

COMPARATIVE PROPERTIES OF PURE AND SULPHONATED DYES EXTRACTED FROM HENNA (*Lawsonia inermis* (Linnaeus) AND KOLANUT (*Cola nitida* (Vert.) Schott & Endl.) PLANTS**^{1*}Abba, H., ²Musa, H. and ²Ado, A.**¹Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.²Department of Pure and Industrial Chemistry, Bayero University, Kano, Nigeria.*Corresponding e-mail: hamza.abbah@gmail.com.

(Received: May, 2013; Accepted: September: 2013)

ABSTRACT

In continuation of our research on the extraction and application of plants, we report the results of the dyeing and fastness properties of dyes extracted from the leaves of Henna and Kolanut plants in chrome-tanned (Wet-Blue) leather. Dyes were extracted from Henna (*Lawsonia inermis*) and Kolanut (*Cola nitida*) plants using chloroform and acetone as solvents. The extracted dyes were subsequently sulphonated with chlorosulphonic acid. Both the extracted and sulphonated dyes were applied on chrome-tanned leather using 2% and liquor-to-good ratio of 50:1 dyeing conditions and the dyeing properties (exhaustion, fixation, glazing, levelness, migration and penetration) assessed. The light, wash and rub fastness properties of the dyeings were investigated. From the results, the λ_{\max} values of the crude dyes were found to be higher than those of the sulphonated derivative dyes in all the three solvents. The dyeing properties of Henna dyes were found to be higher than those of Kolanut dyes, with the sulphonated dyes being better than the crude extracts for both plants. Exhaustion, fixation, and migration properties of all the dyes are very good, while bleeding, glazing, levelness, and penetration of the dyes are, on the average, good. Exhaustion range from 52.23% for crude Kolanut dye to 85.04% for sulphonated Henna dye, fixation range from 50.72% for crude Kolanut dye to 63.32% for sulphonated Henna dye and migration range from 48.85% for crude Kolanut dye to 82.33% for sulphonated Henna dye. The fastness ratings of the sulphonated dyes were found to be higher than those of the crude dyes, suggesting that sulphonation has increased the affinity and substantivity of the crude dyes to leather.

Keywords: Affinity, Chrome Tanning, Dye Migration, Leather, Substantivity**INTRODUCTION**

Archaeological evidences have shown that dyeing has been extensively carried out for over 5000 years, particularly in India and Phoenicia (Kvavadze *et al.*, 2009). The dyes were obtained from animal, vegetable or mineral origin, with no or very little processing. By far the largest source of natural dyes has been from the plant kingdom, notably roots, bark, leaves and wood (Wouters and Rosario-Chirinos, 1992). Colorants improve the appearance, add culinary effect and promote acceptability of substrates (Kazaure and Abba, 2002). Although the *Colour Index* categorizes all colouring matters according to application characteristics, dyes can also be classified according to their chemical structure, shade, fastness, etc (Weiss, 1997).

Among the various substrates to which natural colourants have found application, leather is still one of the most favourable (Uppal, 2005). Over the years, colour chemists were (and still are) concerned with improving the existing methods of synthesizing natural dyes as well as developing more environment

friendly methods of preparing derivatives from the crude natural dyes. With increase in awareness of environmental protection and green house issues comes an increased interest in the synthesis, modification and use of natural dyes, hence the renewed interest in the use of natural dyes in textile industries and tanneries (Khopkar, 2008). Consequently, there is an increase in research and development activities by some of the dyestuffs giants towards production of natural dyes for use in various substrates because coloration of textiles, wood, leather and other substrates with natural dyes from plants is currently receiving increasing attention (Osabohien and Ukponmwam, 2002).

