SAWTRI
TECHNICAL REPORT

108

CONTINUOUS REACTIVE DYEING OF WOOL IN UREA MEDIUM

by

O. A. SWANEPOEL
and
J. P. VAN DER MERWE

SOUTH AFRICAN WOOL TEXTILE RESEARCH INSTITUTE
P.O. BOX 1124
PORT ELIZABETH

CONTINUOUS REACTIVE DYEING OF WOOL IN UREA MEDIUM

by

O. A. SWANEPOEL and J. P. VAN DER MERWE

ABSTRACT

Wool was dyed by a continuous pad-steam process with reactive dyes dissolved in concentrated solutions of urea. The extent of covalent fixation of the dyestuff molecules was determined. Levelness of the dyeings as well as their fastness to washing, to alkaline perspiration, and to rubbing were investigated. The influence of time of steaming, nature of the added tenside, squeeze roller pressure, and urea concentration on the properties and appearance of the dyed wool was examined.

INTRODUCTION

Concentrated solutions of urea are useful media for the continuous dyeing of wool by a pad-steam process[1,2]. Urea is inexpensive and its recovery is therefore not required. It is also non-toxic, non-corrosive and readily available.

Urea reacts[3] with the reactive groups of certain types of fibre-reactive dyestuffs to form derivatives which are no longer able to establish covalent linkages with the substrate. The presence of such "deactivated" dyestuff derivatives on wool — and it follows that this situation may conceivably arise in the application of reactive dyestuffs to wool in the presence of urea — has a detrimental effect on the fastness properties of the dyeing.

In view of the industrial potential of the continuous urea dyeing method and of the ever increasing importance of reactive wool dyeing, the present investigation was undertaken to establish the fastness and levelness of reactive dyeings obtained by this process.

EXPERIMENTAL

Materials

Cibacrolan (CIBA), Drimalan (S), Lanasol (CIBA), Levafix (By), Procilan (ICI), and Remazolan (FH) dyestuffs were used in this investigation.

The nonionic surfactant, *NS1,* was a trimethylnonyl ether of polyethylene glycol containing 6 mols of ethylene oxide and was obtained from commercial sources in the form of a 90% solution.

The nonionic surfactant, *NS2,* a commercial product, was the ethylene oxide condensate of nonyl phenol containing 10 mols of ethylene oxide.

The anionic surfactant, sodium dodecyl sulphate (SDS), was of laboratory reagent quality and was obtained from Koch-Light Laboratories.

The following dye assistants were used: Albegal B (CIBA), Avolan SC (By), Ekaline F (S), Lyogen BPN (S), Neovadine AN (CIBA), and Remol GE (FH).

The top used was prepared from a 60/64's quality merino wool. The linear density of the top was 17 g/m.

Preparation of dye liquors

A solution of each dyestuff was prepared to contain the dyestuff (10 g/*l*), sufficient urea to give the required concentration, and tenside (surfactant or dye assistant; 5 g/*l*). The pH was adjusted with acetic acid to 4.5 – 5.0, except for the solutions of the Procilan dyes where the pH was set at 6.5.

Remazolan dyestuffs require activation before dyeing. This was carried out before addition of urea and the other additives by treating the dissolved dyestuff for 30 min with trisodium phosphate at room temperature.

Dyeing

All dyeings were carried out on a Benz apparatus with the wool top encased in polyester netting. The process entailed a single dip with a dwell time of about 3 sec, immediately followed by a nip. The time interval between passage through the squeeze rollers and entry into the steam box was about 20 sec. Care was taken to ensure that the steam used was not oversaturated in order to avoid the occurrence of a grey veil effect. The pressure on the squeeze rollers (50 degrees shore) was 10 Kg/cm^2 except when this was specifically varied to study the effect of roller pressure on the dyeing.

The pick-up was usually about 80%.

