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Application of an Epoxy-Functional Polyacrylate Emulsion to Textiles

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ABSTRACT

A thermosetting composition consisting of an epoxy-functional polyacrylate emulsion and a minor proportion of polyethylenimine (PEI) is shown to form a durable finish on textile fabrics when applied by padding or exhaustion from a long liquor. In this system, the PEI plays a dual role of cross-linking agent and deposition aid (the latter in exhaust application). The properties of treated fabrics are modified by the deposition of polymer on fiber surfaces and the formation of bonds between adjacent fibers. The frequency of formation of interfiber bonds depends on the method of application and appears to determine such properties as shrink-resistance in wool and improved wrinkle recovery in nylon and cotton. Pad application is the more efficient on wool and nylon, whereas on cotton, both methods of application confer similar performance. The treatment is

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superior to treatment with commercial self-cross-linking polyacrylate emulsions in forming a highly durable finish on unmodified wool which, because of the hydrophobic character of its surface is a poor substrate for conventional textile adhesives.

INTRODUCTION

Polymers are applied to textile fabrics to improve such diverse properties as dimensional stability, crease recovery, tensile strength, abrasion resistance, soil release, and handle. The practical value of these finishes is often critically dependent on their durability to repeated laundering, a function of their chemical resistance and adhesion to the particular fiber.

With self-cross-linking acrylic emulsions, curing can impart adequate chemical resistance [1]. However, despite this, they have limited durability on hydrophobic fibers such as wool and this has been attributed to their poor adhesion [2]. This contrasts with their widespread use as textile adhesives on the more polar cellulosic fibers [3] where adhesion is presumably satisfactory.

We have recently developed an epoxy-functional polyacrylate emulsion which, when cured with high molecular weight polyethylene polyamines, forms a highly durable shrink-resist finish on wool [4-6]. When high molecular weight polyethylenimine (PEI) is used as the cross-linking agent, the polymer can be applied by exhaustion as well as by the more conventional pad application, and the product has been proposed as an alternative commercial shrink-resist treatment for wool-containing fabrics [6]. The durability of the polymer on wool suggests that it may have other uses as a functional finish on other hydrophobic fibers.

The use of epoxy-functional polyacrylate emulsions as finishes for wool fabrics has been claimed in an early patents [7], but the products described have severely limited shrink-resist efficiency. More recently, some water-soluble polyacrylates have been investigated [8, 9]. Various polyacrylate emulsions have also been shown to improve the crease-resistance of cotton [10] and nylon [11], and the use of an epoxy-functional system on cotton has recently been suggested [12]. Some properties of various polyethylenimine derivatives in the finishing of wool [13] and cotton fabrics [14] have also been investigated along with various suggested mechanisms for their substantivity [15-17].

In practice, polymer-based finishes are generally applied to textile fabrics by padding (i.e., impregnation) and only in relatively few instances have methods been developed for exhaust application (i.e., wet deposition). Exhaustion could offer significant practical advantages for it may be carried out in common textile dyeing machinery such as winches or side paddles, perhaps in sequence with the dyeing operation. In previous investigations, exhaust application of a polyacrylate emulsion [18, 19] and other disperse systems [20] to wool has been shown to occur under conditions where destabilization of the disperse phase was apparent. The study of surface interactions [21] in the deposition of latex particles onto cellulosic [22] and nylon [23] fibers has been more extensively investigated.

We report here on the application of an epoxy-functional polyacrylate-PEI system by both padding and exhaustion to wool, cotton, and nylon. Appropriate conditions for exhaust application are investigated, and the properties of the treated textile are compared with those achieved by pad application.

EXPERIMENTAL

Polymers

Polyacrylate Emulsion. This was synthesized by conventional emulsion polymerization procedures using nonionic emulsifiers and a continuous monomer feed containing butyl acrylate, ethyl acrylate, and glycidyl methacrylate (65:25:10). It had a solids content of 41% and an epoxide content of 0.62 meq/g (calc 0.66) determined by hydrochlorination [24]. The polymer had a glass transition temperature (T_g by ASTM D3418-75) of -36°C.

