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DYEING OF WOOL WITH REACTIVE DYES AT TEMPERATURES BELOW THE BOIL

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ABSTRACT

Wool was dyed at temperatures below the boil with reactive dyestuffs. Methods were developed to dye wool at 60°C from a solvent assisted medium and at 80°C in the presence of a reducing agent. The fastness properties and the covalent dyestuff fixation attained was determined. A one bath shrinkproofing-dyeing method is also described.

KEYWORDS

Dyeing, reactive dyes, low temperature dyeing, solvent assisted dyeing, reducing agent, one bath shrinkproofing and dyeing.

INTRODUCTION

In conventional dyeing reversible attachment to active sites is usually responsible for the absorption of soluble dyestuff by the fibrous substrate. The fastness of a non-reactive dyestuff is determined by hydrogen bonding, strong electrovalent links and non-polar Van der Waals forces.

The characterising feature of reactive dyes is that they form a stable covalent linkage with the substrate. The wet fastness of reactive dyes is therefore superior to that of conventional dyes. In many reactive dyeings the covalent link is established by the substitution of an active halogen on the dyestuff molecule by an hydroxy-, amino- or thiol group belonging to the substrate:

$$\text{Wool} - \text{OH} + \text{Dye} - \text{Cl} \rightarrow \text{Wool} - \text{O} - \text{Dye} + \text{HCl}$$
$$\text{Wool} - \text{NH}_2 + \text{Dye} - \text{Cl} \rightarrow \text{Wool} - \text{NH} - \text{Dye} + \text{HCl}$$
$$\text{Wool} - \text{SH} + \text{Dye} - \text{Cl} \rightarrow \text{Wool} - \text{S} - \text{Dye} + \text{HCl}$$

The covalent link can also be established by addition of an hydroxy-, amino-, imino-, thiol- or a similar reactive fibre site to a reactive vinyl bond attached to the chromophoric group of the dyestuff:

$$\text{Wool} - \text{OH} + \text{CH}_2 = \text{CH} - \text{Dye} \rightarrow \text{Wool} - \text{O} - \text{CH}_2 - \text{CH}_2 - \text{Dye}$$
$$\text{Wool} - \text{NH}_2 + \text{CH}_2 = \text{CH} - \text{Dye} \rightarrow \text{Wool} - \text{NH} - \text{CH}_2 - \text{CH}_2 - \text{Dye}$$
$$\text{Wool} - \text{SH} + \text{CH}_2 = \text{CH} - \text{Dye} \rightarrow \text{Wool} - \text{S} - \text{CH}_2 - \text{CH}_2 - \text{Dye}$$

In wool dyeing relatively high standards of wet fastness over a wide range of shades have been obtainable for many years with conventional acid milling, pre-metallized and chrome dyes. In dyeing wool to brilliant shades, however, many of the conventional methods have often failed to supply good fastness properties and it is particularly in this category that reactive wool dyeing finds its major attraction.

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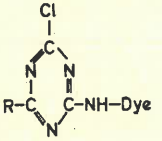
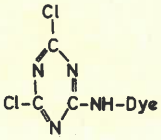
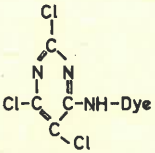
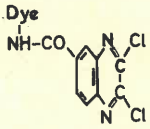
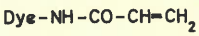
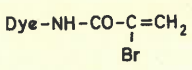
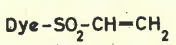
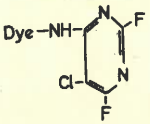
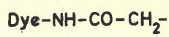
	Monochloro-triazinyl	Procion H Cibacron Cibacrolan	I.C.I. Ciba Ciba
	Dichloro-triazinyl	Procion M	I.C.I.
	Trichloro pyrimidyl	Drimarene Reactone	Sandoz Geigy
	Dichloro-quinoxalino	Levafix E	Bayer
	Acrylamido	Procilan	I.C.I.
	Bromo-acryl-amido	Lanasol	Ciba
	Vinyl sulphonyl	Remazolan	Hoechst
	Chloro-difluoro pyrimidyl	Verofix Reactolan Drimarene	Bayer Geigy Sandoz
	Chloro-acetyl	Cibalan Brilliant	Ciba

FIGURE 1

Structures of Reactive Dyes

The chemical structure of reactive dyes (see fig. I) usually consists essentially of highly sulphonated acid dyes to which the reactive group is attached. Since the chromophoric structures of these dyes are similar to those of ordinary non-reactive dyes, the dyestuff will have an affinity for wool in acid medium and will be retained on the fibre by electrostatic interaction even if no covalent bonding is established. In sharp contrast, however, to the excellent wet fastness of covalently bonded dyestuff molecules, the wet fastness of the unfixed dye is usually poor. The presence of even relatively small concentrations of unfixed dye, therefore, impairs the wet fastness of the reactive dye considerably and it is consequently important that dyeing methods, which will ensure the highest degree of fixation possible, be employed.