Rinsing

Each sample of dyed top, weighing approximately 60g, was rinsed continuously by a single dip and nip. The bowl contained 3*l* of water and the dwell time was about 15 sec. An aliquot of the rinse water, which also contained the liquor extruded from the top by the rollers, was centrifuged and the concentration of dyestuff determined colorimetrically.

Pyridine extractions

Dyestuff not covalently linked to the wool was removed by exhaustive extraction with 20% aqueous pyridine at about 50°C. The pyridine extracts were subsequently made up to a specific volume, centrifuged, and the dyestuff concentration determined colorimetrically.

Determination of pick-up

It is advisable in pad-steam processes that the material enters the steamer as soon as possible after the dyestuff has been padded on. In view hereof pick-up was determined using separate pieces of top which were weighed before and after application of the dye liquor. These samples were subsequently discarded.

Calculation of degree of covalent dyestuff fixation

The total weight of dyestuff padded onto the wool could be calculated from the pick-up values. The difference between these values and the amount of dyestuff lost during rinsing gave the concentration of the dyeing. By subtracting that fraction of the dyestuff extractable by pyridine from the concentration of the dyeing and dividing by the latter, the fraction of covalently linked dyestuff could be calculated.

Dye fastness determinations

Fastness of the dyeings to washing[4] in commercial soap solutions (pH 9 – 9.5), to alkaline perspiration[5], and to rubbing[6] were carried out by established methods.

Investigation of the occurrence of ring dyeing

This was done microscopically on cross-sections of dyed fibres embedded in methyl methacrylate.

Thin layer chromatography (TLC)

Dyestuff samples were chromatographed on layers of Silica Gel G (Merck), 200 microns thick, prepared and activated in the usual manner. The solvent used was n-butanol, ethanol, water (4 : 1 : 1).

Determination of the free amino groups in wool

The free amino group content of samples of top was determined by the method of Leach *et al*[7]. In the case of wool which had been treated with urea solution, residual urea was removed by extraction with water before the analysis was carried out.

Determination of thiol groups

Thiol groups were determined as described by du Toit *et al*[8].

Wetting tests

Samples of 20% aqueous urea containing the various surfactants or dye assistants were placed in 500 ml beakers. A 1 inch square of 2/2 twill worsted cloth was cut and carefully placed on the surface of each of the solutions and the time for it to wet out and sink was recorded. The process was repeated ten times and the average value calculated. In some cases where wetting action was poor a weight was placed on the cloth square to cause the cloth to wet out and sink in a convenient time.

RESULTS AND DISCUSSION

The reproducibility of the values obtained for covalent dyestuff fixation on wool tops dyed by the urea process was not very high. The reason for this is not clear but it is possible that the lack of precise control of wet pick-up and of the volume of the rinse water (a feature of the particular experimental set-up) could have affected the calculation of fixation values. Nevertheless, the fixation values given in Table I, which are averages of several experiments, are sufficiently reliable to prove that the degree of dyestuff fixation attained in the continuous urea process is in many cases somewhat lower than that obtained in conventional dyeing. (The latter values are also listed in Table I to facilitate comparison.)

Low fixation values may result when the time of heating is insufficient to permit reaction between the dyestuff and the wool to proceed to completion.

TABLE I

Degree of Covalent Dyestuff Fixation and Dye-fastness Properties of Wool Dyed by the Continuous Urea Method