Polymin P (BASF). A polyethylenimine, molecular weight 30-40 × 10^3, supplied as 50% solids aqueous solution.

Fabrics

Three light-weight plain-weave fabrics were used: an all-wool worsted fabric (150 g/m^2) having high felting propensity, a nylon fabric (190 g/m^2), and a cotton fabric (244 g/m^2).

Polymer Application to the Fabrics

The polyacrylate emulsion was applied by padding and by exhaustion. The pad liquor contained the emulsion, PEI, acetic acid, and a nonionic wetting agent [1.0 g/L Antarox CO630 (GAF)]. The polymer concentration was varied to give the required add-on at 50% expression (i.e., wet pick-up). PEI was used at a constant 0.1% on mass of fabric (omf), and a 1:5 ratio of acetic acid to PEI ensured emulsion stability (pH 8) of pad baths. Samples were padded and then dried and cured in a laboratory stenter at 150°C for 3 min.

A Pretema Multicolor (system Ellner) machine was used for the exhaust application of the polyacrylate emulsion at a liquor:fabric ratio of 30:1. The fabric was wetted out [a 0.05 g/L solution of Teric N8 (ICI) was used for wool samples] and the polyacrylate, PEI [10% on mass of polyacrylate (omp) except where specified otherwise] and acid were added either as a stable premix or separately. Exhaustion occurred at room temperature when the pH was raised by adding a base (e.g., sodium carbonate). In an alternative procedure, the initial addition of a nonionic surfactant [Teric N8 (ICI)] was used to induce exhaustion at elevated temperatures, the bath being heated to 70°C over 30 min. Exhaustion was assumed to be complete when the liquor had cleared. The fabric was then hydroextracted and cured in a stenter for 3 min at 150°C.

Test Methods

Felting shrinkage of wool samples measured after wash testing was carried out in a 50-L Cubex International machine containing 15 L of wash liquor (0.05 g/L sodium dodecylbenzene sulfonate, pH 6.8 phosphate buffer, 40°C) and a 1-kg load of samples and polyester make-weights. The wrinkle recovery of samples was determined using the multiple pleat test [25]. Samples were wetted out to remove effects caused by aging and reconditioned prior to testing.

RESULTS AND DISCUSSION

Application of Polymer by Exhaustion

In an exhaust process the polymer emulsion particles selectively deposit onto the surface of the textile fibers from a well-agitated aqueous system. It was observed that with polyacrylate-PEI compositions this is favored under the conditions of high dilution which exist in exhaust treatment baths. Exhaustion occurred readily at PEI concentrations up to 4% omp with wool and nylon fabrics or at 10% omp with cotton, the bath eventually becoming clear.

When the PEI concentration exceeded 4% omp (for wool and nylon), exhaustion could be promoted by two different Methods, A and B.

Method A

At given proportions of the three basic components, polyacrylate latex, PEI, and fabric, exhaustion could be achieved by raising the pH of the bath by the addition of a base such as sodium carbonate, sodium hydroxide, or ammonia. In its application to wool fabrics, the important features of the process were:

(a) Higher pH values required to achieve exhaustion at increasing PEI concentration as shown in Fig. 1

