de-acidify stage used before dyeing included sodium bicarbonate,

sodium formate and surfactant. The dyeing used a dispersant, an auxiliary dyeing compound and two additions of dye. Formic acid was used for the fixation.

The natural dyes employed were urucum and cochineal carmine, which were used separately. An experimental design was constructed to determine the influence of the temperature and the addition of antioxidants on the dyeing process. The experimental plan was composed of 16 tests using 15 x 15 cm<sup>2</sup> leather samples and processed in bench drums.

The dyeing was performed in two additions, each one containing 2% dye of the mass of leather used. The process temperature was held at 25°C until the fixing step. Because of the characteristics of natural dyes, which can be degraded when exposed to high temperatures, the fixing step was performed at two temperatures, 25°C and 50°C. To improve the characteristics and light fastness, the addition of Tocopherol in two levels was tested. The low level was without the addition of Tocopherol, and the high level included the addition of 1% Tocopherol together with dye addition. Table 1 shows the parameters used in the experimental design.

The response variables were the amount of dye that remains in the dyeing bath (in percent) and the color intensity. The amount of dye in the bath was analyzed by collecting UV-VIS absorption spectra. The color intensity was estimated with an arbitrary visual scale of 1 to 5, with 5 being the most intense color.

In the second experiment, the dyeing ability of natural dyes was compared on wet blue and wet white leather substrates. This test was performed with a fixing temperature of 50°C, with one dye addition and without Tocopherol. The response variable was the percent of dye that remained in the bath.

Table 1: Parameters used in the experimental design for leather dyeing

Test	Temperature (°C)	Tocopherol 1*	Tocopherol 2**	Dye
1	25	no	no	Urucum
2	50	no	no	Urucum
3	25	yes	no	Urucum
4	50	yes	no	Urucum
5	25	no	yes	Urucum
6	50	no	yes	Urucum
7	25	yes	yes	Urucum
8	50	yes	yes	Urucum
9	25	no	no	Carmine
10	50	no	no	Carmine
11	25	yes	no	Carmine
12	50	yes	no	Carmine
13	25	no	yes	Carmine
14	50	no	yes	Carmine
15	25	yes	yes	Carmine
16	50	yes	yes	Carmine

\* Tocopherol addition together with first dye addition

\*\* Tocopherol addition together with second dye addition

### 3. Results and discussion

The results obtained in the experiments are shown in Table 2. The factorial design 2<sup>4</sup> with a confidence level of 95% was separately performed on the response variables. According to the ANOVA statistic analysis, the residual dye in the bath was controlled by the following parameters: temperature, Tocopherol 2, type of dye, the interaction between Tocopherol 2 and temperature and the interaction between Tocopherol 2 and dye. The results are presented in Figures 3 to 7.

Figure 3 presents the influence of temperature on the amount of dye that remained in the bath after the dyeing process. This shows that as the temperature increases, the amount of dye in the bath decreases, which means that higher temperatures promote dye exhaustion.

The addition of Tocopherol in the second stage (Tocopherol 2) of the dyeing resulted in larger amounts of residual dye in the bath (Figure 4); thus, this substance is not a good dyeing additive.

Figure 5 shows the influence of the type of dye on the amount of dye remaining in the bath,

and it can be seen that more dye remains in the bath if cochineal carmine is used.

Figure 6 shows the influence of the interaction between the Tocopherol 2 and temperature. For the high temperature, the amount of dye that remains in the bath is lower than with the low temperature, showing a positive effect of temperature in cases with or without Tocopherol.

Figure 7 presents the influence of the type of dye and Tocopherol 2, and it was determined that using urucum dye lowers the amount remaining in the bath compared to carmine dye. Tocopherol 2 showed less influence with urucum than with carmine, where the fixation of the latter has been negatively influenced.