Dyestuff	% Fixation in conventional dyeing*	% Fixation obtained with steaming time (min)			Concentration of dyeing (%)	% Dyestuff lost in rinsing	Fastness** to						
							Washing		Alkaline perspiration			Rubbing	
		5	7.5	10			Change in shade	Staining of wool	Change in shade	Staining of wool	Staining of cotton	Dry	Wet
Remazolan Orange GG	87	77	–	–	0.7	9	3	5–4	3	3	3–4	5–4	4
Remazolan Brilliant Blue R	85	75	75	75	0.7	6	2–3	4–5	4–3	3	4	5	5–4
Lanasol Blue eR	80	68	68	66	0.7	5	3	4–5	4	3–4	4	5	5
Lanasol Red B	87	80	86	83	0.6	5	5–4	3	3–4	4	4	5–4	4–5
Drimalan Scarlet WL	68	64	69	66	0.7	11	2–3	5–2	3–2	3–4	4	5–4	4
Drimalan Yellow 4GL	74	74	65	73	0.6	5	2–3	5–4	3–2	4	4–5	5–4	5–4
Cibacrolan Yellow 2G	40	39	–	–	0.7	14	3–2	5	3–4	4–3	4	5	5–4
Cibacrolan Blue 8GK	42	38	34	34	0.6	14	2–3	4	4–3	3–2	3–2	5–4	4
Procilan Yellow 2RS	58	38	43	54	0.6	4	3–4	5–4	4	5	5–4	5–4	4–5
Procilan Red GS	47	40	–	–	0.7	3	3–4	5–4	4–5	4–5	4–5	5–4	4–5
Procilan Brilliant Yellow 4GS	–	78	–	–	0.6	6	3–2	5	4	4	5–4	5	5
Levafix Brilliant Red E3B	–	79	78	80	0.5	17	2–3	5	3	3	3–2	5–4	4

*Dyeing for 60 min at 100°C.
**Values given with 5 min steaming.

If that were the position, extension of the time of steaming would improve the degree of fixation. This was not the case in the present investigation since, as shown by Table I, the extent of covalent fixation remained virtually unchanged when the steaming time was increased by 50% and even by 100%.

Since inadequate steaming times are not responsible for the reduced fixation values, reaction of urea with the amino groups of the wool and also with the reactive groups of the dyestuffs may be considered as possible explanations. It is known (see for instance ref. 9) that urea reacts with aliphatic amino groups. Therefore, boiling wool in a 20% solution of urea for 60 min has been found[3] to eliminate about half the free amino groups in the keratin. As is to be expected, the rate of dyestuff fixation in fibres thus treated was greatly diminished. In contrast, however, analysis of wool steamed for 10 min after a solution of 20% urea had been padded on, showed that the free amino group content had only been reduced by about 4% (see Table II). The thiol groups are more reactive than amino groups but because of their relatively low concentration in wool protein, thiols are probably less important than amino groups in the fixation of reactive dyestuffs. In any event, the effect of steaming wool in the presence of urea decreased the concentration of thiol groups by only 4 micromoles per gram of wool (Table II) and it seems unlikely that such a slight decrease could have a significant effect on the dyestuff fixation. Moreover, unless so few amino and thiol groups remain that all the reactive dyestuff molecules cannot be accommodated (for a 1% dyeing this would require removal of about 90% of these groups) the rate rather than the extent of dyestuff fixation would be affected. Fixation is already at its final value after 5 min of heating and the decreased fixation values can therefore not be a factor since this will only reduce the reaction rate. Consequently, reaction between urea and the amino groups in the protein must be ruled out as a possible contributing influence.

TABLE II

Effect of Steaming in Presence of 20% Urea on the Amino- and Thiol Group Concentration in Wool

	Amino groups as m.eq. leucine/g wool	Thiols as micromols/g wool
Untreated	183	24
After 5 min steaming	175	20