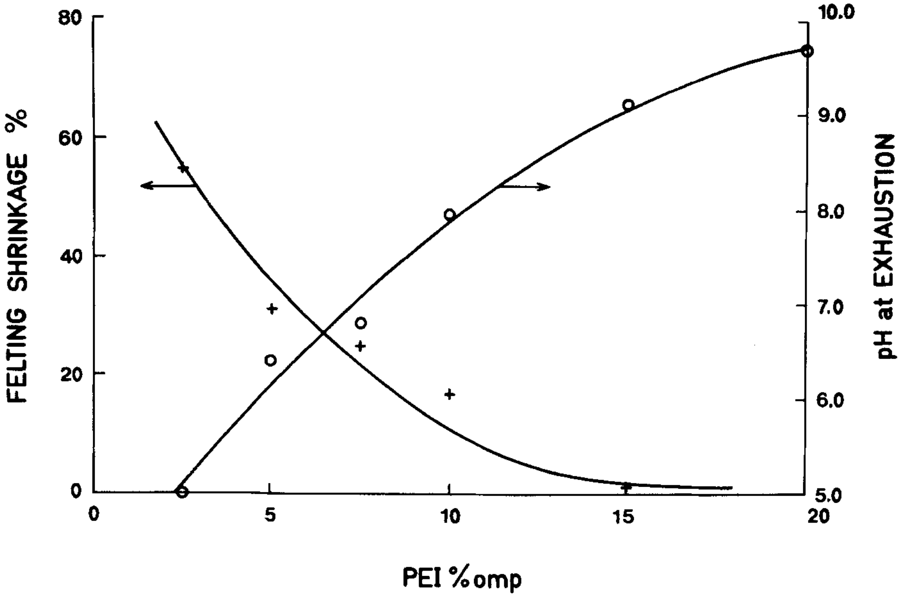

FIG. 1. Effect of PEI concentration on the pH at exhaustion (o) and area felting shrinkage (+) of wool fabric treated at 2.8% polyacrylate omf.

(b) The shrink-resist properties of wool treated in this way were good at PEI concentrations in excess of 10% omp (Fig. 1).

Method B

Exhaustion could be achieved (at a constant pH) by heating the bath in the presence of a heat sensitizing agent to at least 60°C. Suitable heat sensitizers were nonionic surfactants of low cloud point such as the nonylphenol ethoxylates containing from 7 to 12 ethylene oxide units. The important feature of this process with wool was that more surfactant was required with:

(a) Increasing PEI concentration (Fig. 2)
(b) Increasing acetic acid concentration (Figs. 2-4)
(c) Increasing polyacrylate concentration at a fixed ratio of PEI to polyacrylate (Fig. 3)

Mechanism of Exhaustion

Earlier work [5] showed that PEI can effectively cross-link the polyacrylate latex upon film formation to impart a level of durability

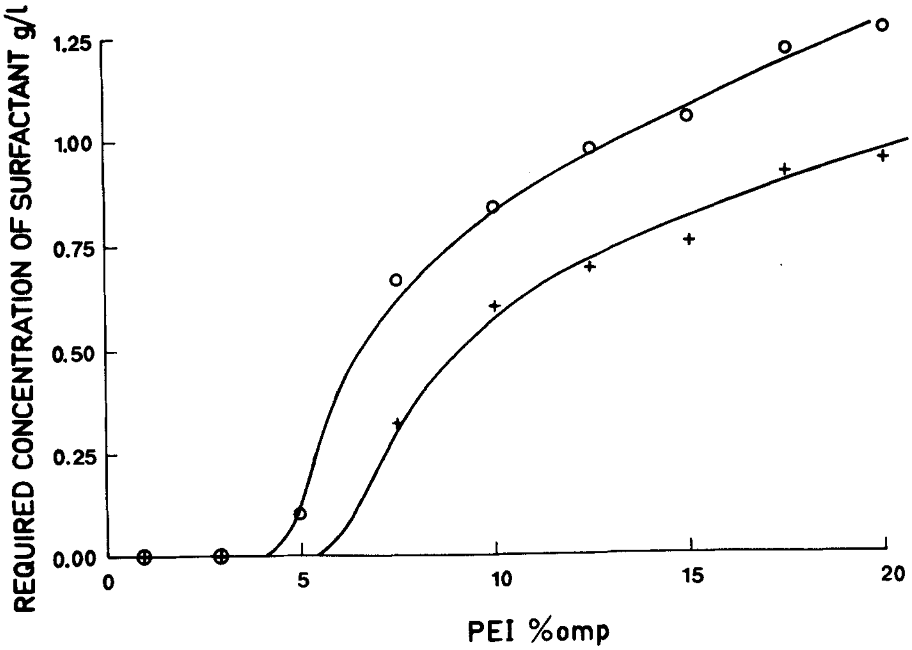

FIG. 2. Effect of PEI concentration on the amount of surfactant required to promote exhaustion of 4% polyacrylate omf onto wool fabric with no acid (+) and 25% acetic acid on mass of PEI (○).

