

Preparation of Dye Fixatives from Leather Solid Waste

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I. INTRODUCTION

In India more than 24 million pieces of cattle hides, 22 million of buffalo hides, 106 million of goat skins and 37 million of sheep skins are processed in about 1600 tanneries. Approximately 2 lakhs tones of solid waste are generated annually from leather industry. In that around 110kgs of hairs are generated around 1- metric tons of raw hides/skins and this is utilised as a low value end products like painting brushes and woollen making etc.. The ultimate aim of this research is to develop dye fixatives from hairs which are generated in the unhairing operation.

The leather manufacture is one of the oldest technologies. Its empirical development is shrouded in the antiquity of man's history. Higher literacy, Fashion and improved economy of people brought in their wake inventions oriented to make life easier and fashionable. Coloring leathers intended to improve its aesthetic appeal and them sartiggy fashion demands necessarily results in increased sales value of the commodity, the ultimate goal of all technology.

1.1 Classification of dyes

The dyes, which are usually used by leather industry, can be broadly grouped in the following

1. Acid dye
2. Direct dye
3. Basic dye
4. Pre metallised dye
5. Reactive dye.

1.2 Mordant and their importance in dyeing

A mordant is a substance used in dyeing process either before or after the application of dyestuff to enable the dyestuff to on the leather or to develop a particular color or to enable the leather to have some affinity for the dye stuff or damper the dye's astringency to leather. Chrome leather can be dyed with acid dyestuffs but the leather may be uneven in shade to the rapidly with which the dyestuff is fixed by the leather. If the leather is treated with mordent like vegetable tannins/synthetic tannins a uniform shade is obtained owing to the good penetration.

1.3 The chemical and physical nature of leather fibres in Relation to dyeing

Leather consists of a three dimensional anisotropic network of tanned collagen fibres. The top surface (grain) consists of very tightly woven fine fibres interspersed with deep pores/pockets whereas the main portion of the leather consists of much coarser fibres arranged in three dimensions and containing no pores. The heterogeneous nature of the raw stock is fully reflected in its colouring properties. But, the affinity of the dyes and consequently the levelness of shade, depend not only on the chemical and physical structure of protein fibres but also on the character and the distribution of the tanning agents, fat liquors and other reagents that follow colouring. Both chemical nature of individual fibres and the physical nature of the fibre may affect the dyeing properties.

1.4 Dyeing on which penetration is desired

Essentially there are two ways in which the required penetration is obtained. However; this procedure employed depends on the depth of shade. The available methods are,

1. Selection of dyes that have inherent penetration
2. By alteration of the conditions of application and of the leather so as to reduce its affinity for the dye. So, once the affinity is reduced, it is possible to force through the surface layers of the leather even those dyes that have comparatively low inherent rates of penetration.

Since penetration is associated with affinity the former can be altered by changing the affinity of the leather for the dyestuff. This can be accomplished by,

1. Blocking the reactive groups of the leather or by adding other groups that can be utilized by the dyestuffs.
2. Changing the pH of the dye-leather system.
3. Changing the concentration of the dye bath (float)
4. The effect of solvent on the dye leather system (acetone)

1.5 Theory of dye fixation

The dyewoods, being closely related to the vegetable tannins, are similar to the vegetable tannins in their theory of fixation. The dyewoods are less colloidal in nature and will penetrate more easily than the vegetable tannins; but the general principles involved are the same. Since fixation is by hydrogen bonding, the lower pH, the greater is the fixation.

The direct dyes are attracted to leather fibres and will be absorbed in the surface of the leather by physical forces rather than by strong chemical bonds. Direct dyes are not penetrating when used on chrome or vegetable tanned leather; rather they are absorbed on the surface.

Acid dyes behave as weak acids in respect of absorption by the hides. The fixation and penetration of an acid dye follows the same general laws that apply to the acid syntans. The acid dyes are attracted to the leather through the positively charged groups of the hide/skin. Therefore, the undissociated carboxyl acid group on the hide will be able to form hydrogen bonds with the appropriate centers on the dye molecule and will be fixed at low pH. And yet, they will penetrate deeper into the skins as the pH value decreases. Since dyestuffs vary in molecular size, degree of solubility and acid-base characteristics, fixation of the dye on the leather will depend on all three factors, as well. Under given condition, the dyes will vary in these characteristics from one another. Negatively charged groups on the leather attract the basic dyes. Under acid condition, leather like untanned proteins will absorb hydrogen ions and assume a positive charge. The basic dye also positively charged will have little affinity for leather. As the pH is raised, the leather becomes more negatively charged and fixation of the basic dye takes place.