Deactivation of the dyestuff by reaction between the reactive side chain of the dyestuff molecule and urea, or between the dyestuff and the decomposition products of urea, could possibly take place in the pad bowl and also during steaming. To investigate this point Remazolan Orange GG was used because vinyl sulphones which form the reactive group of all Remazolan dyestuffs, are known[3] definitely to react with urea. Thin layer chromatograms were obtained of aliquots of a solution of this dyestuff in concentrated aqueous urea after 60 min in the pad bowl and also after 10 min in the steam box. As explained under *Experimental* above the dyestuff in the latter treatment was carried through the steam box by polyester fabric onto which the liquor had been padded. Polyester is a non-substantive support for the reactive dyestuff so that subsequent removal of the dyestuff from the fabric after steaming was simple. It also does not react with the dyestuff, an aspect which may well have complicated interpretation of the results of the reaction between the dyestuff and the urea. A measure of the extent of the reaction between the dyestuff and urea is provided by the intensity of the various bands on the TLC plates. Thus plate A, Fig. 1 shows that although unreacted dyestuff (band F) was still the major component in the dyestuff solution after steaming, the concentrations of the derivatives at positions E and D were appreciable. In contrast, very little of these derivatives had been formed in the pad bowl. It is therefore concluded that deactivation of the dyestuff occurs predominantly in the steam box rather than in the pad bowl.

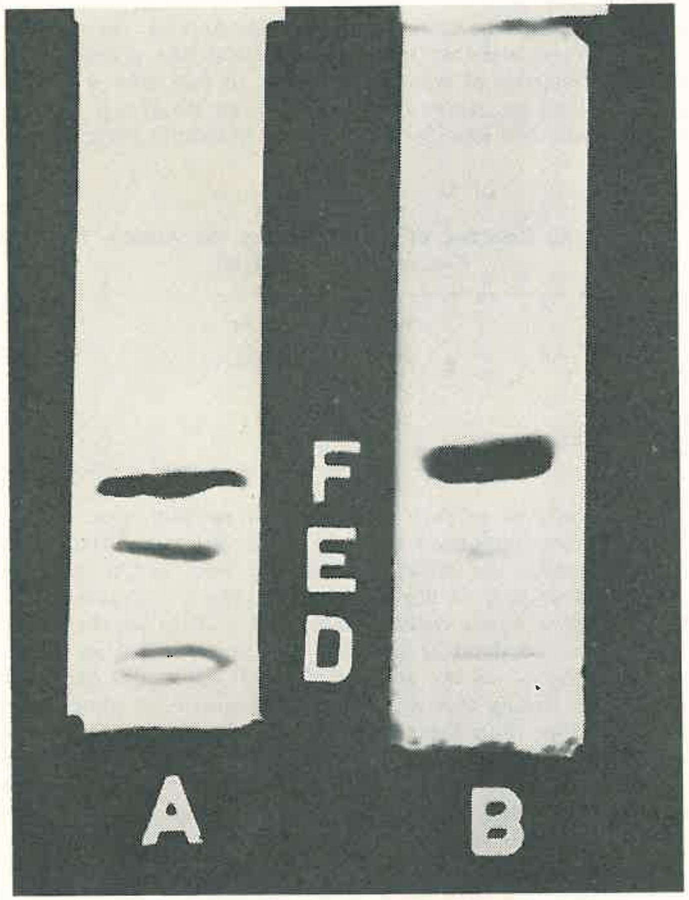

Figure 1: Thin layer chromatograms of Remazolan Orange GG dyestuff heated in 20% aqueous urea. Sample shown in Plate A had been steamed for 10 min whilst that in plate B had been kept in the pad bowl for 60 min at 45°C. Band F is unchanged vinyl sulphone dyestuff whilst E and D are unreactive dyestuff derivatives.

It is interesting to note the absence of *betha*-hydroxyethyl sulphone derivative between bands E and F on both TLC plates in Fig. 1. This derivative is the hydrolysis product of vinyl sulphones and its absence shows that little, if any, hydrolysis occurred either in the pad bowl or during steaming.

