

THE EFFECT OF ACID DYES ON PAKISTANI WOOL FIBRES

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In order to obtain dyed material of level dyeing and better shades on Pakistani wool fibres, the effect of acid dyes, especially that of levelling and milling acid dyes was studied. To achieve better exhaustion of the dyebath at the shortest possible time at low temperatures and at the same time to obtain uniformity of dyed material, experiments have been carried out by adding certain dye assistants to the dyebath. The diameter of wool fibres have been determined with the various depths of shade, and to avoid the breakdown of peptide linkages, which results in the loss of strength of wool fibres, suitable pH values have been found out from the experimental work. It was found that 90% exhaustion of the dyebath occurs in 30 minutes by the addition of 3% amyl alcohol. The maximum dye uptake of true wool fibres was found to be 32.4%. The loss in strength of fibres were considerably reduced by controlling pH at 2-4 in levelling dyes and 4-6 in the case of milling (I.C.I.) acid dyes. The tensile strength of undyed wool fibres was found out to be 2010 kg./2cm.², while that of dyed wool fibres, 2016 kg./cm.².

Introduction

A good deal of research work has been done on acid dyes for wool fibres in advanced countries in this specific field, so that it was found befitting to start work on dyeing of Pakistani wool fibres, using the most recent technique. Generally, wool can be dyed with a wide variety of dyes.¹ Our study at this stage is confined to simple acid dyes, specially levelling and milling (Coomasie) I. C. I. acid dyes.

In order to meet the complaints of tippy² dyeing, (unequal absorption of dyes by different portions of the fibre) poor shades other than the specified standards, loss in the strength of dyes wool fibres, Lindberg³ has shown that the epicuticle of the fibre is mainly responsible for the rate of dyeing and felting properties of fibres. Accordingly, tippy dyeing, which is due to fibre degradation through atmospheric conditions, has been considerably improved by pretreatment of Pakistani wool fibres with certain chemicals, e. g. alcoholic potash, without changing the mechanical properties of wool fibres. The rate of dyeing, exhaustion of the dyebath, and the uniform levelling of dyes at the shortest possible time at low temperatures has further been increased by adding 3% amyl alcohol or 5% butyl alcohol (bath volume) as a carrier⁴ to the dyebath with or without the pretreatment of wool fibres by alcoholic potash.

The change in the diameter of wool fibres with the varying percentage of dye content was undertaken. The loss in the strength of dyed wool fibres was considerably improved through pH control,⁵ as at the lower pH values of the dyebath chemical degradation of wool fibres occurs, resulting in the complete breakdown of peptide linkages in the fibre and subsequently a decrease in fibre strength.

To promote level dyeing and exhaustion, anhydrous sodium sulphate and acid (depending upon the dyeing properties of dye) were used.

Experimental

1. *Purification of Water Soluble Acid Dyes.*—The method consisted⁶ in the precipitation of the dye from the hot concentrated aqueous solution by the addition of sodium acetate. The precipitate was filtered, redissolved and reprecipitated several times. The precipitate was treated with boiling ethyl alcohol in which sodium acetate is soluble. When the product gave no reaction for acetate, the extraction was stopped, dried and tested for the purity.

2. *Scouring.*—The raw wool was thoroughly scoured before dyeing by treating wool with 2% synthetic detergent 'Surf' and 1% soda ash (on the dry weight of goods being scoured) for 20 minutes at 49-60°C. The goods were rinsed and dried before being subjected to the dyeing operation.

3. *Pretreatment of Wool Fibres.*—The scoured wool was conditioned at 65% R. H. before treatment. The wool was then immersed in 100 times its weight of a solution containing 2g. potassium hydroxide in 96 ml. ethyl alcohol (100%) and 4 ml. water for 15 minutes. Immediately after removing the wool from the alcoholic potash solution it was put into a solution containing 1 ml. conc. sulphuric acid in 96 ml. ethyl alcohol (100%) and 4 ml. water. After a few minutes' steeping in this solution, the wool was rinsed with distilled water and dried at 70°C. overnight.