unattainable by polyamines not of the polyethylene polyamine type. High molecular weight PEI can also act as a deposition aid in exhaust application by effectively modifying the stability of disperse systems. In the present system we expect this to occur as a result of its adsorption onto the surfaces of both the textile fibers and the latex particles. The degree of surface coverage imparted by this adsorbed film and the resulting electrical potentials of the respective surfaces would then determine whether particle deposition (heterocoagulation) [21] can take place. One would expect that both the charge and the degree of surface coverage of adsorbed PEI would be influenced by its concentration and the pH of the medium.

In the absence of PEI and at a pH greater than 4, it would be expected that the surface potentials of both the textile fibers [26] and the latex particles are negative, that of the latter being due to anionic end-groups formed during initiation. Accordingly, in the presence of PEI the stability of the system will be determined by the extent to which these charges are reversed [27] and its degree of surface coverage.

In Method A it is believed that, initially, a surplus of PEI is present

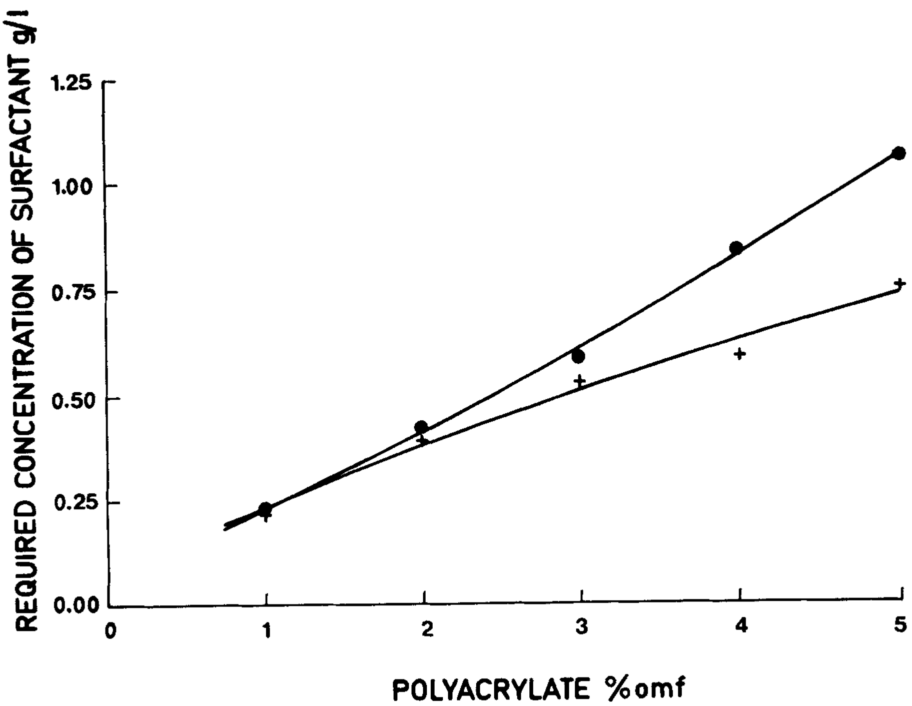

FIG. 3. Effect of polyacrylate concentration (containing 10% PEI omp) on the amount of surfactant required to promote exhaustion onto wool fabric using no acid (+) and 25% acetic acid on mass of PEI (●).

carrying sufficient positive charge to prevent particle deposition. By raising the pH, the charge on both surfaces would approach zero, thereby removing the electrical barriers to deposition. It is also possible that raising the pH reduces surface coverage sufficiently to allow particle deposition to occur by a "bridging" [28] or "patch-charge neutralization" [29] mechanism. Accordingly, the pH required for exhaustion should increase with increasing PEI concentration, as was observed (Fig. 1).

