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MACHINE WASHABLE HAND KNITTING YARNS

by

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INTRODUCTION

Consumer surveys carried out in Europe have placed renewed emphasis on the desirability of having available on the market pure wool hand knitting yarns which would be suitable for washing in household washing machines. Although a number of trials directed at the achievement of this goal has met with some success overseas, many problems still remained and, particularly in the case of finer wools, the necessity of further investigation existed. This prompted the undertaking of the present investigation which concerns the dyeing, shrinkproofing and subsequent performance-testing of locally available, commercial hand knitting yarns.

EXPERIMENTAL

Materials

The hand knitting yarns had the following characteristics:

Yarn A: Crêpe yarn spun from 60/64's South African Merino wool; count = R333 tex/3/2 (3/2/16's w.c.) with twist = 419 t.p.m. (Z) x 423 t.p.m. (S) x 86 t.p.m. (Z).

Yarn B: Crêpe yarn; 60/64's South African Merino wool; count = R569 tex/3/3 (3/3/14's w.c.) with twist = 346 t.p.m. (Z) x 133 t.p.m. (S) x 42 t.p.m. (Z).

Yarn C: Four-fold yarn spun from 56's quality wool; count = R282 tex/4 (4/12.5's w.c.) and twist = 272 t.p.m. (Z) x 126 t.p.m. (S).

The sodium salt of dichloroisocyanuric acid (DCCA) was purchased as the commercial product Fi-Clor 60 S (Fisons).

The softening agents Belfasin 615 (Henkel) and Waxol HE (I.C.I.) were commercial products.

Shrinkproofing treatments

All shrinkproofing treatments were carried out on yarn in hank form.

In the Dylan ZB method the wool was wetted at room temperature in a solution containing 0.5g/*l* Tergitol TMN (Union Carbide). After addition of $CaCl_2$ (10%) the pH was adjusted to 10 — 10.5 and the liquor circulated through the package for 10 min. The required amount of $KMnO_4$ was then added and circulation continued for a further 5 min followed by addition of the appropriate quantity of sodium hypochlorite. Reaction was continued until 90% of the available chlorine had been consumed. Antichlorination treatment involved treatment in a fresh solution of sodium bisulphite to which 0.5 g/*l* formic acid was added after the initial 10 min. Circulation was then continued for a further 30 min at 35°C after which the treatment was concluded by two rinses, hydro-extraction, and drying.

In the DCCA treatment the yarns were wetted in a solution containing Tergitol TMN (0.5 g/*l*) and NaCl (2 g/*l*) at room temperature and at a pH 6 — 6.5 for 30 min. The wool was then lifted from the machine and the pre-dissolved DCCA powder added to the liquor. Uniform distribution of reagent in the bath was ensured by circulating the liquor for 1 min before lowering the hank carrier into the bath. After 35 min the temperature was raised to 35°C and reaction continued until exhaustion of 95% of the avialable chlorine. Finally, sodium bisulphite (3%), followed after 5 min by sufficient acetic acid to give a pH of 4.5, was added for the antichlorination treatment. The temperature was raised to 40°C and reaction continued for 20 min. The yarn was subsequently rinsed twice and dried.

Dyeing

The wool was dyed in hank form and involved the usual methods recommended by the dyestuff manufacturers. The maximum dyeing temperature was 100°C at which the bath was held for 1 hour. The dyestuffs employed are listed in the various Tables. The strength of the dyeings was 2% throughout.

Neutralisation

Material requiring neutralisation was treated with a solution of tetra-sodium pyrophosphate at room temperature for 10 min. The temperature was then increased to 40°C, held for 10 min and finally raised to 45°C where treatment continued for yet a further 10 min. Unless stated otherwise the quantity of pyrophosphate was 4% on the dry weight of the wool.

Determination of felting shrinkage

After having received the required shrinkproofing and dyeing treatments the yarn was knitted into fabric of plain-knit construction having a cover factor of 0.9. (The corresponding value is 1.06 when the tex system is employed.) Samples of these were wet relaxed[1] and then agitated in a 50 *l* Cubex[2] containing 12.5 *l* of phosphate buffer (1.25%) at pH 7 and 40°C. Three samples of each specimen were treated simultaneously and the load was made up to 1000g with standard knitted cotton makeweights[2]. Area shrinkage was determined every 30 min to a maximum of 2 hours.