Table 2: Residual dye concentration in the bath and color intensity for the dyeing tests

Test	Dye in the bath (%)	Color Intensity of leather
1	0.0018	1
2	0.0018	2
3	0.0020	3
4	0.0018	3
5	0.0031	4
6	0.0019	1
7	0.0027	4
8	0.0024	5
9	0.0078	4
10	0.0075	5
11	0.0090	2
12	0.0084	5
13	0.0273	2
14	0.0192	4
15	0.0271	1
16	0.0211	3

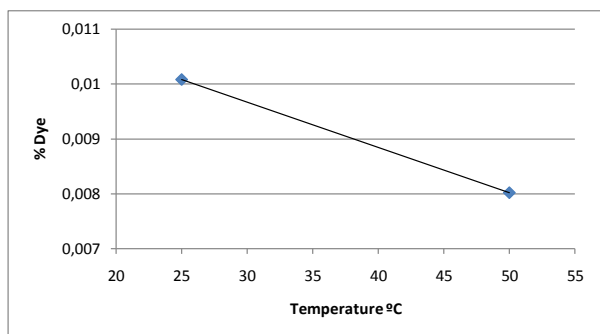


Figure 3: Influence of temperature on the amount of dye remaining in the bath

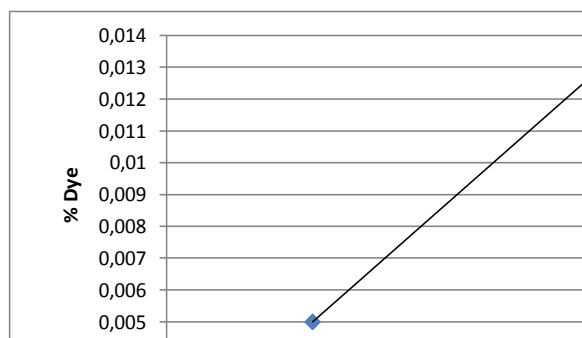


Figure 4: Influence of Tocopherol addition in the dyeing tests

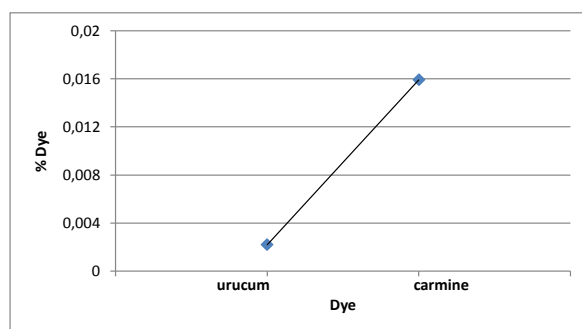


Figure 5: Influence of the type of dye on the amount of dye remaining in the bath

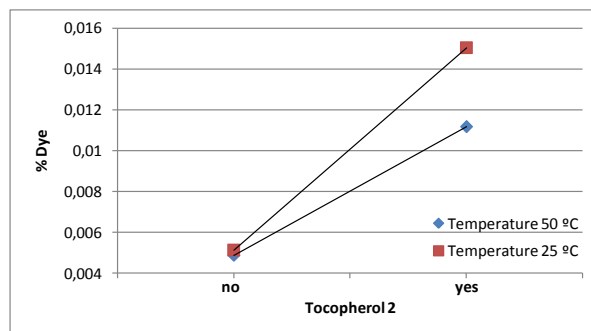


Figure 6: Influence of temperature and Tocopherol 2 on the amount of dye remaining in the bath

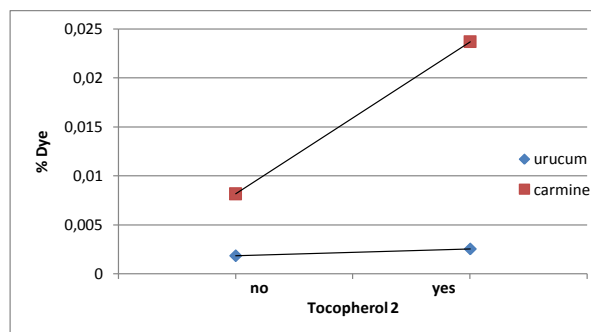


Figure 7: Influence of the type of dye and Tocopherol 2 on the amount of dye remaining in the bath

According to the experimental data, none of the tested factors alone influenced the color intensity; however, interactions between Tocopherol 1 and the type of dye and Tocopherol 2 and the type of dye did influence the color intensity of leather on the grain surface. In Figure 8, the influence of the interaction of Tocopherol 1 and the type of dye on the color intensity is shown. This indicates that the urucum dye with the addition of Tocopherol in the first stage of dyeing provides a more intense color, and the reverse occurs for the cochineal carmine dye.