In the fixation of the dye, in addition to the pH factor discussed above, the presence of other materials on the leather fibre is also important to the behaviour of the dye in relation to the leather. Chrome tanned leather carries an additional positive charge due to the presence of the chromium cat ion that has combined with the hide. The acid dyes therefore, will be more strongly attracted to the chrome leather and will fix directly to it. Basic dyes, on the other hand have little affinity for chrome leather. In order to fix a basic dye onto chrome leather, a negative charge must be introduced on the leather. Mordanting chrome-tanned leather by adding a vegetable tanning material or an anionic syntan does this pretty well. The basic dye thus will be very strongly attracted to the mordant fibre and stable fixation will take place.

Factor that affect dye fixation

The dye stuff molecules are large complexes and can exhibit high secondary valency forces due to dipole moment and hydrogen bonding which play a significant part, once the dye molecule is drawn into close proximity of the fibres by the ionic forces. This accounts for the fact that whilst the dye may be fixed by acid, it is not entirely unfixed or stripped from the leather, if the acid neutralized subsequently with alkali. The factors which are affecting the dye fixations are

1. pH
2. Temperature
3. Concentration
4. Micelle formation
5. Tannage
6. Fixing agent
7. Exhaustion

1.6 Spectrophotometric curves and their relationship to color

It is possible to measure the colour of a transparent or opaque medium by irradiating it with, for example, tungsten light and measuring the amount that is transmitted or reflected respectively as a function of wavelength. A spectrophotometer is used to carry out this function and the graph that is produced is termed a spectrophotometer curve, which as long no fluorescence has taken place, provides a 'fingerprint' of that colour.

1.7 Stock solution preparation

A solution of the dye was made by dissolving the dye Dermapel BRL(02 gm) in distilled water taken in a 100ml standard flask and made up to the mark so as to give a 0.2% solution. From this stock solution 1.25ml was pipette out into a 50ml standard flask so that the concentration was 0.005%. This stock solution was used in all subsequent studies.

1.8 Preparation of Keratin hydrolysate

Around 100gms of cleaned sheep wools are taken in a 1000 ml conical flask and 800 ml of water and 100 ml of N/10 HCL added to extract Acidic keratin hydrolysate from keratin. Similarly instead of N/10 HCL added N/10 Na₂CO₃ to get alkaline keratin hydrolysate solution

II. SCOPE OF WORK

Two commercially available cationic dye fixatives have been chosen for the initial screening studies and a detailed investigation has been carried out with the two dye fixatives screened based on the results obtained in the screening studies. The performance of these dye fixatives in comparison with a natural based product based on mixed amino acid and low molecular weight peptides have been assessed at different concentrations and various pH condition.

To start with, a standard commercial recipe has been selected which makes use of a different parameters of various dye fixatives, the generic nature of which are as follows.

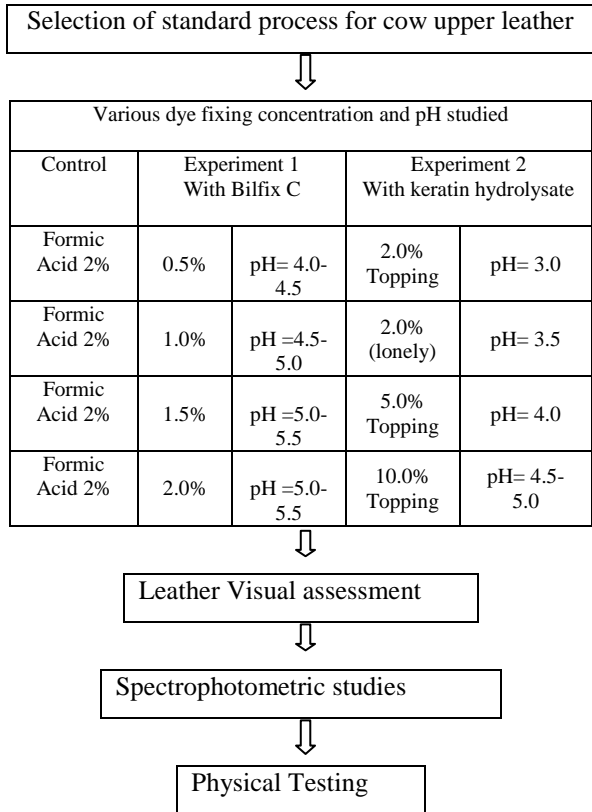
1. Bilfix C
2. Mixed Amino-Acid (natural product derived from denaturated keratin)

