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The Application of Mixed Surfactant Micelles in Wool Textile Finishing

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Anti-shrinkage procedures based on the deposition of Hercosett on untreated wool fibres combined with either the use of an amphoteric surfactant or mixed micelles of amphoteric/anionic surfactants are described. Specific molar ratios of the surfactants were found to promote good stability of the bath, giving area felting shrinkage values of the treated fabrics less than 10%.

INTRODUCTION

Many of the polymer shrinkproofing processes developed for wool [1–3] are dependent on chemical pretreatment of the fibre in order to increase its surface energy. Consequently the efficiency of both polymer adhesion and spreading on the fibre surface are considerably improved, especially for certain oxidative pretreatments. The most widely used shrink-resist process of this type is the CSIRO chlorine–Hercosett process [4,5], which may be applied on a continuous basis to tops or batchwise to knitwear.

The chlorination step is critical and must be carefully controlled in order to minimise degradation and to give regular deposition of resin on the fibre, the Hercosett resin distribution being highly dependent on the levelness of chlorination pretreatment. Additionally chlorination may have a deleterious effect on the colour fastness of the treated wool, whether dyeing is carried out before or after chlorination.

As an alternative procedure, the formation of Hercosett–anionic surfactant complexes can be considered to avoid the need for oxidative pretreatment of the fibres [6–8]. However, it is essential to use the correct concentration of both components, and the stability of the systems in aqueous media is not very satisfactory.

The use of an amphoteric surfactant (dodecylamidopropylbetaine) and/or mixed micelles of amphoteric/anionic surfactants has been reported to be very useful in the study of chemical modifications of wool fibres, due to the surfactants' adsorption and permeability on keratinous proteins [9]. This paper reports a study of the deposition of Hercosett resin on wool in the presence of an amphoteric surfactant or mixed amphoteric/anionic surfactant micelles at different molar ratios.

EXPERIMENTAL

Materials

The knitted fabrics used were botany wool: R64/2 tex (count 2/28) yarns.

The Hercosett 125 (polyamide–epichlorohydrin polymer) used was a commercial sample supplied as a 125 g/l aqueous solution by Hercules Inc. Sodium lauryl sulphate (SLS) was analytical grade (BDH) and dodecylamidopropylbetaine (DAPB) was supplied by Tensia Surfac. Lanasol Orange G (CGY, C.I. Reactive Orange 29) was used in the work.

Methods

The shrinkage testing was carried out at a liquor ratio of 30:1, load 1 kg, for 3 h at 40°C; the pH was held at 7.5 using a phosphate buffer according to IWS test method 185.

Laboratory dyeings were carried out in a Multi-Dye dyeing machine under standard conditions. Exhaustion of the dyebaths was determined by a spectrophotometric method using a Unicam SP600 spectrophotometer.

The distribution of the resin on the wool surface was assessed using a scanning electron microscope (Cambridge Stereoscan S-4-10). The samples were coated with a gold film about 40 nm thick.

A Box–Hunter central rotatable plan [10] was used to optimise the concentration of SLS and DAPB present in the bath (0–6 mol of each surfactant per mol resin) to give maximum shrink resistance in the botany wool fabrics and minimum absorbance in the treatment bath. The following treatment parameters were constant:

- Hercosett concentration, 2 g/l
- Liquor ratio, 30:1
- Temperature, 50°C
- Time, 15 min.

The optimisation of the process was carried out at pH values of 5.0, 7.0, 9.0 and 11.0.

Treatment with Mixtures of Hercosett Resin and SLS–DAPB

Previously some solutions of anionic/amphoteric surfactants with different molar ratios where prepared, as shown in Table 1. A series of treatments of wool (10 g) with Hercosett resin (0.6 g) in the presence of several 5.00 mmol/l aliquots of SLS–DAPB mixture was carried out at constant pH in the range 5.0–11.0 and subsequently the area felting shrinkage of the fabric determined. Afterwards the samples were extracted to approximately 80% pick-up and then dried and cured in a forced-air oven at 80°C for 60 min.