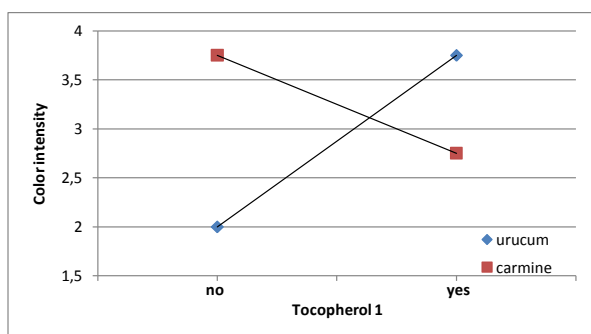


Figure 8: Influence of Tocopherol 1 addition on the color intensity

Figure 9 shows the influence of the interaction between Tocopherol 2 and the type of dye on color intensity. This indicates that the urucum dye with the addition of Tocopherol in the second stage of dyeing has a similar influence as Tocopherol 1 with the two dyes.

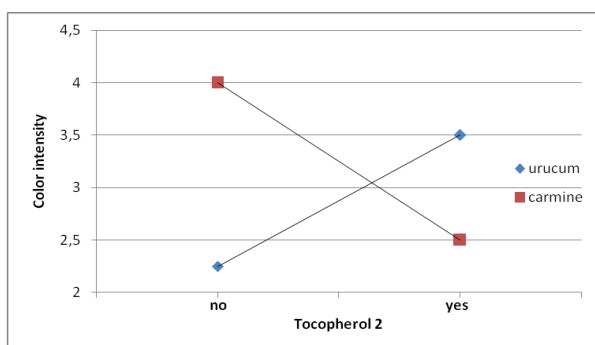


Figure 9: Influence of the interaction of Tocopherol 2 and dye on the color intensity

In the tests comparing the wet blue and wet white leather substrates (Figure 10), it was observed that wet blue leather has more affinity for the dye. The residual dye

concentration is lower with wet blue than with wet white leather.

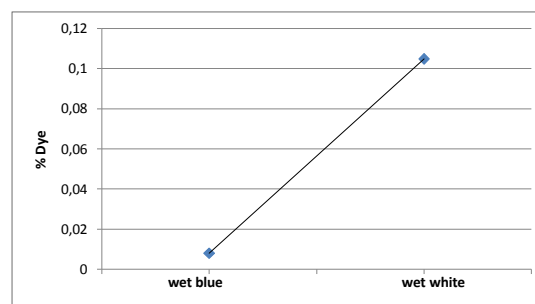


Figura 10: Concentración del colorante residual en el baño para el cuero wet-blue y wet-white

#### 4. Conclusions

The parameters tested that influenced the residual dye concentration were the temperature, Tocopherol 2, the type of dye, the Tocopherol 2/temperature interaction and the Tocopherol 2/type of dye interaction. For the color intensity, the influential parameters were the Tocopherol 1/type of dye interaction and the Tocopherol 2/type of dye interaction. The ability of the leather to absorb the dye was better at 50°C than at 25°C. The addition of Tocopherol was positive only when using urucum dye and when added together with second dye addition. The tests performed with wet white leather and wet blue leather showed that when using wet blue leather, a lower amount of dye remained in the bath.

Other studies are still required to identify the types of chemical bonds that form between these natural dyes and the wet leathers. Understanding these chemical bonds will make it possible to identify compatible products for use in the wet finishing process or additives that can enhance or interfere with the dye/leather interactions. Properties such as color fastness, PVC migration and thermal resistance should be tested to determinate the influence of natural dyes in the leather dyeing and finishing processes. It is important that other natural dyes be tested to verify the feasibility of producing different leather colors.

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