Henna (*Lawsonia inermis*) is a herb that is widely distributed in the tropics and may be found widely grown in Iran, Western India, Middle East, and West Africa (Kukowitsch, 1996). In Nigeria, the plant is cultivated mostly in the northern parts where it is used on hands and feet by ladies (Noah, 1995). The dye present in Henna is called Lawsone [2-hydroxy-1,2-naphthoquinone ($C_{10}H_6O_3$)] and is mostly present in its leaves at concentrations of up

to 2% (Booth, 1998). Cola is a genus of about 125 species of trees native to the tropical rain forests of West Africa (Akpuaka *et al.*, 1998). It is an evergreen tree growing up to 20 meters, with glossy and ovoid leaves. Cola trees are best known for their seeds or nuts which are rich in caffeine and thymolepte (Tende *et al.*, 2011). In Nigeria, the tree is grown mostly in the western part, but consumed mostly in the northern and eastern parts, especially during ceremonial occasions (Noah, 1995).

Leather is a durable and flexible material created via the tanning of putrescible animal raw hides and skins, primarily cattle hide (Askeland and Pradeep, 2005). Leather-making is now a scientifically-based industry that holds a constant challenge for chemists who, through research and understanding of the underlying principles, can control the quality of the leather and leather products to a much greater degree as chemists now have a better understanding of the chemistry of collagen, keratin and the various tanning-materials (Okonkwo, 2004). In chrome tanned leathers, the most reactive sites are the chromium nuclei, and these form the main points of fixation for dyestuffs (Hjeresen *et al.*, 2000).

The application of dyes on chrome-tanned leather in some cases has been carried out without mordanting as the chromium in the leather easily complexes with electron-donating groups of the dyes to produce good dyeings with improved fastness (Gordon, 1994). By far the most important class of dyes for dyeing leather is acid dyes and (1-hydroxy-2-methyl anthraquinone was reported (Guthrie *et al.*, 1992) to have less affinity than its sulphonated derivative, 1-hydroxy-2-methyl anthraquinone-4-sulphonic acid, for leather due to the higher solubility of the latter in water.

The present study was designed to extract dyes from Henna (*Lawsonia inermis*) and Kolanut (*Cola nitida*) plants using chloroform and acetone as solvents, sulphonate the extracts, apply the extracted and the sulphonated dyes on chrome-tanned leather and investigate the spectroscopic, dyeing and fastness properties of the dyes and the dyeings.

MATERIALS AND METHODS

Pretreatment

2.5 kg of fresh leaves of Henna (*Lawsonia inermis*) and Kolanut (*Cola nitida*) plants were separately heated at 85°C for 2hrs and air dried. The dried leaves were ground into fine powder and made to pass through sieves of mesh size 50-70µm screen.

Extraction of the Dyes

50g of the finely ground powder of the leaves was weighed, placed into the extraction thimble (Whatman 33mm X 94mm) of the Soxhlet extraction apparatus and the dye extracted with 250ml each of chloroform and acetone (Aldrich). The two extracts were concentrated by vacuum evaporation using rotary evaporator (Buchi, Rotavapor-RE, 218336).

Sulphonation

To 20g each of the concentrated crude dye extracts in 20 ml of distilled water was added, drop-wise, 15 ml of Chlorosulphonic acid (BDH) with gentle but constant stirring in a fume cupboard. 20 ml of sodium hydroxide (M and B) was later added. The product was stirred for 30 minutes and then heated to the boil for 30 minutes and left overnight extracted with ethanol. The sulphonated extract was further concentrated with rotary evaporator.

Determination of λ_{\max}

Standard solutions of the crude extracts and the sulphonated derivative dyes were prepared in n-hexane, ethanol and water and the wavelengths of maximum absorption (λ_{\max}) and the extinction coefficients of the crude extract and the sulphonated derivative dyes were determined in each case.

Dyebath Preparation

2g each of the crude extract and the sulphonated derivative dyes were placed in 250ml conical flask. 10ml of distilled water and two drops of formic acid (M and B) were added into the conical flask to serve as dyebath.

Dyeing the Leather

65g of the chrome-tanned leather was spread out on a glass tray and neutralized with 30ml of 0.1M sodium trioxocarbonate (IV) (BDH) and then

dyed separately with the crude extract and the sulphonated dye solutions using a liquor-to-solid ratio of 50:1.

