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ASPECTS OF THE SHRINKPROOFING AND BLEACHING OF WOOL

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INTRODUCTION

The production of whites and of pastel shades in wool is complicated by the fibres' natural cream to yellow ground colour and their tendency to yellow during certain processing operations. Yellowing which takes place during exposure of the manufactured article to sunlight, may affect the appearance of the article and is of importance to the manufacturer as well as to the consumer. The acquisition of information concerning the yellowing of wool, both during and subsequent to the application of a particular treatment, is therefore highly desirable.

The shrinkproofing of wool by chlorination methods generally causes some yellowing. This also happens when salts of dichloroisocyanurates (DCCA) are employed as the source of chlorine. This particular type of reagent has many commendable features such as ease of application and retention of fabric strength, and is employed in the production of shrinkproofed and flat-set fabrics suitable for the manufacture of items such as shirts and blouses. Many of these garments are required as whites or in pastel shades and the yellowing behaviour during or after processing is therefore particularly important. The present investigation was undertaken to obtain information on this subject.

EXPERIMENTAL

Materials

Wool fabric: Unfinished plain weave; square set (55 ends and picks per inch) fabric made from R37 Tex/2 (2/47's worsted) in warp as well as weft. Weight per square yard = 5.3 oz.

DCCA: The sodium salt of dichloroisocyanuric acid was purchased as the commercial product Fichlor 60S (Fisons).

Shrinkproofing:

Initial experiments were carried out on a laboratory scale winch but in the final experiments 6 meter lengths of material were treated on a winch of 150 *l* capacity. Reagent concentrations were selected to produce an area shrinkage of less than 2% after machine washing (see later) for 3 hours.

Prior to all shrinkproofings, the material was scoured in a solution containing 0.5 g/*l* Eriopon HD (Geigy) and 4% NaCl (on the weight of the fabric).

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Shrinkproofing with 4.5% DCCA: The fabric was run for 15 min in a solution containing 4.5% DCCA and 10% Na_2SO_4, adjusted to pH 6.0 by addition of acetic acid. The temperature of the solution was 20°C. After 20 min the pH was lowered to 5.0 (acetic acid) and this was followed by a further decrease to pH 4.0 – 4.5 after another 20 min. Exhaustion was allowed to proceed to a value of 85% of the active chlorine whereafter clearing was commenced by the addition of 10% sodium bisulphite. After 10 min running, the temperature was increased to 45°C and the process continued for a further 20 min.

The fabric was rinsed and dried unless bleaching was required in which case it was proceeded with as described under *Bleaching* below.

Shrinkproofing with 4.5% DCCA and 0.2% potassium permanganate: After running the fabric for 15 min at pH 6.0 and 20°C in a bath containing 10% glauber salt, 4.5% DCCA was added. At 60% exhaustion of the DCCA, 0.2% permanganate was added. The run was allowed to proceed until the complete discharge of the permanganate colour (ca. 30 min). The pH was then lowered to 4.0 – 4.5 (acetic acid) and clearing carried out with 10% sodium bisulphite as described in the previous paragraph.

Unless subsequent bleaching of the fabric was required, rinsing and drying were carried out by the usual methods.

Shrinkproofing with 3% DCCA and 2% potassium permanganate: The bath was set at 20°C and pH 6.0 with 10 g/*l* glauber salt. After 15 min running 3% DCCA and 2% permanganate were added. The reaction was allowed to proceed for 60 min after which the wool was cleared as before.

Bleaching:

Bleaching was carried out immediately after shrinkproofing and clearing using the same bath as in these preceeding processes.

Bleaching with sodium formaldehyde sulphoxylate: Sulphoxylate* (5%) was added to the clearing bath and after running the wool for 5 min, the temperature was rapidly increased to 85°C and held for 30 min. The wool was then rinsed and dried.

Bleaching with sulphoxylate and fluorescent brightening agent: This operation corresponded in every respect with the previous except for the addition of 1% Leucophor PAF (Sandoz) to the bath with the 5% sulphoxylate.