Fastness of dyeing to washing and perspiration

These were carried out by the usual methods[3] and involved determination of the change of shade and staining onto wool and cotton when the wool was washed in a solution of industrial soap flakes at pH 9.9 or subjected to testing of fastness to alkaline perspiration.

Tensile strength

The tensile properties of yarns conditioned to 20°C and 65% relative humidity were determined on an Instron tensile testing machine at a rate of extension of 200% per min.

Abrasion resistance

The yarn flex abrasion resistance was determined on a Stoll Quartermaster Abrasion Tester with headweight of 1 lb and flexing bar weight of 4 lb.

RESULTS AND DISCUSSION

The phrase "machine washability" can clearly be interpreted in various ways, each requiring compliance with its own set of standards in testing conditions and sample performance. The instrument chosen in the present investigation was the Cubex which is reputed[2] to provide results of excellent reproducibility in addition to being commonly available to laboratories and testing houses in many countries. The conditions of testing in the Cubex, as given under *Experimental* were milder than those normally employed for woven fabrics[4] but were deliberately chosen in the expectation that machine washable knitwear would normally be washed in machines with special wool-washing cycles involving rather mild conditions. Concerning the required standards of fabric performance, Dixie[5] suggested that adults' knitted outerwear should not shrink more than 10 — 12% area-wise when washed 20 times whilst childrens' wear is permitted the same shrinkage tolerance in a total of 40 washes. In the authors' laboratory an area shrinkage tolerance of 7 — 9% was considered more realistic while a total washing time of 120 min was chosen for adults' as well as childrens' wear. (A single test was decided upon since it may be difficult for the finisher to determine whether the wool is ultimately intended for the manufacture of childrens' or for adults' wear.) These were then the criteria by which the effectiveness of shrinkproofing treatments discussed below was judged.

Various methods of shrinkproofing were examined on a preliminary basis before a final method was selected for more extensive investigation. These shrinkproofing methods involved treatment of yarn A by the Dylan ZB used and the DCCA methods.

The Dylan ZB method, involving the simultaneous application of $KMnO_4$ and chlorine (the latter in the form of hypochlorite), gave a reasonable shrinkproofing effect at the higher of the two reagent concentrations used (see Table I). It was, however, still not adequate in terms of the requirements for machine

TABLE I

Shrinkage behaviour of fabrics knitted from yarn A treated after dyeing* by various shrink-resist processes

Treatment	% Area felting shrinkage after 30 min	60 min	90 min	120 min
Dylan ZB (2% $KMnO_4$ + 2.5% Cl)	11.9	39.4		
Dylan ZB (2.5% $KMnO_4$ + 3% Cl)	-6.0	-1.2	12.0	
5.5% DCCA	-4.7	-4.1	-3.3	3.0
5.5% DCCA; Belfasin (1%) + Waxol (1%)	-5.2	1.2	16.4	

*Dyeing carried out with Cibacrolan dyestuffs at pH 4.5

washability specified above. Since a further increase in reagent concentration was precluded by the excessive damage to the material which treatment at such high concentration levels is known to incur, the Dylan ZB method was also considered unsuitable for the production of machine washable hand knitting yarns.

The second process, viz. that involving the use of DCCA, produced excellent shrink resistance at 5.5% treatment level and was therefore selected for further investigation. Unfortunately the DCCA treatment produced a handle which was somewhat harsher than that obtained with the Dylan ZB method and first efforts were consequently directed towards possible means of mitigating this effect by a concluding treatment with softening agents. The results obtained with a mixture of Belfasin 615 (1%) and Waxol HE (1%), a combination found effective in improving the handle, was disappointing in that the treated wool shrunk more than 16% in only 90 minutes washing and did therefore not conform to machine washability requirements. The explanation for this increased felting rate is considered to be the lubricating action of the softening agents. The problem is currently being investigated in some detail and will form the subject of a further report.