Determination of Fastness Properties

Light, wash fastness (change in shade and degree of staining) and rub (wet and dry) ratings of the dyes in leather were determined by standard methods (Ingamells, 1993; Sperling, 2006).

Evaluation of Dye Migration

5cm X 30cm swatch of a substrate was separately padded in the dye liquor at 65°C for 45min and the swatch immediately placed on a horizontal glass plate. 10cm-diameter watch glass was placed on portions of the wet substrate. The substrate was then dyed at room temperature and the watch glass removed. The degree of migration of the dye particles was evaluated in comparison to the dye concentration in the area of the substrate covered by the watch glass to the dye concentration in the uncovered area of the substrate. The dye is quantitatively extracted with a suitable solvent from disks of the substrate of equal size of covered and uncovered areas. The percent migration is then calculated from the formula:

$$\% \text{ Dye Migration} = \left(\frac{1 - A_c}{A_u} \right) \times 100$$

where A_c is the absorbance of the dye extracted from the covered area and A_u is the absorbance of the dye extracted from the uncovered area.

Determination of Dye Exhaustion:

15cm³ of the dye solution from the dyebath was taken and its optical density measured at its λ_{\max} using Helios Alpha Unicam UV-Visible spectrophotometer. After completion of the

dyeing operation, the substrate is removed and the excess liquor squeezed back into the dyebath. The dyebath was then cooled to room temperature and made up to its original volume with distilled water. 15cm of this diluted dye solution is taken and its optical density measured at its λ_{\max} . The percent dye exhaustion on the substrate (the amount of dye absorbed) is then calculated from the two sets of measurements using the formula:

$$\% \text{ dye exhaustion} = \frac{(\text{Initial optical density} - \text{final optical density})}{(\text{Initial optical density})} \times 100$$

Triplicate measurements were made and the average value obtained in a dye solution for a substrate was recorded.

RESULTS AND DISCUSSION

The wavelengths of maximum absorption (λ_{\max}) of the dyes extracted from Henna (*Lawsonia inermis*) and Kolanut (*Cola nitida*) plants and their sulphonated derivatives in n-hexane, ethanol and water, with the associated eight wavebands are presented in Table 1 below. It can be seen that the wavelengths of maximum absorption (λ_{\max}) of the crude extract and the sulphonated dyes vary from 420 to 695nm which falls within the visible range. The λ_{\max} values of the crude dyes are higher than those of the sulphonated derivative dyes in all the three solvents compared in the table by 15 to 50nm. Comparing the λ_{\max} values of the extracted and sulphonated dyes in the solvents, a hypsochromic shift in the λ_{\max} values is seen. The hypsochromic shift in the values of the λ_{\max} is attributed to the electron-withdrawing effect of the sulphonic acid (SO₃H) group which decreases the electron density.

Table 1: Wavelengths of Maximum Absorption (λ_{\max}) of the Extracted and Sulphonated Dyes in n-hexane, Ethanol, and Water using Liquor-to-solid Ratio of 50:1.

Band	Wavelengths of Maximum Absorption (λ_{\max}) (nm)					
	n-hexane		Ethanol		Water	
	Extract	Sulphonated	Extract	Sulphonated	Extract	Sulphonated
1	465	450	470	460	440	420
2	470	460	490	480	460	450
3	490	480	535	530	490	480
4	540	520	585	575	540	510
5	570	555	610	595	580	575
6	610	590	640	620	630	605
7	650	630	665	635	670	645
8	685	680	690	685	695	690

Table 2 below shows the results of the dyeing properties (exhaustion, fixation and migration) of the n-hexane-extracted crude dyes and their sulphonated derivatives in chrome-tanned leather. From the table, it can be observed that the exhaustion (amount of dye absorbed) of the crude dyes and their sulphonated derivatives is generally very good (ranging from 52.23%, given by the crude dye extracted from Kolanut to 85.04%, given by the sulphonated dye derived from Henna). This very good exhaustion rating implies that all the four dyes exhaust well in leather. Migration of the four dyes from dyebath to leather is, although slightly lower than exhaustion, on the average, also very good. The values range from 48.85%, given by the crude dye extracted from

Kolanut to 82.33%, given by the sulphonated dye from Henna. These results suggest that leather is very much receptive to the dyes, although it is more receptive to the sulphonated dyes than the crude extracts.