Flat-setting:

The fabric was padded (100% expression) with a 1% solution of sodium bisulphite and steamed on a decatizing machine for 10 min.

Application of formaldehyde/thiourea resin[1]:

The fabric was padded (100% expression) with a solution of thiourea (2.5%), formaldehyde (25% of a 35% solution) and 0.1% wetting agent (Tergitol TMN – Union Carbide) in water and was subsequently dried in a tenter at 100°C for 12 min.

*For the sake of brevity, "sulphoxylate" is used for sodium formaldehyde sulphoxylate. This compound is commercially available as Formosul (ACC), Rongalit C (B.A.S.F.), etc.

Washing:

Samples of finished fabric were washed in a household washing machine (Bendix) to determine the influence of washing on the subsequent light fastness. The wash liquor was a 0.2% solution of Softly (Lever Bros) at a temperature of 40°C. The duration of the wash was 15 min. A double rinse and drying concluded the process.

Determination of fabric performance:

Yellowness[2], abrasion resistance[3], bursting strength[4] and colour fastness to sunlight[5] were determined by standard methods.

Felting shrinkage was measured after 3 hours washing in a Bendix washing machine charged with 20 *l* of a 0.2% solution of Softly at 40°C and a total load of 700 g. Percentage shrinkage is expressed in terms of the wet relaxed state of the fabric.

RESULTS AND DISCUSSION

Yellowing which takes place when wool is treated with DCCA can be diminished by a lowering of either the concentration[6] of the reagent or the temperature[7] and the pH[6] at which the reaction is carried out. The concentration of the DCCA is determined by the minimum quantity necessary to produce the required degree of shrink resistance and can therefore not be reduced in order to limit yellowing. Temperature and pH are adjustable but practical considerations impose definite limits within which these adjustments may take place. For example, it is impractical to work much below ambient temperature because cooling facilities are generally not available in textile mills. Only a small quantity of ice was needed to reduce the temperature of the liquor to 20°C on a hot day. However, if lower temperatures were required increasingly more ice had to be employed. At very low temperatures the rate of reaction is also reduced and exhaustion of the bath may take longer than is commercially acceptable. Lowering of the pH is restricted by the inferiority of the handle obtained and the danger of non-uniform treatment at low pH[6]. The pH values and the temperature (*ca.* 20°C) finally used in the experiments described above were selected on the basis of these considerations. The duration of the treatment was about 90 min for the worsted fabric employed and subsequent dyeing with a variety of dyestuffs showed that treatment had been level. These conditions of shrinkproofing were however not entirely satisfactory in terms of the whiteness of the fabric. The results (Table I) show that considerable yellowing still occurred during the shrink-resist treatment with DCCA alone. In an effort to reduce this still further, the use of permanganate in conjunction with DCCA was investigated.

Methods of shrinkproofing wool with a combination of DCCA and permanganate have been described[8–11] in the literature. The combined use of the DCCA and the permanganate permits the achievement of a specific degree of shrink resistance with less DCCA than would be the case when only the chlorinat-

TABLE I

Properties of Wool Fabrics Subjected to Various Finishing Treatments

Treatment of fabric*									
Shrinkproofing		Bleaching		Resin		Fastness to light	Yellowness index	Abrasion resistance (cycles to hole)	Bursting strength (lb/in²)
DCCA conc.	KMnO₄ conc.	5% sulphoxylate	1% Leucophor PAF	application	Washing				
0	0					4–5	36.2	367	130
4.5%	0					4–5	44.7	304	117
4.5%	0				+	4–5			
4.5%	0			+		4–3b	44.6	317	127
4.5%	0			+	+	4b			
4.5%	0	+				4–5	42.4	317	121
4.5%	0	+			+	4–5			
4.5%	0	+		+		4b	41.9	309	124
4.5%	0	+		+	+	4b			
4.5%	0.2%						43.7	318	
3.0%	2.0%						42.9	271	
4.5%	0.2%	+				4–5	41.5	313	
4.5%	0.2%	+			+	4–5			
4.5%	0.2%	+		+		4–3b	41.5	304	
4.5%	0.2%	+		+	+	4b			
4.5%	0.2%	+	+			3–2		314	117
4.5%	0.2%	+	+		+	3–2			
4.5%	0.2%	+	+	+		4–3		320	122
4.5%	0.2%	+	+	+	+	3–4			