Dyers frequently prefer to dye their material only after it has been shrinkproofed so as to avoid the complications in matching and the limitations imposed on the selection of dyestuffs which may be experienced if the sequence is reversed. It is therefore important to know the effect of subsequent dyeing on the performance of shrinkproofed fabrics during washing. In this connection it was not unrealistic to anticipate that at least certain dyeing procedures may have an adverse influence on the shrink resistance of material previously treated with DCCA. For example, some dyeing procedures involve the use of liquors of which the pH is relatively low and it is known that acidic liquors tend to restore the shrinkage propensity of wool materials shrinkproofed by oxidative treatments[6, 7]. Table II shows that, depending on the dyestuff used, the shrink resistance of DCCA-treated wool can indeed be impaired by subsequent dyeing. Although this effect can sometimes be eliminated by a neutralisation treatment, the results (Table II) also show that such treatment is not always effective (see also ref. 8 on the shrinkage behaviour of wool dyed with 1:1 premetalised dyestuff in H_2SO_4 medium). The value of neutralisation is nevertheless not to be underestimated and even where dyeing preceded shrinkproofing, the degree of shrink resistance can be improved by following the shrinkproofing treatment by neutralisation in a solution of tetra-sodium pyrophosphate (see Table II). Such a neutralisation treatment following shrink resist treatment may well permit the use of lower DCCA concentrations thus decreasing the amount of fibre damage induced by the treatment. Since it is undesireable if the amount of stretching (negative shrinkage) becomes as high as that obtained with the last sample in Table II, reduction of the concentration of shrinkproofing agent in such cases becomes not only desireable but essential.

TABLE II

Influence of sequence of dyeing and shrinkproofing and of neutralisation on the shrink resist properties of yarn A

Treatment of yarn*	% Area felting shrinkage after			
	30 min	60 min	90 min	120 min
Dyed (Neopolar, pH 3.5); 5.5% DCCA ...	0.1	5.9	19.4	35.4
5.5% DCCA, dyed (Neopolar, pH 3.5) ...	12.9	41.8		
5.5% DCCA, dyed (Neopolar, pH 3.5); neutralised with 6% pyrophosphate	–1.8	7.2	24.2	35.7
Dyed (Neopolar, pH 3.5); 5.5% DCCA; neutralised with 6% pyrophosphate	–0.5	0.2	4.9	11.8
Dyed (Cibalan); 5.5% DCCA; neutralised	–7.3	–7.3	–8.1	–4.0

*Where treatment with DCCA followed dyeing at pH 3.5, neutralisation with 6% pyrophosphate before application of DCCA reagent was required.

Based on the above results and conclusions the yarns described under *Experimental* were dyed, shrinkproofed, and neutralised in that sequence and, as shown by the results in Table III, the products were eminently suitable for machine washing. The lower concentration of DCCA used with yarn A compared to the others was necessary because yarn A tends to stretch excessively during washing if a 5.5% DCCA treatment is followed by neutralisation in pyrophosphate (Table II). It may be added that similar experiments on wool dyed with Carbolan instead of Cibalan dyestuffs gave results almost identical to those displayed in Table III.

TABLE III

Shrinkage behaviour of fabrics knitted from various yarns dyed at pH 5 — 5.5 with Cibalan dyestuffs, shrinkproofed by treatment with DCCA, and neutralised with tetra-sodium pyrophosphate — in that order

	DCCA conc.*	% Area felting shrinkage after			
		30 min	60 min	90 min	120 min
Yarn A	5.0	–2.1	–1.9	–0.1	2.4
Yarn B	5.5	–2.2	–4.2	–1.8	–0.3
Yarn C	5.5	–3.6	–4.6	–3.2	0.6

*Calculated on the dry weight of the wool.

The tensile properties and abrasion resistance of the various machine washable yarns are given in Table IV which shows that loss of tensile strength due to shrinkproofing was not more than 10%. The corresponding loss in abrasion resistance was also not large, except in the case of yarn C where the rather high reduction in this parameter is perhaps attributable to the loose construction of the yarn.