The amount of unreactive derivatives formed during steaming was not determined quantitatively but visual comparison of the intensity of the bands makes it clear that the concentration of these undesirable products is sufficiently high in the case of plate A, Fig. 1 to have an effect on the degree of fixation. It is, however, necessary to point out that the relative quantity of deactivated dyestuff formed during steaming in the actual dyeing of wool may be considerably less than the proportion depicted by Fig. 1, plate A. This is because of competition between the wool and the urea for reaction with the dyestuff. Since the rate of reaction of dyestuff with wool is very much higher than with urea[3], such competition would limit the occurrence of the urea-dyestuff reaction. This theory is supported by the results given in Table III which show that the degree of covalent fixation taking place is essentially independent of the concentration of urea in the liquor. The rate and therefore the extent of the reaction between dyestuff and urea would be proportional to the concentration of the reagents. Since the degree of covalent dyestuff fixation is not decreased with increasing

TABLE III

Covalent Dyestuff Fixation of Wool Dyed* in Liquors containing various Concentrations of Urea

		% Fixation attained by dyeing at urea conc. of		
Dyestuff	Tenside	10%	20%	35%
Remazolan Orange GG	Remol G.E.	80.2	76.9	73.6
	SN1	79.8	77.8	75.3
Procilan Red GS	Procilan Salt L	40.7	39.6	38.6
	SN1	38.5	44.2	38.7
Levafix Brilliant Red E2B	Avolan SC	79.3	84.1	84.7
	SN1	85.1	86.4	86.8

*Steaming time 5 min.

TABLE IV

Values of Covalent Dyestuff Fixation and Fastness to Washing of Wool Dyed in the presence of various Tensides

	% Fixation when using as tensides*				Change in shade during washing				Staining of wool during washing			
Dyestuff	*NS1*	*NS2*	*SDS*	Other	*NS1*	*NS2*	*SDS*	Other	*NS1*	*NS2*	*SDS*	Other
Remazolan Orange GG	77	80	75	80[a]	3	3–4	3	3–2	5–4	5–4	5–4	5–4[a]
Lanasol Red B	82	76	79	80[b]	3	3–2	3	2	5–4	5–4	5–4	5–4[b]
Drimalan Scarlet WL	64	66	68	67[c]	2–3	3–2	2–3	5–4	5–4	5–4	5–4	5–4[c]
Cibacrolan Yellow 2G	39	41	36	39[d]	3–2	3–4	3	3–2	5	5	5	5[d]
Procilan Red GS	40	46	37	45[e]	2–3	2	2	2	4–5	4–5	4–5	5–4[e]
Levafix Brilliant Red E2B	79	80	81	79[f]	2–3	3	2	2–3	5	4–5	4–5	5[f]

* Unless stated otherwise, concentration of tenside was 0.5%.

[a]Remol GE; [b]Albegal B; [c]Ekaline F (0.38%) + Lyogen BPN (0.12%); [d]Neovadine AN; [e]Procilan Salt L; [f]Avolan SC.

urea concentration, it is concluded that the influence of the urea-dyestuff reaction on the degree of fixation attained is relatively unimportant.

Although the formation of unreactive derivatives by reaction of urea with Remazolan dyestuffs has been established beyond any doubt, other dyestuff classes, e.g. Lanasols, do not appear to be deactivated by urea[3]. Yet, as shown by the results in Table I, Lanasol dyestuffs also suffer a reduction in their usually high fixation values when applied by the urea method. It is therefore clear that factors other than the deactivation of dyestuff molecules also influence the degree of covalent fixation. The nature of these influences and the manner in which they operate are not yet understood.

Table I shows that the amount of dyestuff lost in the rinse bowl differs for the various dyestuffs and can sometimes be considerable. This may complicate shade matching while the cost of the wasted dyestuff must also be considered.

Table I contains the ratings for fastness to washing, to alkaline perspiration and to rubbing. Since increased steaming times had no effect on the ratings, only those obtained on wool steamed for 5 minutes have been included in this table. The independence of fastness properties on increased steaming times is not surprising considering that fixation values were not influenced by an extension of the steaming period.