Based on the results, the two dye fixatives have been taken for detailed studies and the results have been discussed.

III. INVESTIGATION METHODS

1. Visual assessment
2. Instrumental color measurement
3. Rub fastness testing.

IV. EXPERIMENTS



V. RESULTS AND DISCUSSION

The following equipments are used for testing

1. Reference spectrophotometer

Milton Roy Colour mate HDS reflectance spectrophotometer.

2. Rub fastness Testing

Rub fastness tester from SASTRA based on the IS 6171:1971 LF: 9

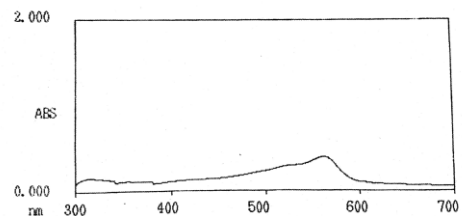
5.1 Spectral characteristics of Bilfix C

S.No	Characteristics	Dye Solution	Dye Soln.+ Bilfix C	Dye Soln.+ Bilfix C +HCL	Dye Soln.+ Bilfix C +Na ₂ CO ₃
1	pH	5.8	7.7	2.2	9.8
2	OD	0.422	0.933	0.413	1.033
3	Solution	Clear	Turbid	Clear	Turbid
4	Peaks	315.5	331.5	310.5	332.0

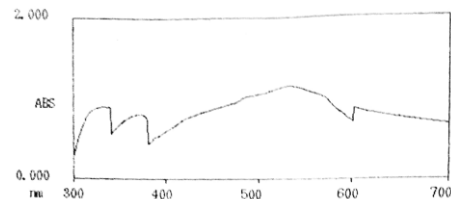
		355.0	371.5	356.5	371.5
		524.5	536.0	529.0	542.5
		559.5	602.0	602.0	602.0
5.	Absorbance	0.218	0.836	0.588	0.832
		0.138	0.741	0.192	0.750
		0.446	1.023	0.448	1.126
		0.438	0.890	0.168	1.256

6.1. Spectral characteristics of Keratin hydrolysate

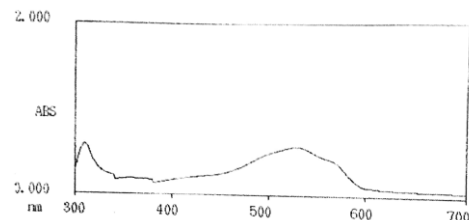
S.No	Characteristics	Dye solution	Dye Soln.+ keratin	Dye Soln.+ keratin +HCL	Dye Soln.+ keratin +Na ₂ CO ₃
1	pH	5.8	3.0	2.0	9.8
2	OD	0.436	0.359	0.367	0.649
3	Solution	Clear	Clear	Clear	Clear
4	Peaks	353.5	313.0	313.0	317.0
		379.5	355.5	357.0	364.0
		529.5	396.0	397.0	499.0
		559.0	560.0	505.0	602.0
5.	Absorbance	0.124	0.904	0.902	0.947
		0.125	0.622	0.635	0.635
		0.463	0.347	0.360	0.656
		0.403	0.477	0.373	0.259