TABLE 1

Molar Ratios of Surfactants

Molar ratio (SLS:DAPB)	SLS (mmol/l)	DAPB (mmol/l)
0:1	0.00	5.00
1:8	0.56	4.45
1:6	0.70	4.30
1:4	1.00	4.00
1:2	1.65	3.35
1:1	2.50	2.50
2:1	3.35	1.65
4:1	4.00	1.00
6:1	4.30	0.70
8:1	4.45	0.56
1:0	5.00	0.00

RESULTS AND DISCUSSION

Wool Fabric Treated with Hercosett–Surfactant Mixtures

It is well known that the addition of an anionic surfactant to Hercosett solutions forms milky dispersions when the resin:surfactant ratio lies within certain limits. Using an amphoteric surfactant such as DAPB at alkaline pH values, the interaction of DAPB with Hercosett also promotes a certain amount of turbidity.

In Figure 1 the absorbance of DAPB–Hercosett mixtures at pH 10.5 is shown as a function of different ratios of both components. As a comparison, also included in Figure 1 is the spectrophotometric behaviour of SLS–Hercosett mixtures at pH 5.0 [7]. The DAPB–Hercosett system can be seen to be more stable than SLS–Hercosett, the absorbance values for specific surfactant/resin ratios being lower. Also, when wool fabrics were treated with

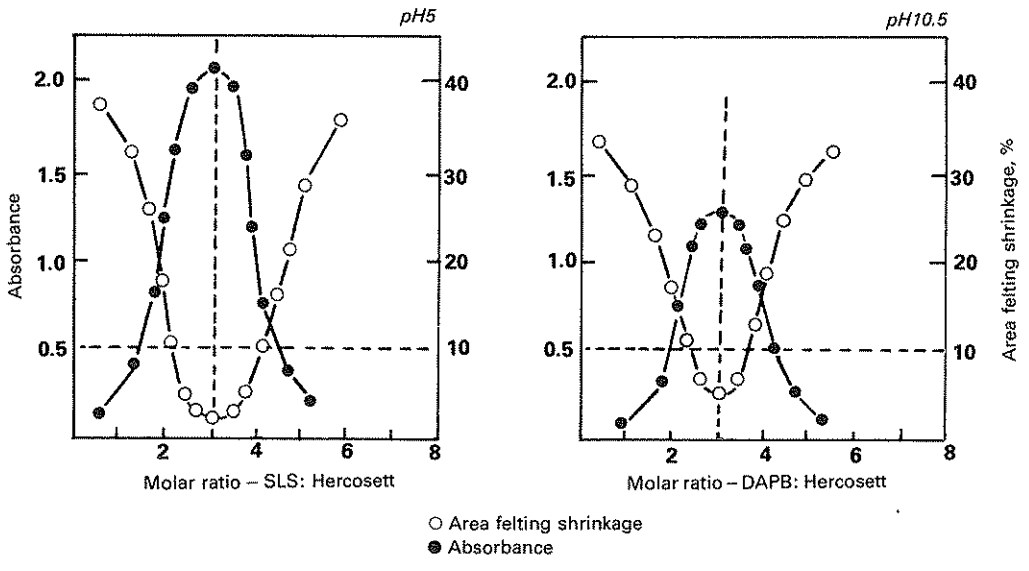

Figure 1 – Absorbance of Hercosett–SLS and Hercosett–DAPB systems and area felting shrinkage of samples treated with them