In Method B it was found that certain polymers or surfactants known to have an inverse solubility-temperature relationship were effective in inducing exhaustion at elevated temperature. One of the most effective of these was a polyethoxylated (8EO) nonylphenol surfactant (Teric N8) having a low cloud point. It is suggested that phase separation of the surfactant, induced at elevated temperature, leads to an increase in the surface area of the disperse phase and a redistribution of the adsorbed PEI. This dilution of adsorbed PEI

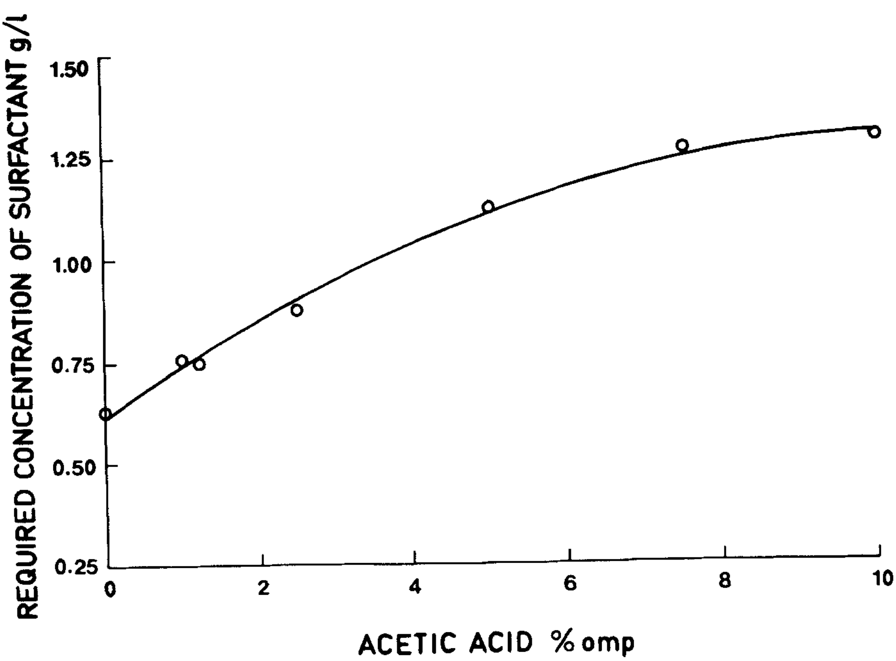

FIG. 4. Effect of acetic acid concentration on the amount of surfactant required to promote exhaustion of 4% polyacrylate omf (10% PEI omp) onto wool fabric.

at fixed pH provides alternative conditions for exhaustion. The quantity of surfactant required therefore depended on the quantity of latex to be deposited (Fig. 3) and the degree of stabilization afforded it by increased PEI and acid concentration (Figs. 2-4).

Application of Polymer by Padding

In the application of polymer by padding, it is important to prevent exhaustion (or flocculation) of the latex. This can be achieved at the optimum proportion of PEI to polyacrylate by the addition of sufficient acid. The very much higher polymer concentration employed in pad baths is also beneficial in this respect since the ratio of PEI to fabric is correspondingly higher, leading to a greater likelihood of the saturation of fiber surfaces by adsorbed PEI [27]. Presumably both latex and fibers are positively charged over a wide pH range (< 8.5) so that exhaustion does not occur.

Optimum PEI Concentrations

In the application of polymer by padding, at treatment levels above 3% omf, about 2-5% PEI omp has been shown to be optimum for curing [5]. However, at lower treatment levels (i.e., lower bath concentrations) where a significant proportion of PEI is presumably adsorbed on the fibers, it is preferable to use a fixed proportion of PEI to fabric of 0.1% omf [6], as in the present work. A still further (~100-fold) dilution occurs in exhaust treatment baths leading to a still higher proportion of PEI associated with the fibers. If much of this is unavailable for cross-linking the polyacrylate, then the requirement for higher proportions of PEI to polyacrylate (> 10% omp) in exhaust treatments (Fig. 1) can be understood.