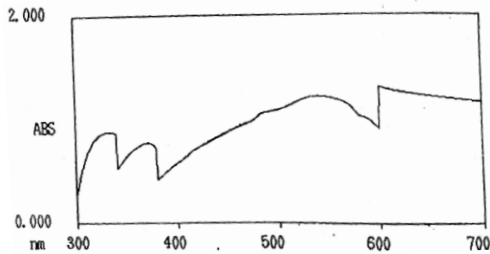
5.1.a. Fig Stock solution



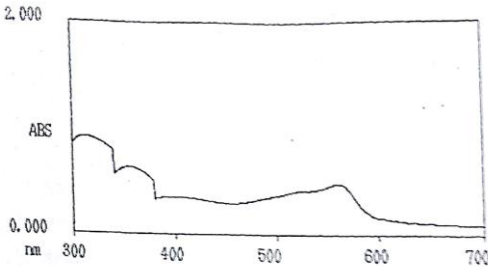
5.1. b. Fig Dye solution and Bilfix C



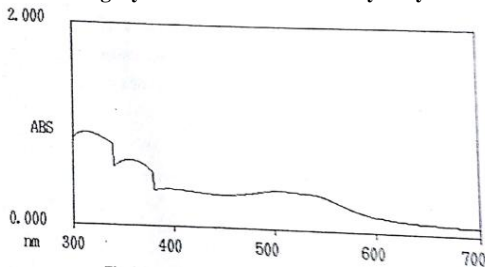
5.1.c. Fig Dye solution, Bilfix -C and HCL



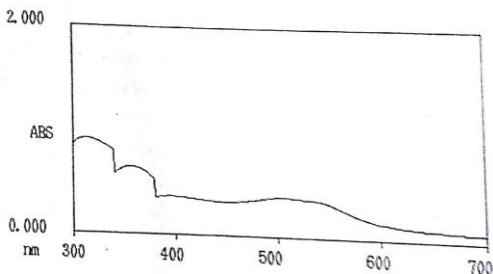
5.1.d. Dye solution , Bilfix C and Na₂CO₃



6.1.a.Fig Dye solution and Keratin Hydrolysate



6.1.b.Fig. Dye solution, Keratin Hydrolysate and HCL



6.1 c.. Dye solution, Keratin Hydrolysate and Na₂CO₃

3.1 Wet and Dry Rub Fastness Test- Bilfix- C

S.No	Samples	Dry Rub	Wet Rub
1	Formic Acid	4-5	4
2	Bilfix C- 0.5%	4	3-4
3	Bilfix C- 1.0%	4-5	4
4	Bilfix C- 1.5%	4-5	4
5	Bilfix C- 2.0%	4	3-4

3.1 Wet and Dry Rub Fastness Test- Keratin Hydrolysate

S.No	Samples	Dry Rub	Wet Rub
1	Formic Acid	4-5	4
2	Keratin.-2.0%	4-5	4
3	Keratin.-5.0%	4-5	5
4	Keratin.-10.0%	4-5	5

VII. CONCLUSION

From the comparative study of the spectral characteristics and run spectra of the dye fixatives in different pH, the keratin hydrolysate has better characteristics than commercial product Bilfix-C. It is clear that the precipitation of the Bilfix c with dye solution shown a higher OD values. In the visual assessment, Physical testing and based on the colour measurement results, it is clear that keratin product gave better results. These are all due to the secondary valency forces and also due to covalent bonding.

REFERENCES

- [1]. Ramamoorthy.G, Sehgal.P.K, Mahendra Kumar, Journal of society of Leather Technologists and chemists, Vol-73, P-168, 1989.
- [2]. Journal of American Leather Chemists Association, Vol-90, P-161, 1995.
- [3]. Journal of American Leather Chemists Association, Vol-82, P-1309, 1987.
- [4]. Journal of American Leather Chemists Association, Vol-90, P-365, 1995.
- [5]. Keratin & keratinization p236, 1968.
- [6]. T.P.S Astry, P.K.Sehal and T.Ramasami: Value added eco friendly products from tannery solid wastes. Journal of Environmental science & engineering.
- [7]. Srinivasan T S., MAnendrakumal: Krishnan T S and K.J Scaria (1985) "Chrome Shavings-a tannery waste, current practice and future trends for its utilization" Presented in the 3rd AAP Animal Science Congress, Seoul, Korea.