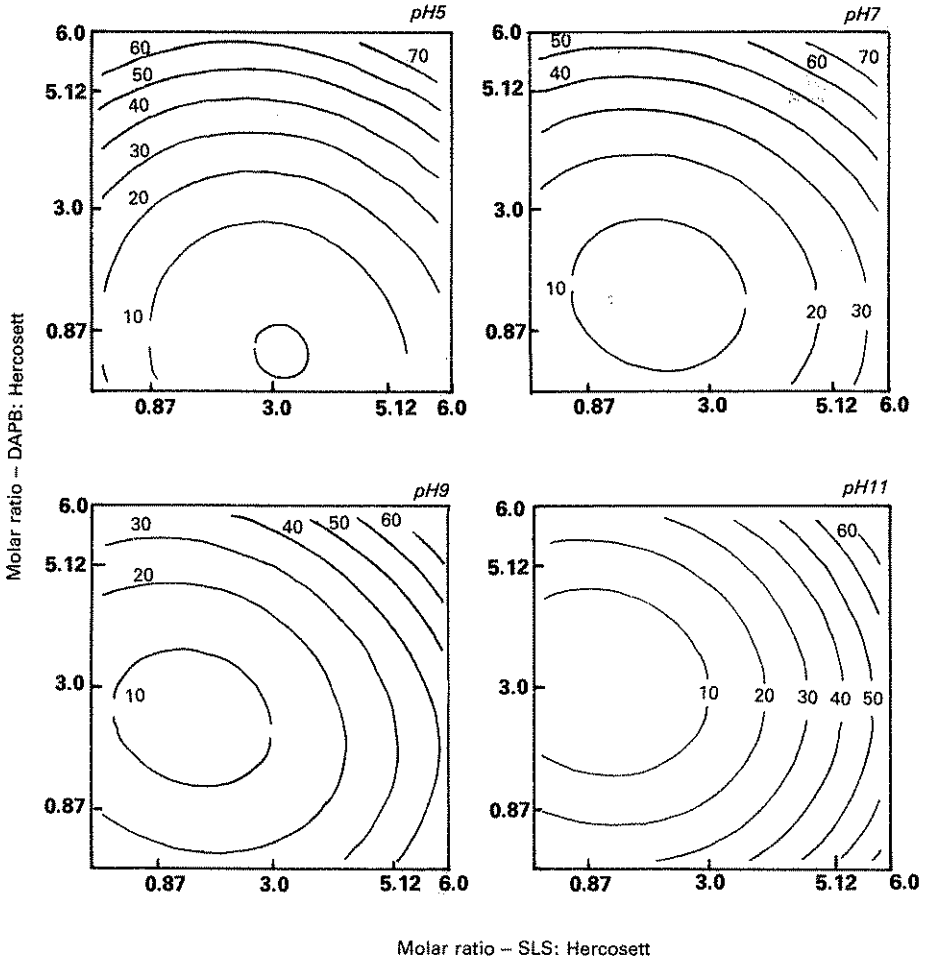

Figure 2 – Area felting shrinkage of samples treated with Hercosett–SLS–DAPB systems

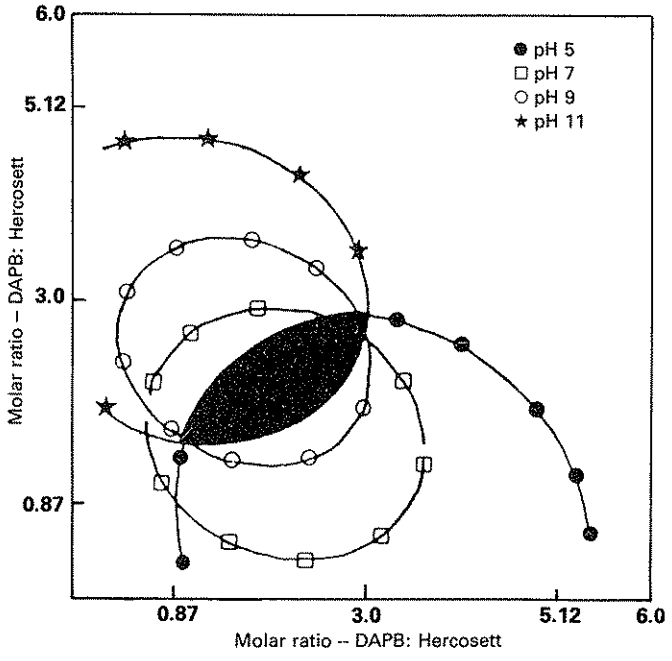

Figure 3 – Contours of 10% area felting shrinkage of wool treated with Hercosett–SLS–DAPB systems at various pH values

DAPB–Hercosett (pH 10.5) or SLS–Hercosett (pH 5.0) the reduction in shrinkage was greater with higher values of absorbance for specific surfactant:resin ratios.

As the pH interval between SLS–Hercosett and DAPB–Hercosett was wide (5.0–10.5), and, depending on the specific physico-chemical properties of SLS–DAPB mixed micelles [9], it is possible to obtain stable micellar associations including Hercosett. An optimisation study was therefore performed on the basis of the treatment of wool fabrics with Hercosett included in surfactant solutions. The treatments were carried out at pH values of 5.0, 7.0, 9.0 and 11.0, with the time of treatment being 15 min and the temperature 50°C as above.