TABLE IV

Tensile properties and abrasion resistance of dyed yarns before and after shrinkproofing with DCCA

	DCCA conc. (%)	Breaking strength (Kg)*	Breaking extension (%)*	Abrasion Resistance**
Yarn A: Untreated		2.73 (0.127)	36.2 (3.80)	211
Shrinkproofed	5	2.97 (0.491)	38.8 (3.44)	217
Yarn B: Untreated		4.09 (0.121)	31.2 (4.43)	538
Shrinkproofed	5.5	4.44 (0.154)	37.2 (2.27)	485
Yarn C: Untreated		2.20 (0.126)	31.0 (2.87)	190
Shrinkproofed	5.5	2.14 (0.146)	32.3 (3.08)	144

*Values of standard deviation given in parentheses.
**Number of cycles to collapse of yarn

It may be added, that the main obstacle to neutralisation of wool which has been dyed lies in bleeding of the dyestuff in the essentially alkaline liquor. With reactive dyestuff this problem naturally does not exist since this kind of dyestuff is dependent on covalent rather than physical forces for its retention on the fibre. Dyeings with metal complex dyestuff of the 1:2 premetalised type were also found to be quite stable to treatment with tetra-sodium pyrophosphate solution whilst other dyestuff types varied in their fastness properties from one type to the next. This is indeed a point which may be decisive in determining whether neutralisation of a dyed material, irrespective of the sequence of dyeing and shrinkproofing, is permissible and must be decided for individual dyestuffs.

The effect of shrinkproofing with 5.5% DCCA on the shade of wool fabrics previously dyed with various dyestuffs commonly used for the local production of washable wool products is shown in Table V. This table also contains the evaluations of the wash and perspiration fastness for the various yarns. It is noticeable that the change in shade due to the DCCA treatment is usually small and never more than one point on the standard scale. The results of the fastness evaluations confirm previous conclusions that shrink-resist treatment with chlorinating agents leads to a reduction in fastness properties. Thus, in some cases fastness ratings of 3 were obtained which, according to IWS specifications, are insufficient for Woolmark washable articles. Minimum requirements for such articles being fastness properties of 3—4, it follows that even in the limited number of dyestuff investigated a predominant portion was suitable.

SUMMARY

Hand knitting yarns of sufficient dimensional stability to be suitable for washing in household washing machines can be obtained by shrinkproofing with DCCA of sufficient strength to give 3.3% active chlorine on the weight of the wool.

TABLE V

Fastness Properties of Dyed Yarns

DYESTUFF	FASTNESS OF DYEING TO TREATMENT IN						
	5% DCCA	5 g/l soap flakes			Alkaline perspiration		
	Change in shade	Change in shade	Staining of wool	Staining of cotton	Change in shade	Staining of wool	Staining of cotton
C.I. Acid Red 122 ...	5	4BL	4—5	5	4—5	3—4	3
C.I. Acid Red 211 ...	5	4D	5	5	4—5D	4—5	4
Polar Brilliant Red GE (Geigy) ...	5	4—5	5	4—5	4—5D	3	3
C.I. Acid Yellow 110	5—4D	3D	4—5	5	4—5G	4	4
C.I. Acid Yellow 116	4Y	4D	4—5	5	4—5Y	5—4	5
C.I. Acid Yellow 128	4—5D	4—5D	5	5	4—5G	3—4	4—3
C.I. Acid Blue 126 ...	4—5D	3D	4—5	5	4—5	3—4	4—5
C.I. Acid Blue 143 ...	4—5D	3G	5	5	4—5	4	4—5
C.I. Acid Blue 181 ...	4G	3G	4	5	4—5	3	4—3
C.I. Acid Blue 227 ...	4D	3—4D	5	5	4—5BL	3	4—5
Brilliant Alizarine Milling Blue BL 150% (Sandoz) ...	4G	3D	5	5	4G	4	5
C.I. Acid Green 27 ...	4—5BL	4—5D	5	5	4—5Y	4—5	5
Carbolan Brilliant Green 5 GS (I.C.I.)	4—5BL	4—5D	5	5	4—5Y	4—5	4—5
C.I. Acid Brown 19 ...	4BL	4G	5	5	4—5G	4	4
C.I. Acid Brown 224 ...	4—5BL	4—5	5	5	4—5	4—5	4
Coomassie Fast Grey 3GS (I.C.I.) ...	5	4—5G	5	5	4—5G	4	4—5
C.I. Acid Black 60 ...	5—4	4G	5	5	4—5G	4	4

D — Duller, G — Greener, BL — Bluer, Y — Yellower

The sequence of shrinkproofing and dyeing of the yarn may influence the dimensional stability of the end product but whichever sequence is employed special care should be exercised to ensure that the goods are subsequently neutralised. Proper neutralisation is however not readily achieved when dyeing has been carried out under strongly acidic conditions.

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