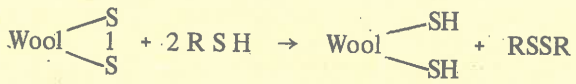
The rate of reaction between the dyestuff and the wool is dependent both on temperature and the duration of the dyeing. The degree of covalent fixation can therefore be improved either by dyeing at higher temperatures or by extending the duration of the dyeing. It is, however, known that the boiling of wool leads to a certain amount of damage such as some yellowing and that this increases as the duration of the boiling is increased. Yellowing can, however, be inhibited by dyeing at lower temperatures but the degree of covalent fixation is low and the wet fastness properties therefore poor.

The purpose of the investigation reported below was to find a method by which the rate of reaction between wool and reactive dyestuff could be increased. It was hoped that this would facilitate covalent fixation even when dyeing at relatively low temperatures without having to extend the duration of the dyeing beyond that which would be acceptable in practice.

As is shown above, the reactions between wool and dyestuff can involve either dyestuffs in which a halogen is replaceable or a dyestuff in which an addition to an activated double bond takes place, while the hydroxyl-, amino-, or thiol groups of the wool can be involved in the reaction. There is a fair abundance of hydroxyl groups in wool but these groups are relatively unreactive. Schöberl[1] showed that hydroxyl groups are about a 100 times less reactive than amino groups and 10,000 times less reactive than thiol groups. It is therefore unlikely that the reaction between the dyestuff and the hydroxyl groups in the wool fibre will be very great.

The highly reactive thiol groups are present in normal wool fibres only in relatively low concentrations and it is therefore probably the amino groups which are primarily involved in this type of reaction. If it were possible to increase the reactive thiol groups in the wool to a sufficiently high concentration, their very high reactivity could be utilized to give rapid fixation of the reactive dyestuff.

Schöberl[1] has shown that rapid fixation of reactive dyestuffs is possible onto wool which had been treated with mercaptans which, by means of a thiol-disulphide interchange reaction, increases the thiol content of the wool:



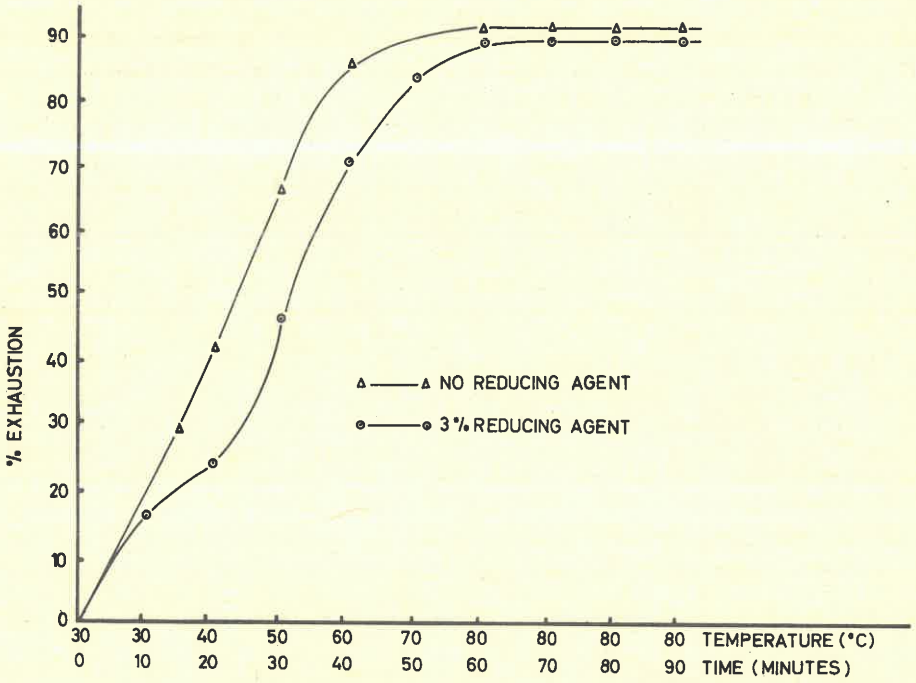


FIGURE II(b)

Exhaustion Curves for Remazolan Brilliant Blue R

Each dyeing was duplicated, once exactly as described above and once with 3% sodium bisulphite added. The temperature was raised at 1°C/min to 80°C and dyeing continued at this temperature for 30 min.