While rubbing fastness was invariably good in both wet and dry testing, change in shade during alkaline perspiration testing and during washing was considerable. The latter observation is consistent with the relatively low fixation values recorded throughout, which means that a comparatively large proportion of the dyestuff on the wool is not covalently bound and therefore capable of bleeding during alkaline treatment. Procilan dyes, being of the 1:2 premetalised type, have better fastness properties in the unfixed state than unreacted molecules of the non-metalised reactive dyes. This explains why shade changing during alkaline washing or perspiration testing is somewhat better with Procilans than with the other reactive dyestuffs.

Staining of adjacent wool during washing was not extensive, a fact to which the poor affinity of the dyestuffs at higher pH values no doubt contributed. During alkaline perspiration testing cotton did not stain excessively but staining of wool was generally somewhat worse.

To determine the influence of the wetting agent on the efficacy of the urea continuous process, three different surfactants were investigated. Dyeings were also carried out with various dye assistants commonly used in conventional dyeing procedures. The results, given in Table IV, show that the nature of the tenside had little effect on either the degree of dyestuff fixation or on the fastness of the dyeings to washing. Ratings obtained for fastness to rubbing and to alkaline perspiration (not given in Table IV) were similarly independent of the nature of the additive.

Although the nature of the tenside had little effect on either the fastness properties of the dyed goods or on the degree of covalent dyestuff fixation, its influence on the levelness of the dyeings obtained was found to be of the greatest importance. Only those additives with the most powerful wetting action were found to be suitable for the production of level dyed tops. The sinking times listed

TABLE V

Sinking Times of Wool Cloth Samples in Solutions of 20% Urea containing 5% of various Tensides

Tenside	Sinking times (sec) of sample carrying			
	0 g	0.5 g	1 g	2 g
NS1	4.6	–	–	–
NS2	3.6	1.1	–	–
SDS	–	18.3	–	4.8
Remol GE	–	–	26.4	–
Albegal B	–	–	17.5	–
Ekaline F (0.38%) + Lyogen BPN (0.12%)	–	–	28.2	15.4
Neovadine AN	–	–	6.6	–
Procilan Salt L	–	–	–	82
Avolan SC	–	–	–	330

in Table V show that surfactant *NS1* is a most effective wetting agent and, accordingly, dyeings produced with this additive were invariably level. With less potent wetting agents on the other hand, the ensuing dyeings were frequently unlevel. To illustrate the importance of the wetting properties of the tenside, a photograph is reproduced in Fig. 2 depicting tops dyed with three different dyestuffs in the presence of either *NS1* or one of the tensides with poorer wetting properties. It shows that, in contrast to the level dyeings obtained with the aid of *NS1*, the centres of the tops had not been dyed at all when the poorer wetting agents were employed. The unlevel dyeings shown in Fig. 2 were the worst cases obtained and unlevel effects were usually less striking. In fact, quite level dyeings were obtained in many cases with some of the less effective wetting agents but consistently level dyeings were only possible when *NS1* was used. Levelness can usually be improved slightly by an increase in the pressure of the squeeze rollers. The improvement however is marginal and is unlikely to overcome the problems arising from the use of an inferior wetting agent.

The levelness of dyeings increased with the use of more concentrated solutions of urea. This effect was noticeable when tensides with poorer wetting properties were employed. In the present investigation no difference in levelness could be observed between tops dyed with liquors containing 20% and 35% urea provided *NS1* was employed. It is, however, conceivable that even with a good wetting agent 35% urea may be required if the top used tends to dye unlevel as may be the case with tops made from heavily weathered fibres.

The addition of dye assistants (essential as they are in conventional dyeing) to the dye liquor used in the urea process is not justified. This statement is supported, in the first place, by the fact that the improvement in levelness produced by a good wetting agent cannot be further improved upon and, secondly, by the observation that fixation values were not increased when the dye liquor contained these tensides.