* All samples were flat-set.
b Bleaching during exposure to light.

ing agent is used[11]. A combination of 3% DCCA and 2% permanganate has been recommended[10] as optimal and the process is acclaimed[10] for the softness of handle and the high degree of whiteness of the products thus treated. Comparison of fabrics shrinkproofed by this method with those treated by 4.5% DCCA, shows (Table I) a significant improvement in whiteness but also a decrease in abrasion resistance. It was found in the course of the present investigation that a combination of 4.5% DCCA with 0.2% permanganate gave a product which was appreciably whiter than one treated with 4.5% DCCA only, yet, the abrasion resistance remained unchanged (Table I). This observation prompted the present authors to concentrate on the investigation of shrinkproofing by the use of this particular combination.

The selection of a suitable bleaching method was based on published information[12–14]. It appears to be an accepted fact that bleaches obtained by reduction methods, although initially not quite as white as oxidation-reduction bleaches, are more resistant to yellowing when exposed to sunlight. Therefore, in view of the importance attached to yellowing during wear, oxidation-reduction bleaches were not considered in the present study. The most commonly available reduction bleaches are sodium sulphoxylate, sodium bisulphite and sodium dithionite. Several authors[12–14] have reported that sodium sulphoxylate is a substantially more powerful bleaching agent than the other two and that the resultant bleach has the best light fastness. The shrinkproofed wool was consequently bleached by treatment with sulphoxylate and a substantial increase in whiteness was observed. This applied to the wool shrinkproofed with 4.5% DCCA alone as well as to that treated with the combination of DCCA and permanganate. The whiteness of the latter fabric was however superior to that of the cloth treated with the chlorinating agent alone. Table I also shows that bleaching with sulphoxylate had no influence on the fabric strength or abrasion resistance.

After shrinkproofing (4.5% DCCA and 0.2% permanganate) and bleaching (5% sodium sulphoxylate) the fabric was still yellower than it had been before treatment (Table I). Reflectance spectra revealed the interesting fact that the higher yellowness index was due to an increased reflectance of the longer wavelengths of the spectrum (see Fig. 1). (Increased yellowness is usually the result of a reduction in the reflectance of blue light.). Although yellower, the treated fabrics are actually higher in luminosity and bright dyeings can therefore be obtained quite readily.

Ultramarine Blue (household blue, also frequently used in industry) reduces the reflectivity of the sample to which it is applied in the long wavelength range of the spectrum. It was reasoned that if blue were applied to the treated wool samples with their unusually high reflectivity at the longer wavelengths, the resultant reflectance spectrum should be quite similar to that of a normal wool sample. This was found to be true in practice. It is to be noted that the luminosity of the wool treated with the blue was not lower than that of the untreated fabric and that the usual objection to the use of ultramarine blue, namely greying, did therefore not apply.

The fabrics described above, being at least as bright and as fast to light exposure as the untreated wool (see Table I), were suitable for the production of