Figure 2 shows the levels of area felting shrinkage obtained for wool fabrics treated with Hercosett–SLS–DAPB systems at different pH values. At pH 5.0 there was a minimum level of area felting shrinkage when SLS was the major component in the SLS–DAPB mixture, whereas at pH 11.0 the opposite was true. At pH 7.0 and 9.0 the area felting shrinkage showed intermediate values.

Figure 3 combines the 10% area felting shrinkage contours from Figure 2. The black area shows where the level of felting shrinkage of treated samples is lower than 10% for all pH values between 5.0 and 11.0.

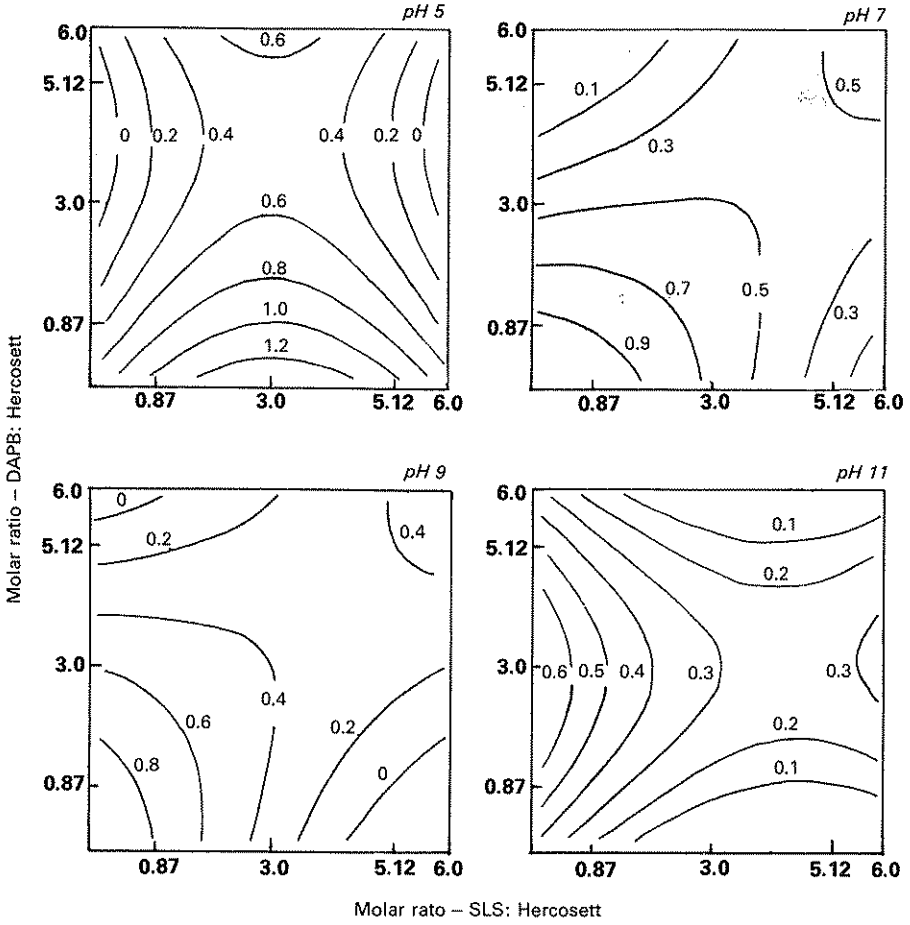

Figure 4 – Absorbance of Hercosett–SLS–DAPB systems

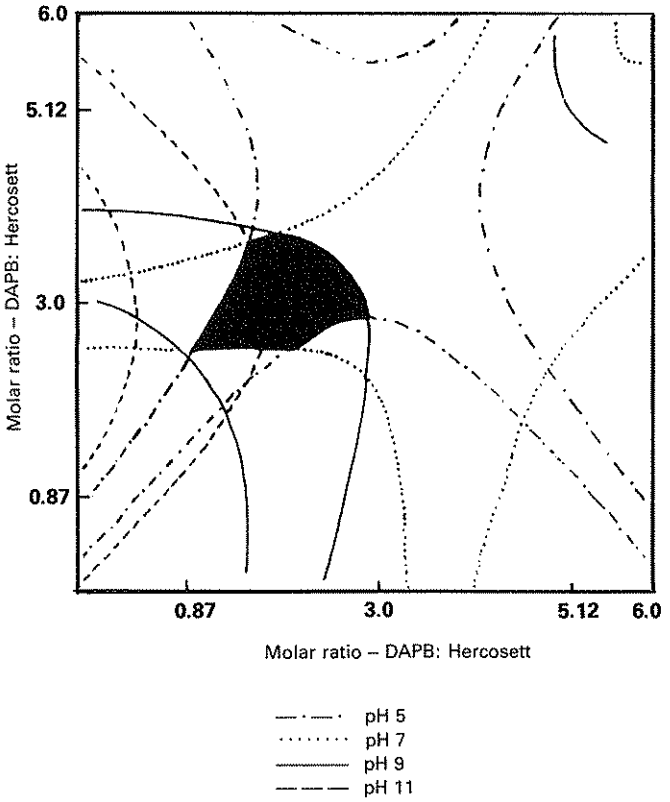

Figure 5 – Contours of 0.4 and 0.6 absorbance levels of Hercosett–SLS–DAPB systems at various pH values

As it seems that the turbidity of the resin–surfactant mixture is an important factor in promoting the deposition of resin on wool fibres, a spectrophotometric study was carried out with Hercosett–SLS–DAPB at different pH values. Figure 4 shows levels of absorbance of the mixed micellar systems. As with the case of area felting shrinkage, the relative concentrations of surfactant where the maximum absorbance values were found are clearly shown.

Grouping together the four parts of Figure 4, Figure 5 is obtained, the black area showing the region where the absorbance values lie between 0.4 and 0.6 in the pH range studied in the mixed micellar systems.

By comparing Figures 3 and 5 it is possible to establish a direct relationship between the optimum absorbance of the solutions and the minimum area felting shrinkage of wool samples treated with these solutions.

In Figure 6 the shaded areas represent the optimum area felting shrinkage (Figure 3) and absorbance (Figure 5) regions. It can be seen that an area of overlap exists where relative concentrations of mixed micellar systems give rise to absorbance values ranging between 0.4 and 0.6, and where the relative concentrations applied promote area felting shrinkage values lower than 10%, at pH values between 5.0 and 11.0, the Hercosett concentration value being 6% in all cases. Thus the application of Hercosett resin together with mixed micelles of SLS–DAPB promotes an improvement in the deposition of the resin on wool, as compared with other methods using binary dispersions of Hercosett with only one of these surfactants.