Comparison of Pad and Exhaust Applications on Fabric Properties

The development of improved fabric properties by polymer treatments is dependent on both the durability of the finish and its distribution on the fibers. The presence of epoxy functionality imparts a cross-linking capability to the polyacrylate and has been shown to be a critical requirement for high washfastness [5]. The additional requirement for particular polyalkylene polyamine cross-linking agents [5] may reflect their greater contribution to adhesion, particularly with nonpolar surfaces. The effect of the polyacrylate on the subsequent properties of the treated fabrics is shown in Figs. 5-7.

The felting of wool during machine washing was greatly reduced by this treatment. As with most other polymer-based shrink-resist treatments, the effect was attributed to the formation of bonds by polymer between adjacent fibers [30, 31]. These bonds inhibit the relative movement of adjacent fibers, thus preventing felting in machine washing. The level of treatment required to prevent felting depended on its method of application. Pad application was considerably more effective than exhaust application (Fig. 5).

The polyacrylate emulsion also improved the wrinkle recovery of nylon fabric (Fig. 6), an effect which is also thought to result from the formation of polymeric interfiber bonds. A large component of the wrinkle recovery of nylon arises from the contribution of interfiber friction which prevents the return of fibers to their original conformation when the deforming force is removed. Interfiber bonds reduce this frictional component by limiting fiber movement [10] when the fabric is bent. In addition some polymers provide elastic restoring couples which aid the recovery of the fabric from deformation [32]. The polymer applied by padding improved wrinkle recovery at a lower concentration than that applied by exhaustion.

The polymer improved the wrinkle recovery of cotton (Fig. 7) as well as other properties such as its abrasion resistance [33]. As on

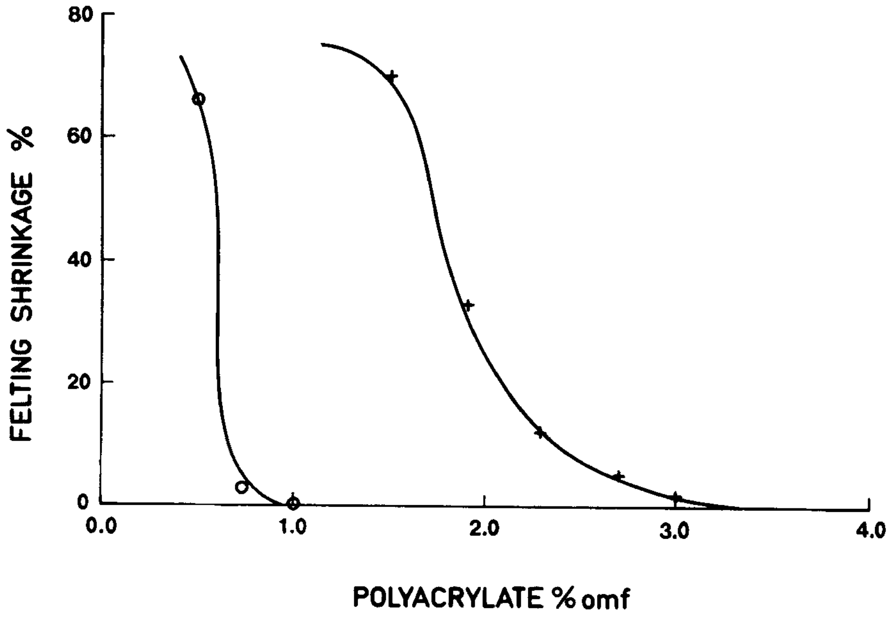

FIG. 5. Variation of area felting shrinkage of wool fabric in a 3-h wash test with the level of polyacrylate applied by padding (o) and exhaustion (Method B) (+).

nylon, polymers are thought to improve the wrinkle recovery of cotton by forming interfiber bonds. In this instance, however, the polyacrylate was equally effective whether applied by exhaustion or by padding.