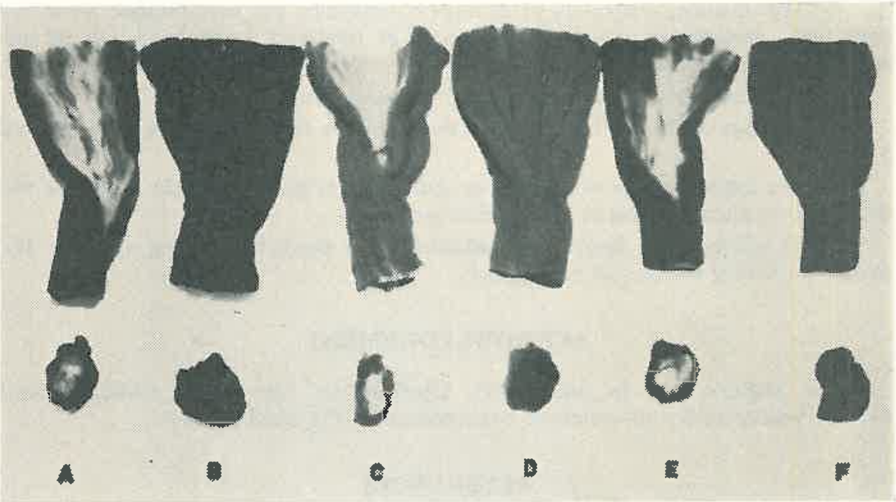

Figure 2: Dyed tops showing the inability of dyestuff to penetrate to the fibres in the centre of the top when tensides with poor wetting properties were used. Partially opened tops are shown in the top row whilst the lower row shows cross-sections of the wool top.

A = Levafix Brilliant Red E2B with Avolan SC.
B = Levafix Brilliant Red E2B with *NS1*.
C = Remazolan Orange GG with Remol GE.
D = Remazolan Orange GG with *NS1*.
E = Procilan Red GS with Procilan Salt L.
F = Procilan Red GS with *NS1*.

In view of the unlevelness of dyeings sometimes obtained with the use of less effective wetting agents, it was surprising to find that the occurrence of ring dyeing was not extensive. Some cases of ring dyeing were actually observed but these were infrequent and, once again, none of them included wool dyed in the presence of the good wetting agent *NS1*.

CONCLUSIONS

(a) Reactive dyeing of wool by conventional methods usually gave higher values of covalent dyestuff fixation than the continuous urea method of dyeing. The magnitude of this effect however is not such that it precludes the use of reactive dyestuffs in the urea method.

(b) Wet-fastness properties of dyeings obtained by the urea method were not very high, presumably due to the presence of relatively large quantities of unreacted dyestuff on the wool.

(c) Fastness of the dyeings to rubbing was satisfactory.

(d) Dyeings could not be improved by extending the time of steaming beyond 5 min.

(e) The nature of the surfactant or dye assistant added did not influence the degree of covalent fixation or the fastness properties.

(f) To ensure level dyeings the addition of a powerful wetting agent to the dye liquor was of the utmost importance.

ACKNOWLEDGEMENT

The authors wish to thank Mrs. Gloria Spies for skilfull assistance and Mr. G. Scheepers for microscopic examination of the dyed tops.

REFERENCES

1. Angliss, I. B., and Delmenico, J., *J. Soc. Dyers Col.* **80,** 543 (1964).
2. Anon, *Wool Text. Ind.* p. 7 (March, 1967).
3. Swanepoel, O. A., unpublished results.
4. Society of Dyers and Colorists, "Standard Methods for the Determination of the Colour Fastness in Textiles", 3rd Edit., Bradford, 1962, p. 104.
5. *Ibid.* p. 71.
6. *Ibid.* p. 83.
7. Leach, S. J., and Hill, J., *Biochemistry* **2,** 807 (1963).
8. Du Toit, E. H., van Rensburg, N. J. J., and Swanepoel, O. A., *J. S. African Chem. Inst.* **18,** 52 (1965).
9. Wild, F., "Characterisation of Organic Compounds", Cambridge Univ. Press, 1947, p. 170.

N.K.BPK,P.E.11174