4. *Preparation of Dyebath.*—For levelling acid dyes the dyebath was prepared at the ratio (1:50) with 5-10% of anhydrous sodium sulphate and

3-4% of sulphuric acid (96%) and the proper percentage of well dissolved dye (all assistants and chemicals were calculated on the original weight of the fibres). The scoured wool fibres introduced into the dyebath at 49-60°C. at pH 2-4, the temperature was raised to the boil in 45-60 minutes and boiling continued for another 45-90 minutes. In the place of sulphuric acid the same quantity of formic acid can be used. In milling acid dyes the initial sulphuric acid content was replaced by 3-5% of 28% acetic acid, while keeping pH values 4-6 and temperature 70°C. a critical temperature below which little dyeing occurs for some milling dyes.

5. *Diameter Measurements.*—The diameter of the three types of fibres i.e. true, heterotypical and medullated fibres (usually at the central portion of the fibre) were determined by projectional microscope (Lanameter) at fixed relative humidity and percentage regain before and after dyeing it with the various percentages of dyes.

6. *Colorimetric Measurements.*—In the case of change in diameter of untreated wool fibres with Napthalene Red J.S. (C.I. No. 176), the percentage strength of the dye extracted from the fibre with the help of 2.5% aqueous pyridine and sometimes subsequently with sodium borate, was estimated colorimetrically. The percentage of accessible dye on the fibre at different intervals while determining the rate of dyeing has also been found out with the same apparatus.

7. *Dynamometric Measurements.*—The mean strength of the wool fibres were determined before and after dyeing with single fibre testing machine.

8. *Amyl Alcohol Treatment.*—3% amyl alcohol as a carrier (on bath volume) was added to the above prepared bath but at a ratio (1:250) keeping the temperature of the dyebath at 60°C. and pH at 6.4, the effect of the carrier on the rate of dyeing was observed on alcoholic potash treated and untreated wool fibres.

9. *Specific Gravity Bottle Method.*—The percentage volume increase of the dyed and undyed wool fibres, as in diameter measurements, were determined by specific gravity bottle method using toluene as inert liquid for dyed and undyed wool fibres.

Discussion

The acid dyes include many different groups of chemicals but they are called acid dyes, because they are applied in acid solution. It so happens

that they are all sodium or calcium and alkali salts of sulphonic acids,¹¹ but the sulphonic acid group appears in many dyestuffs for solubilizing purposes and is not the name of a class of dyestuff. It may appear strange that animal fibres can be dyed with either acid or basic dyestuff, but this is due to their amphoteric character for they possess both acid and basic groups, the dyeing is reasonably fast, because of chemical combination. When the amino groups are removed from wool, affinity for the acid colours is theoretically as follows: the wool base first forms a salt with the acid in the dyebath and this compound then reacts with sodium salt of the coloured acid to produce a new combination between the wool base and the coloured acid. The dyed wool is thus a compound of wool (acting as a base) and the coloured acid.⁸

The acid used in the dyebath may be sulphuric acid, formic acid or acetic acid, the first named is the cheapest and most commonly used. In addition to the dye and the acid, a small amount of anhydrous sodium sulphate¹² is also added to prevent the dye rushing on to the fibre and giving uneven results.

While¹³ in recent years dye makers have made much progress towards the provision of dyes having an acceptable degree of water solubility and suitability for the fibres being dyed, the art of dyeing has been aided by the discovery of methods of modifying fibres temporarily, so as to make them more receptive to dye.

In order to remove the possibility of changing the mechanical properties of wool fibres, the wool for experimental work was scoured with the above standard method, using distilled water and taking other necessary precautions, as wrong scouring may cause hinderance in the dyeing of wool.

It has been observed that the large scale unevenness is due to the fact that the fibres in different areas of the cloth may possess different affinity for the dye. This is because the fibre differences are due to varying amount of degradation undergone by the individual fibres which results in differing accessibility to dye. The treatment of wool with alcoholic potash almost eliminates fibre to fibre differences, which under condition of dyeing give marked differences on untreated wool.