If the fixation of the four dyes in the leather are compared, as displayed by Table 2, it can be seen that the fixation of the dyes, on the average, is good. The fixation values range from 50.72% for the crude dye extracted from Kolanut to 63.32% for the sulphonated dye derived from Henna. The good fixation ratings obtained are due to the good affinity of the dyes for the substrate, suggesting the existence of strong intermolecular forces of attraction between the dyes and the substrate.

Table 2: Dyeing Properties (Exhaustion, Fixation and Migration) of the Crude and Sulphonated Dyes in n-hexane in the Chrome-Tanned Leather.

Dye	Dyeing Property		
	Exhaustion (%)	Fixation (%)	Migration (%)
Crude dye from Henna	61.57	56.62	65.54
Sulphonated Henna dye	85.04	63.32	82.33
Crude dye from Kolanut	52.23	50.72	48.85
Sulphonated Kolanut dye	64.45	57.67	61.24

In Table 3 below are shown the dyeing properties (bleeding, glazing, levelness and penetration) of the ethanol-extracted crude dyes and their sulphonated derivatives in chrome-tanned leather. All the properties assessed are, on the average

good. This suggests that the dyes have good affinity (strong attraction between dye and substrate) and good substantivity (suitability of a dye for a particular substrate) for leather.

Table 3: Dyeing Properties (Bleeding, Glazing, Levelness and Penetration) of the Ethanol-Extracted Crude Dyes and their Sulphonated Derivatives in Chrome-Tanned Leather.

Dye	Property rating			
	Bleeding	Glazing	Levelness	Penetration
Crude dye extracted from Henna	Good	Good	Good	Very good
Sulphonated dye from Henna	Fair	Very good	Very good	Excellent
Crude dye extracted from Kolanut	Good	Fair	Fair	Good
Sulphonated dye from Kolanut	Fair	Good	Very good	Good

The comparative light, wash (change in shade and degree of staining adjacent white fabric) and rub (wet and dry) fastness ratings of the crude dyes and their sulphonated derivatives in leather are shown in Table 4 below. From the table, it can be

seen that the fastness ratings of the sulphonated derivative dyes are higher than those of the crude extract dyes. This result suggests that sulphonation has increased the affinity and substantivity of the crude dyes to leather.

Table 4: Light, Wash (Change in shade and degree of staining adjacent white fabric) and Rub (wet and dry) Fastness Ratings of the Water-Extracted Crude Dyes and their Sulphonated Derivatives in Leather at a Liquor-to-Solid Ratio of 50:1.

Dye	Fastness rating				
	Light	Wash		Rub	
		Change in shade	Degree of staining	Wet	Dry
Henna extract	5	2-3	3	2-3	2-3
Henna sulphonated	6	3	3	3	3-4
Kolanut extract	4	3	2-3	2-3	3
Kolanut sulphonated	5	3	3	3	3

CONCLUSION

It is clear from the results of this study that the sulphonated dyes have better dyeing properties and fastness ratings than the crude extracts from both plants, with dyes from Henna being more lightfast than those from Kolanut. As the dyes from both Henna (*Lawsonia inermis*) and Kolanut (*Cola nitida*) plants have shown very good affinity and substantivity for leather new methods of extracting natural dyes from locally-available plants should be explored for dyeing leather with a view to producing non-toxic colourants of improved fastness properties to the various agencies (heat, wet, rub, light, etc) likely to be encountered by the dyed substrates before, during and/or after use.

With the present global economic meltdown, high level of environmental awareness and pollution dangers, Nigeria stands a very good chance of improving her economy if the dyestuffs production potential of the large expanse of her vegetation is exploited to bail out our ailing import-dependent textile, leather and leather products industries, thereby saving foreign exchange.

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