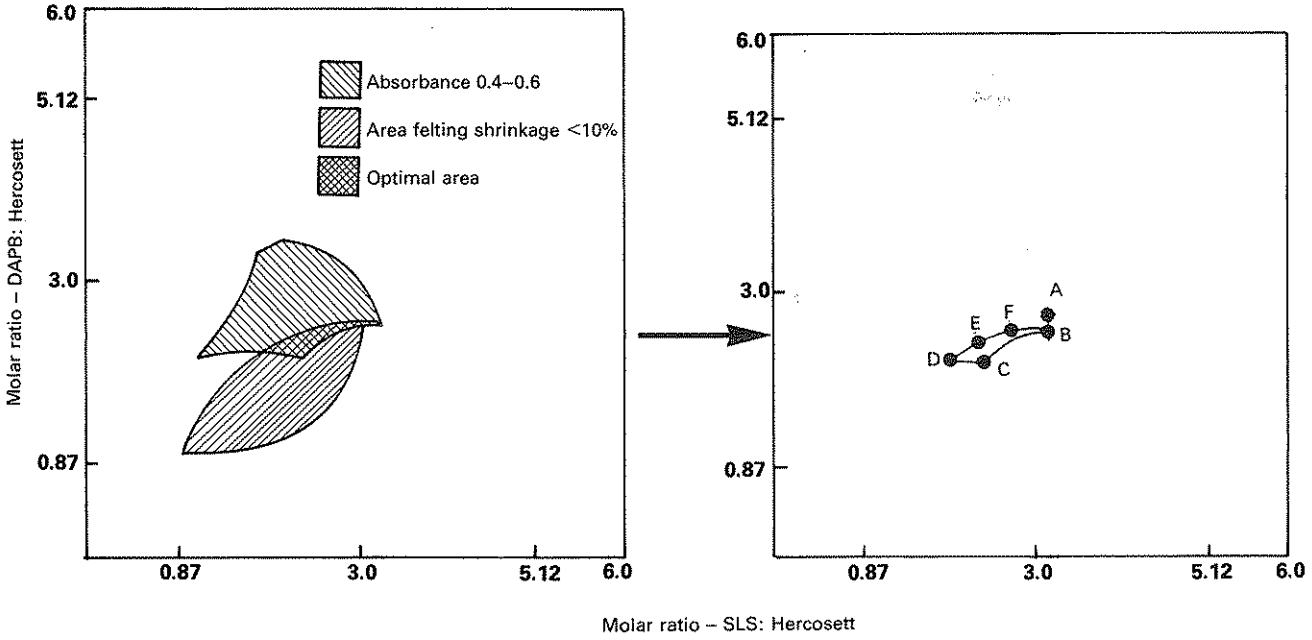

Figure 6 – Combination of Figure 3 and Figure 5

Deposition of Resin on the Surface of Wool Fibres

Using electron microscope techniques, the regularity of deposition of Hercosett resin applied to wool in the presence of mixed micelles of SLS–DAPB was studied. This study was carried out in the optimal area shown in Figure 6 with 24 samples of fibres treated with specific concentrations of SLS and DAPB as indicated in Figure 6 (points A, B, C, D, E and F).

Figure 7 consists of three photomicrographs of wool treated with Hercosett and mixed micelles of SLS–DAPB showing the evenness of deposition and distribution of Hercosett resin on the wool. The resin almost totally covers the surface of the fibres especially those fibres located inside the samples studied.

Several physico-chemical studies (of surface tension and rheological behaviour) carried out with both SLS–DAPB mixed micelles and Hercosett–SLS–DAPB mixtures have permitted the values of area felting shrinkage obtained for wool fabrics to be correlated with the viscoplastic behaviour of the system used during the treatment of wool fabrics [11].

Effect of Subsequent Dyeing on Samples Treated with Hercosett–SLS–DAPB Systems

Figure 8 shows the percentage exhaustion of Lanasol Orange G (2% o.w.f.) on wool treated with Hercosett–SLS–DAPB systems as a function of time, compared with the percentage exhaustion of this dye on untreated wool samples, wool fabrics previously treated with binary systems (Hercosett–SLS or Hercosett–DAPB) and wool sam-

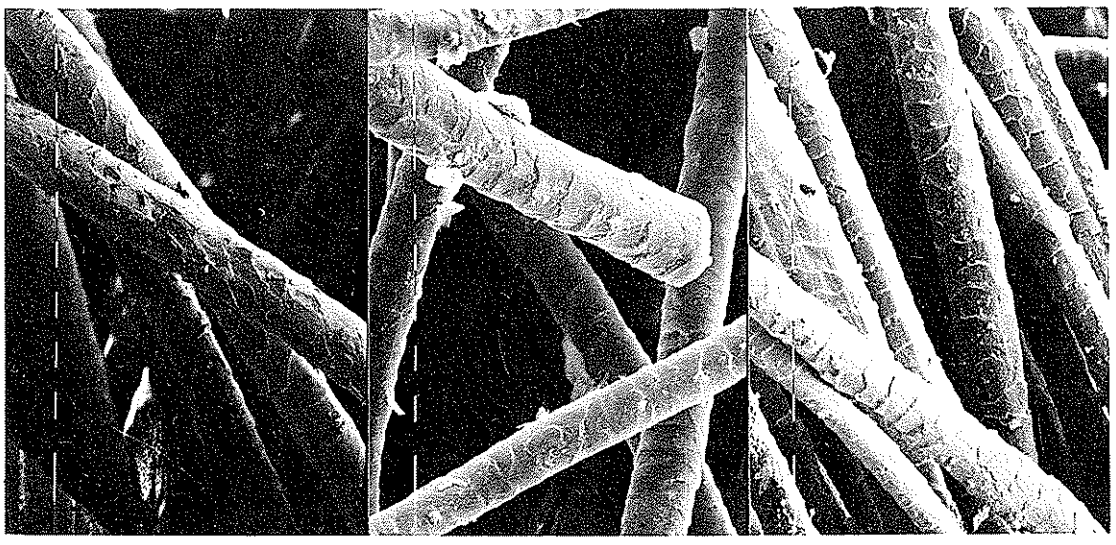

Figure 7 – Scanning electron microscope photomicrographs of wool treated with Hercosett–SLS–DAPB systems