The use of 3% amyl alcohol as a carrier has been shown in Figure 1. The addition of it to the dyebath increases the dyeing rate at the shortest time at a low temperature. It is clear

from Figure 1, that by addition of amyl alcohol, to the dyebath 90% exhaustion occurs in 30 minutes, and 95% in two hours, while without it 60% exhaustion of untreated wool fibres occurs in 7 hours, but even then the uniformity of dye on the fibres was poor. It was found that there is a small difference in the rate of dyeing by the addition of 3% amyl alcohol on treated and untreated wool fibres.

In the case of change in the diameter of wool fibres, with percentages of dye, there was no relation between change in diameter and dye content. However, the relation between change in percent volume determined by projection microscope and specific gravity bottle method, and the percent dye content was found. It has also been found, as shown in Figure 2, that the finer wool absorbs more dye as compared to the coarse wool. The maximum dye uptake of true wool fibres was found to be 32.4%. From Table 2 it is clear that below 10% of dye content no change in diameter was found and that is why the commercial dyed wool fibres are found without change in diameter. The results in Table 2 also indicate that the diameter of dyed wool fibres is definitely larger than that of the undyed fibres and that the differences between the two become increasingly larger as the dye content increases.

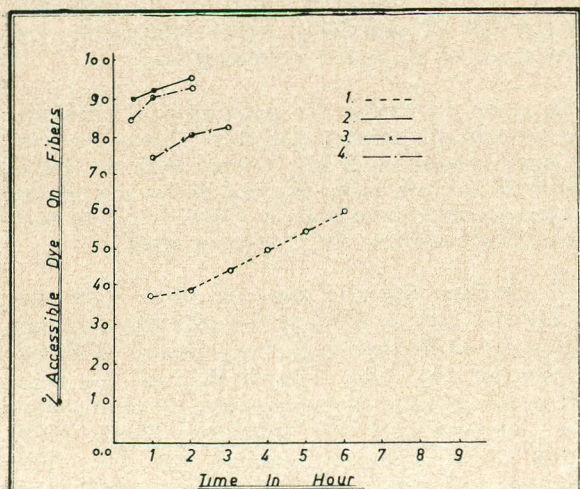


Fig. 1.—Dyeing rate of Naphthalene Red J.S. on wool; Temperature 60°C.; Bath ratio 1:250. Ph-6.2; Depth of shade -2% (on wt. of fibres).

Conclusion

The following conclusions may be drawn from the foregoing discussion:

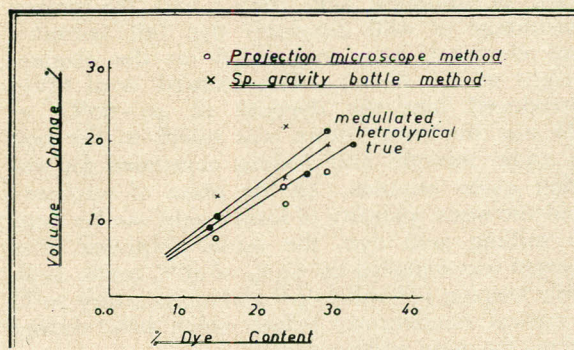


Fig. 2.—Relation between % dyeing content and % change in volume determined by projection microscope and Sp. gravity bottle method.

TABLE I.—RATE OF DYEING AND PERCENTAGE EXHAUSTION OF THE DYEBATH WITH PURIFIED NAPHTHALENE RED. J. S. (C. I. No. 176) AT VARIOUS INTERVALS OF DIFFERENT CHEMICAL TREATED WOOL FIBRES.

Sr. No.	No. of observations	Nature of fibres	Time of dyeing (Hours)	% Exhaustion of dyebath
1.	1	Untreated	1	38
	2	Untreated	2	40
	3	Untreated	3	45
	4	Untreated	4	50
	5	Untreated	5	55
	6	Untreated	6	—
	7	Untreated	7	60
2.	1	Untreated + 3% amyl alcohol to the dyebath	1	92
	2	Do	2	95
3.	1	Treated wool with alcoholic potash	1	75
	2	Do	2	80
	3	Do	3	82
4.	1	Wool treated as (3) + 3% amyl alcohol	1	90
	2	Do	2	92

TABLE 2.—FIBRE DIAMETER IN MICRON (μ) OF DYED AND UNDYED KAGHANI WOOL FIBRES AT 65% RELATIVE HUMIDITY.