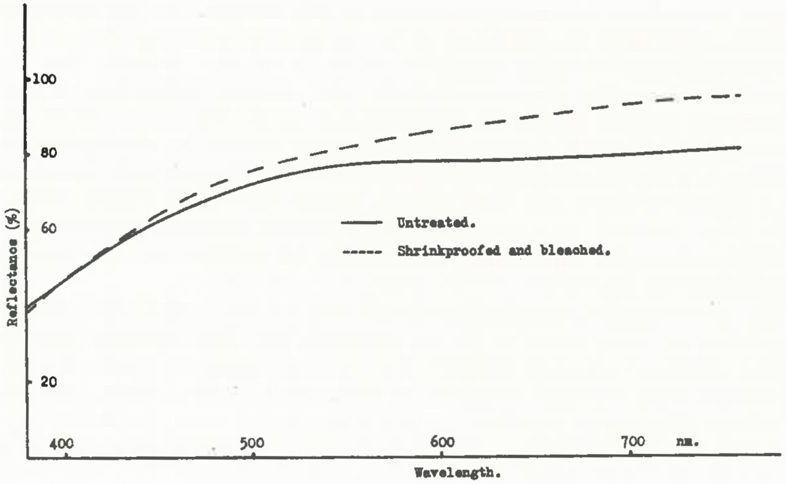

FIG. 1

Reflectance spectra of untreated wool and of wool which has been shrinkproofed and bleached. Magnesium oxide used as reference.

wool goods in pastel and in bright shades. The ground shade was, however, not considered sufficiently white for undyed "whites" and the use of fluorescent brightening agents was therefore unavoidable. Application of this brightening agent was combined with the bleaching process in an effort to limit the number of processes required. The results show that the fluorescent agent and the sodium sulphoxylate were compatible and suitable for simultaneous application. Although instrumentation for the measurement of whiteness in fabrics treated with fluorescent brightening agents was not available, the fabric was assessed visually and considered suitable for the production of white all-wool garments. Unfortunately, application of the fluorescent agent had the expected adverse effect on the light fastness of the fabric which fell from a 4–5 to a 3–2 for the brightened goods.

The light fastness of fluorescent brightened wool material can be improved by the application of a thiourea-formaldehyde resin[1]. This resin was applied to the material containing the fluorescent brightening agent and also to unbrightened fabrics. In the latter cases the observation was made that the light fastness decreased as a result of the application of the resin. It was furthermore noticed that the irradiated wool had bleached and not yellowed during the exposure. These results indicate that the mechanism of the protective action of the resin is one of bleaching which compensates for the natural yellowing of the wool during exposure to sunlight. The wool which did not contain fluorescent brightening agent had a relatively high light fastness. This caused bleaching by the resin to over-compensate for the slight amount of yellowing which occurred; hence, a resultant bleaching action. The rate of yellowing of the fluorescent brightened

material is very much higher and could not be fully compensated for by the bleaching effect of the resin. The resultant yellowing was however considerably less than it was in the absence of the resin (Table I).

Unfortunately the resin is not wash-fast[1]. When application of the resin was followed by washing in a household washing machine, the light fastness of the unbrightened, resin-treated materials increased somewhat (Table I) indicating less efficient bleaching. The light fastness of the brightened, resin-treated material decreased after washing to a value of 3–4. This value is nevertheless a substantial improvement on the 3–2 for the fabric which had not received the resin-treatment. The improvement may well justify the additional padding process required for the application of the resin.

The yellowing indices of the unbrightened materials show that the appearance of the wool was not altered by the application of the resin. (This was also confirmed for the fluorescent brightened fabrics by visual assessment.) The abrasion resistance, bursting strength (Table I), and the handle of the fabrics were similarly unaffected by the resin.

SUMMARY

1. For the production of easy-care wool fabric in pastel or bright shades the following finishing procedure is recommended:
   (a) Shrinkproofing with 4.5% DCCA (85% exhaustion) and 0.2% $KMnO_4$ at pH 6 and 20°C, or at the lowest possible temperature in excess of 20°C.
   (b) Clearing with 10% sodium bisulphite at pH 4.0 – 4.5.
   (c) Bleaching with 5% sodium sulphoxylate, starting at 45°C, increasing the temperature to 85°C, and holding for 30 minutes. Steps (a), (b) and (c) are performed in the same bath.
   (d) Flat-setting with 1% sodium bisulphite on the decatizing machine.
2. For the production of easy-care wool fabrics in undyed "whites", the following finishing procedure is recommended:
   (a) and (b) As in 1.
   (c) As in 1, but with the addition of 1% Leucophor PAF or other suitable fluorescent brightening agent.
   (d) As in 1.
   (e) Pad on thiourea (2.5%) and formaldehyde solution (25%) and dry in tenter for 12 minutes at 100°C.

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