The results of covalent fixation between the dye and the wool are given in Table I which show that the presence of bisulphite had a profound influence on the extent of covalent fixation attained within a specific time. Surprisingly, it was found that this method was applicable not only to those dyestuffs containing the reactive halogen side chain, but also to those depending on activated vinyl groups for their reactivity.

THE EFFECT OF THE REDUCING AGENT ON THE RATE OF DYEING

Addition of bisulphite to the dyeliquor only has a slight influence on the rate of dyeing (see fig. II(a) and (b) This and the fact that high values of covalent fixa-

TABLE I

COVALENT FIXATION VALUES OBTAINED BY DYEING AT 80°C IN THE ABSENCE AND PRESENCE OF SODIUM BISULPHITE

DYE	% COVALENT FIXATION	
	Without $NaHSO_3$	With 3% $NaHSO_3$
Levafix Brilliant Red E – 2B	69.3	89.2
Levafix Brilliant Scarlet E – 3B	64.1	81.0
Lanasol Blue 3G	57.5	89.3
Lanasol Red 6G	59.9	88.9
Primazin Red P3B	40.5	84.3
Primazin Yellow PGL	54.4	88.8
Cibalan Brilliant Red BL	57.2	70.6
Remazolan Red BB	84.8	90.4
Remazolan Brilliant Blue R	91.4	91.5

tion could be obtained in the presence of bisulphite proved that the addition of a reducing agent to the dyebath offers the opportunity of dyeing wool at temperatures below the boil within a relatively short period of time.

EXHAUSTION AND LEVELLING

At low temperatures exhaustion and levelling proved to be major problems because at these temperatures the dye molecules in the dyebath have insufficient kinetic energy to break through the charge barrier surrounding the wool fibre, with the result that exhaustion was very slow. Migration of the dye in the fibre is also known to be slower at low temperatures than at high temperatures and this contributes to the poor levelling. Furthermore, because of the extremely rapid dyestuff fixation which takes place at the freshly created thiol groups, what little opportunity for dyestuff migration has existed is nullified out and levelling problems become severe.

It was thought that the use of organic solvents may assist both in the problems of exhaustion and of levelling.

DYEING FROM A SOLVENT ASSISTED MEDIUM

Peters and Stevens[3] described how the use of alcohols of low miscibility with water but with high dissolving power for the dyestuff, forms thin layers round the wool fibre. Some extraction of dyestuff into this thin layer of solvent then takes place to give an extremely high concentration gradient at the surface of the wool fibre which in term is condusive to rapid exhaustion of the dyestuff. Moreover, because the alcohol forms a thin layer over the entire surface of the wool fibre, absorption is more uniform and levelness is increased. Some experiments with the aid of these solvents led to the adoption of the following procedure:

The bath was set at 30°C with 4% (w/v) n-butanol, 1% Albegal B (Ciba) and 4% Acetic Acid (80%) (pH 4.5–4.7)

The goods were treated for 10 min, the dyestuff added, the temperature raised at a rate of 1°C/min to 60°C, 3% sodium bisulphite added and dyeing continued at this temperature for 30 minutes.

This procedure produced satisfactory levelness and adequate covalent fixation as can be seen in Table II. Exhaustion was also virtually 100%. Although this procedure can therefore be regarded as satisfactory, the high cost of n-butanol and also of other suitable alternatives is prohibitive. Even if this cost could be off-set to some extent by the re-use of the same liquor for consecutive dyeings, recovery procedures may be complicated and the desirability of a simple straight forward and inexpensive procedure is clearly evident.