Dye content (% dry wool)	Fibre diameter in microns (μ)		
	True (4.9% regain)	Heterotypical (5.4% regain)	Medullated (6.2% regain)
0.0	28.23	42.26	56.12
13.6	—	44.12	59.01
14.4	29.23	—	—
23.1	—	45.27	59.42
26.4	30.43	—	—
29.0	—	45.65	61.98
32.4	31.0	—	—

1. In order to attain the correct shade, the dye and assistants should be calculated on the original weight of the material to be dyed.

2. Amyl alcohol as a carrier has proved very effective in promoting fibre to fibre evenness on untreated wool fibres at low temperatures and getting maximum exhaustion of the dyebath in minimum time. By using amyl alcohol, steam, electricity, and time can also be saved considerably.

3. The desirable properties of wool fibres have also been preserved by using amyl alcohol and controlling of pH values i.e. 2-4 in acid dyes while 4-6 in case of milling acid dyes.

4. The finer wool absorbs more dye as compared to the coarse wool. It was also found that below 10% of dye (on wt. of fibres) no appreciable change in diameter occurs, with the result that better results can be achieved below the given limit.

TABLE 3.—VOLUME INCREASE ON DYEING AT 65% RELATIVE HUMIDITY.

Dye content (% dry wool)	Vol. increase of Kaghani wool fibres (%)*		
	True	Heterotypical	Medullated
13.6	—	9.0	10.5
14.4	7.9	—	—
23.1	—	14.9	12.1
26.4	16.1	—	—
29.0	—	16.9	21.9
32.4	20.5	—	—

*Percentage volume change = $100 \left[\left(\frac{D_u}{D_d} \right)^2 - 1 \right]$

TABLE 4.—VOLUME INCREASE OF THE SAME WOOL FIBRES AS IN TABLE 2 DETERMINED BY SPECIFIC GRAVITY BOTTLE METHOD.

Dye content (% dry wool)	Percentage volume increase		
	True	Heterotypical	Medullated
13.3	—	9.0	10.5
14.4	15.5	—	—
23.1	—	15.9	22.3
26.4	16.1	—	—
29.0	—	20.0	21.9
32.4	20.5	—	—

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References

1. R.E. Kirk & D.F. Othmen, *Encyclopaedia of Chemical Technology* (The Interscience Publishers, Inc., New York, 1956), Vol. 15, pp. 115.
2. Von Bergen & R. Mauersberger, *American Wool Handbook* (Book Pub., Inc., New York, 16, N.Y., 1948), 2nd Ed., pp. 777, 759.
3. Joel Lindberg, *Textile Research J.*, **23**, 67, 573, 585, 398, 69 (1953).
4. *Ibid.* **25**, 528 (1956).
5. C. H. Nicholls, *Textile Research J.* **4**, 500-502 (1957).
6. T. Vicker Staff, *The Physical Chemistry of Dyeing* (Oliver and Boyd, London, 1954), 2nd Ed. pp. 19-48.
7. R. E. Kirk & D.F. Othmen, *Encyclopaedia of Chemical Technology* (The Interscience Publishers Inc., New York, 1956), Vol. 5, pp. 366-369.
8. J. Meybeck & G. Gianola, *Proceeding to Intern. Conf. of Austr.* (Morris & Walker Pty., Ltd., Melbourne 1956), Vol A. pp. B-115, 119.
9. E.R. Kaswell, *Textile Fibres Yarn and Fabrics* (330 West Forty Second St. New York, 36, N.Y., 1953), pp. 10.
10. B. E. Hartsuch, *Introduction to Textile Chemistry* (John Wiley and Sons Inc. New York, 1950, pp. 108.
11. J. T. Marsh, *Textile Science* (Chapman & Hall Ltd., London, 1958), 4th Ed. pp. 234.
12. George L. Clark, *The Encycl. of Chem.* (Reinhold Publishing Corp., New York, 1957), pp. 322.
13. A. J. Hall, *Textile J. of Australia*, **1**, 199 (1962).