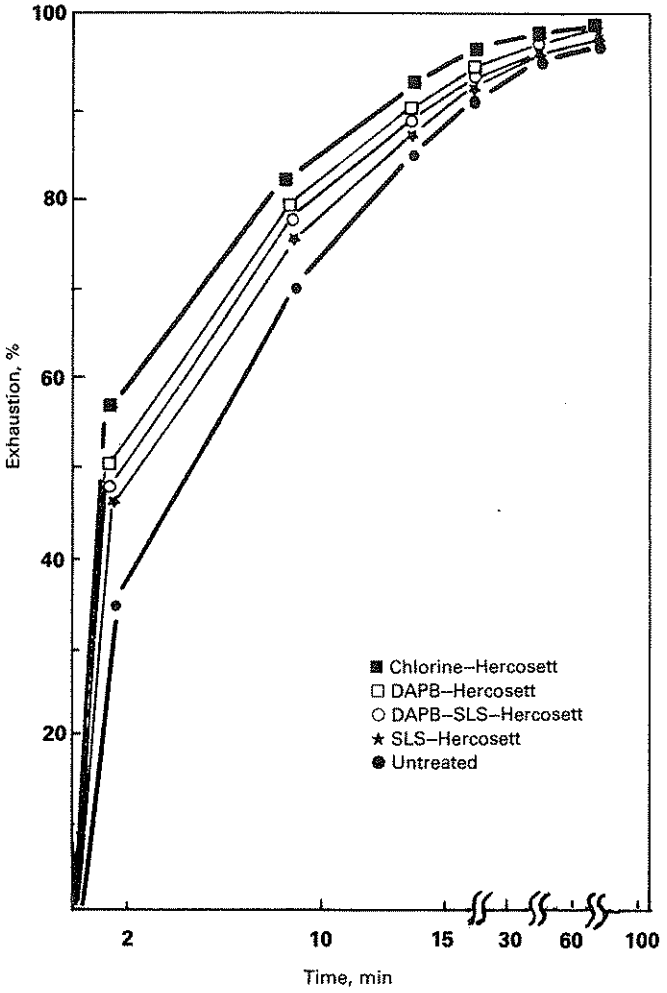

Figure 8 – Exhaustion of Lanasol Orange G on different wool samples

ples previously treated using the chlorine–Hercosett process. It can be observed that the exhaustion of the dye is much quicker at the beginning for the chlorine–Hercosett-treated samples. After 30 min the dyeing follows a similar trend with all the other samples except for the untreated wool. After 100 min the dye exhaustion was approximately 95% in all the cases. Colour fastness both to alkaline perspiration (IWS test method 174) and to washing (IWS test method 193) was well within acceptable limits.

CONCLUSIONS

Deposition of Hercosett resin on wool fabric can be accomplished by forming mixed systems between the resin and an amphoteric surfactant at alkaline pH values. A minimum value of area felting shrinkage is obtained for a specific Hercosett:DAPB molar ratio that aiso promotes an optimum turbidity in the bath.

The use of SLS–DAPB mixed micelles at different molar ratios aids the absorption of Hercosett resin on the surface of the fibres in the pH range 5.0–10.5 and the stability of the bath is improved. For a 1:1 SLS:DAPB molar ratio at neutral pH, a minimum of bath turbidity is obtained and the area felting shrinkage of the treated fabric is lower than 10%.

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Quinone–Quinoneimine Tautomerism of Phenothiazine- and Phenoselenazine-quinonoid Dyes: Isolation of a Quinoneimine Tautomer

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Quinone–quinoneimine tautomerism of phenothiazine- and phenoselenazine-quinonoid dyes has been investigated by means of their visible absorption spectra. Tautomerism was found to be influenced mainly by the nature of the hetero atom in the ring and the polarity of the solvent. Phenothiazine quinonoid dyes usually have been isolated in the quinone form but in this instance the dyes were isolated in their quinoneimine form, and the equilibrium was shifted to the quinone form in more polar solvents. Quinone tautomers absorbed visible light at much longer wavelengths (about 100–150 nm) than the quinoneimine tautomers. Isosbestic points for the tautomerism were observed. The calculated absorption maxima of the tautomers, obtained by means of the PPP MO method, have been correlated with the observed values, and the structures of the tautomers were confirmed by their n.m.r. and u.v. spectra.

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