TABLE II

COVALENT FIXATION VALUES OBTAINED BY DYEING AT 60°C IN THE PRESENCE OF 4% (W/V) N-BUTANOL

DYE	% COVALENT FIXATION
Lanasol Yellow 4G	81.2
Lanasol Red 6G	82.7
Lanasol Blue 3G	77.0
Remazolan Yellow G	69.9
Remazolan Brilliant Blue B	84.2
Remazolan Orange 3R	79.6
Reactofil Blue 2GL	77.1
Reactofil Brilliant Red 2B	91.9
Reactofil Brilliant Yellow 4GL	89.9
Procilan Brilliant Yellow R200	72.4

TABLE III

COVALENT FIXATION VALUES OBTAINED BY DYEING AT 80°C

DYE	% COVALENT FIXATION
Lanasol Yellow 4G	93.9
Lanasol Red 6G	91.8
Lanasol Blue 3G	91.4
Remazolan Yellow G	80.8
Remazolan Brilliant Blue B	82.1
Remazolan Orange 3R	88.7
Reactofil Blue 2GL	90.9
Reactofil Brilliant Red 2B	93.4
Reactofil Brilliant Yellow 4GL	94.6
Procilan Brilliant Yellow R200	82.6
Procilan Yellow GWN	70.1

TABLE IV

BRIGHTNESS VALUES FOR WOOL DYED AT 60°C IN THE PRESENCE OF 4% (W/V) N-BUTANOL, 80°C AND 100°C

DYE	60°C	80°C	100°C
Lanasol Yellow 4G	27.2	27.3	25.9
Lanasol Red 6G	61.4	58.9	53.4
Lanasol Blue 3G	65.1	66.5	51.7
Remazolan Yellow RR	23.7	24.1	19.8
Remazolan Red F3B	50.9	54.4	46.1
Remazolan Brilliant Blue B	49.5	50.7	42.0
Reactofil Brilliant Yellow 4GL	26.5	28.1	26.6
Reactofil Brilliant Red GL	61.9	58.5	55.9

DYEING AT 80°C WITH THE AID OF A REDUCING AGENT

It was decided to investigate the dyeing behaviour at 80°C since this temperature is well above the temperature of strike of most dyestuffs and should therefore produce reasonable exhaustion. Levelness was considered to be still a potential problem but this could be overcome by the use of some of the powerful levelling agents

commercially available. It did soon transpire, however, that it was necessary to prevent the rapid fixation of the dyestuff to the reactive thiol groups of the wool until such time as level uptake of the dyestuff by the fibre had occurred.

Good results were obtained by dyeing at 80°C until such time as most of the dyestuff had been exhausted whereafter the reducing agent was added to give rapid fixation of the dyestuff to the wool. It was found that only 15 minutes of dyeing at 80°C after the addition of the reducing agent was sufficient to bring about satisfactory covalent fixation of the dyestuff. These results are summerised in Table III.

A dyeing procedure which gave satisfactory results is the following:

The bath was set at 40°C with the following:

4% Ammonium sulphate
1% Albegal B
1.5% Acetic acid (80%) (pH 5.3–5.6)

The goods were treated in this liquor for 10 minutes, the dissolved dyestuff added, the temperature raised at 1°C/min to 80°C and a further 2.5% acetic acid (80%) added gradually over 15 minutes to lower the pH to 4.5–4.7 Sodium bisulphite (3%) was then added and the temperature kept at 80°C for a further 15 minutes.

BRIGHTNESS OF DYEINGS OBTAINED AT TEMPERATURES BELOW THE BOIL

Table IV contains the brightness values of dyeings which had been carried out with the aid of n-butanol at 60°C and also those which had been carried out at 80°C. For purposes of comparison brightness values of dyeings which had been carried out in the conventional method at the boil are also given. These results show that a substantial increase in brightness is obtained by reducing the temperature from 100°C to 80°C, but the further reduction from 80°C to 60°C does not appear to have caused any further improvement.

FASTNESS PROPERTIES OF DYEINGS OBTAINED BY DYEING IN THE PRESENCE OF REDUCING AGENTS

(a) **Light Fastness**

Table V gives the fastness rating of dyeings dyed at 60°C in the presence of n-butanol, 80°C, and conventional dyeings at the boil.

It will be observed that the light fastness of the samples dyed at 60°C and 80°C is slightly lower than that of samples dyed at the boil. This effect may however be due to the bleaching which had taken place during dyeing in the presence of bisulphite and the known fact that bleached wool yellows more rapidly than unbleached wool.

TABLE V

LIGHT FASTNESS VALUES FOR WOOL YARN DYED AT 60°C IN THE PRESENCE OF N-BUTANOL, 80°C AND 100°C

DYE	60°C	80°C	100°C
Lanasol Yellow 4G	5 – 6	5 – 6	6
Lanasol Red 6G	5 – 6	5 – 6	6
Lanasol Blue 3G	5 – 6	5	6
Remazolan Orange GR	4	4	4 – 5
Remazolan Red R	3	3	3 – 4
Remazolan Brilliant Blue B	5	5 – 4	5 – 6
Reactofil Brilliant Yellow 4GL	4 – 5	4 – 5	5
Reactofil Brilliant Red 2B	4 – 5	4	5
Reactofil Blue 2GL	5	5	6
Procilan Brilliant Yellow 2GS	6 – 7	6	7
Procilan Red BWN	4	4	5

(b) **Wash and Perspiration Fastness**

According to Swanepoel and Mellet[4] the wet fastness properties of reactive dyeings is a direct function of the degree of covalent fixation. The results summarized in Tables II and III show that covalent fixation and therefore the wet-fastness properties for low temperature dyeings and dyeings dyed at the boil are similar.

BREAKING STRENGTH

Table V contains breaking strength values for wool dyed at 60°C in the presence of n-butanol, wool dyed at 80°C, and wool dyed at 100°C in the conventional manner in the absence of bisulphite. Although it is known that treatment of wool with reducing agents normally decreases the breaking strength of the fibres this effect must have been limited in the dyeings described above as shown by the very slight changes in breaking strength of the wool.

DYEING OF PASTEL SHADES

The described method of dyeing wool at 80°C offers particular advantages in the dyeing of pastel shades. In the dyeing of full shades, slight changes in the ground colour of the material are normally obscured by the depth of the shade itself. However, in pastels the ground colour of the wool has a profound effect on the appearance of the dyed material and it is here that the described method finds particular

TABLE VI

BREAKING STRENGTH VALUES (IN KG) FOR WOOL YARN DYED AT 60°C IN THE PRESENCE OF N-BUTANOL, 80°C AND 100°C

DYE	60°C	80°C	100°C
Lanasol Yellow 4G	2.45	2.48	2.46
Lanasol Red 6G	2.39	2.42	2.43
Remazolan Red F3B	2.59	2.47	2.43
Remazolan Yellow GL	2.57	2.45	2.60
Reactofil Brilliant Red GL	2.39	2.43	2.42
Reactofil Yellow RL	2.40	2.39	2.45
Procilan Brilliant Yellow 2GS	2.48	2.37	2.31
Procilan Red GS	2.58	2.35	2.47

use. However, it must also be emphasized that the reduction in dyeing time and the savings in steam with the dyeing of deeper shades is certainly significant. In the dyeing of pastels, not only is the formation of the yellow tone in the wool inhibited by the use of the lower temperature, but the reducing agent actually functions as a bleaching agent which further enhances the brightness.

Sometimes the brightness of pastel shades can also be affected by a greying effect of metals present in water or in the reagents used and it was found that in most of the treatments where bisulphite was used for the production of bright fast dyeings that this effect could be improved upon by the addition of E D T A to the dyebath.

ONE BATH SHRINKPROOFING-DYEING PROCEDURE

The realisation that bisulphite and many dyestuffs show reasonable compatability in the same dyebath suggested that wool might be shrinkproofed and dyed from one bath. Such a step would be time saving and economical.

In the process finally developed as a result of this reasoning, normal shrinkproofing was carried out with sodium dichloro-isocyanurate and the dechlorination procedure was carried out as usual with sodium bisulphite. The dyestuff was then added at the conclusion of the dechlorination procedure for which 15 minutes was allowed, and the dyeing executed as described above. The resultant dyeings were found to be superior in brightness to those carried out in two stages where the bath was dropped after dechlorination.

It must, however, be emphasized that the dyeings obtained with highly reactive dyes tended to be skittery but that this problem could be overcome by raising the pH of the dechlorination bath to 6 (ammonium acetate) before addition of the

dyestuff. The temperature was then raised to 80°C and the pH gradually lowered to 4.5–4.7 by the addition of acetic acid.

SULPHUR STOVING

Some chromophores are sensitive to sulphur dioxide and reactive dyes which contain such chromophores, will naturally not be suitable for use in the described dyeing procedures. It is therefore necessary to ensure that dyes used in these methods contain chromophores of sufficient stability to the reducing agent to tolerate the presence of the bisulphite.

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