In wool and nylon fabrics, scanning electron microscopy (SEM) studies (Fig. 8) clearly show that at equivalent treatment levels more interfiber bonds were formed when the polymer was applied by padding than when applied by exhaustion. Thus the greater effect of polymer treatment in padded fabrics suggests that it was a result of more efficient interfiber bond formation (Figs. 5 and 6). In SEM studies of cotton fabric (Fig. 8), the prevalence of interfiber bonds in exhaust treatments was comparable with that obtained by padding, and this corresponded well to the similar wrinkle recoveries produced by the two treatments (Fig. 7). Similar observations of polymer distribution have been made in nonwoven webs of cellulosic fibers prepared by the wet-laid process [34]. The prevalence of interfiber bonds in a web formed by "beater addition" of the binder (i.e., deposition onto fibers prior to web formation) using a cationic deposition aid was comparable with that in which the binder was applied by saturation of the preformed web.

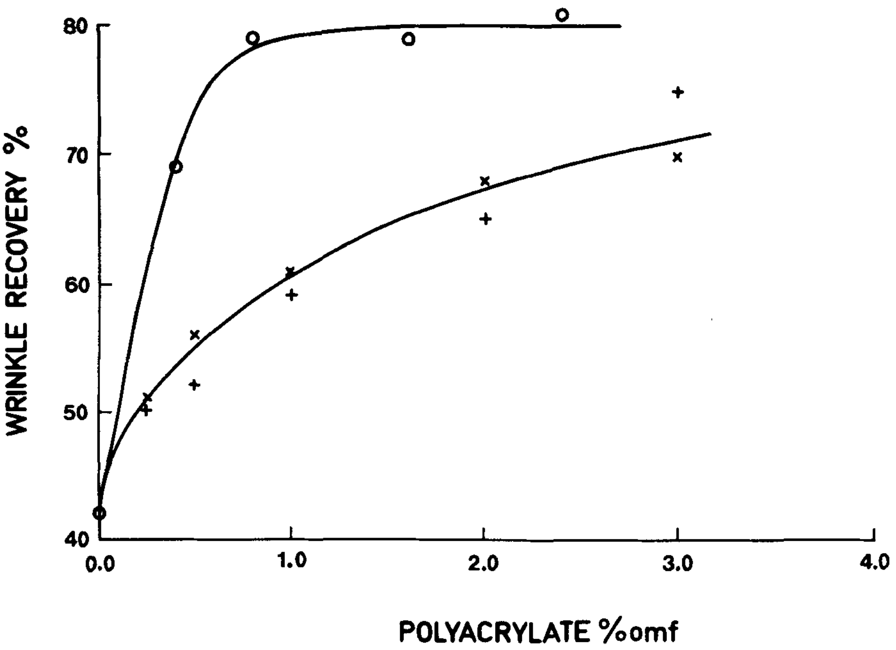

FIG. 6. Variation of wrinkle recovery of nylon fabric with the level polyacrylate applied by padding (o), and exhaustion by Methods A (x) and B (+).

In the application of polymer emulsions by padding, the colloidal stability of the system prevents particle deposition until virtually all of the water is removed during drying [35]. Thus, upon film formation, the polymer is concentrated in capillary spaces between fibers, thereby favoring the formation of interfiber bonds.

In exhaust applications the conditions that favor particle deposition should also allow for competing flocculation of latex particles. Accordingly, deposition may take place as individual particles or as flocs, and the size of flocs that deposit will depend on the rate of flocculation. This may influence the evenness with which the polymer is distributed throughout the textile. Thus not only the process of exhaustion but also its method will have a significant bearing on ultimate textile properties.

Although exhaust techniques may lead to an unfavorable polymer distribution, this may be alleviated to some extent by the spreading characteristics of the polymer over the fiber surfaces after particle coalescence, this being dependent on the wettability of the particular fiber. The apparent independence of polymer distribution in cotton fabrics on its method of application may result from the greater wettability of cellulosic fibers [35], possibly aided by wicking due to

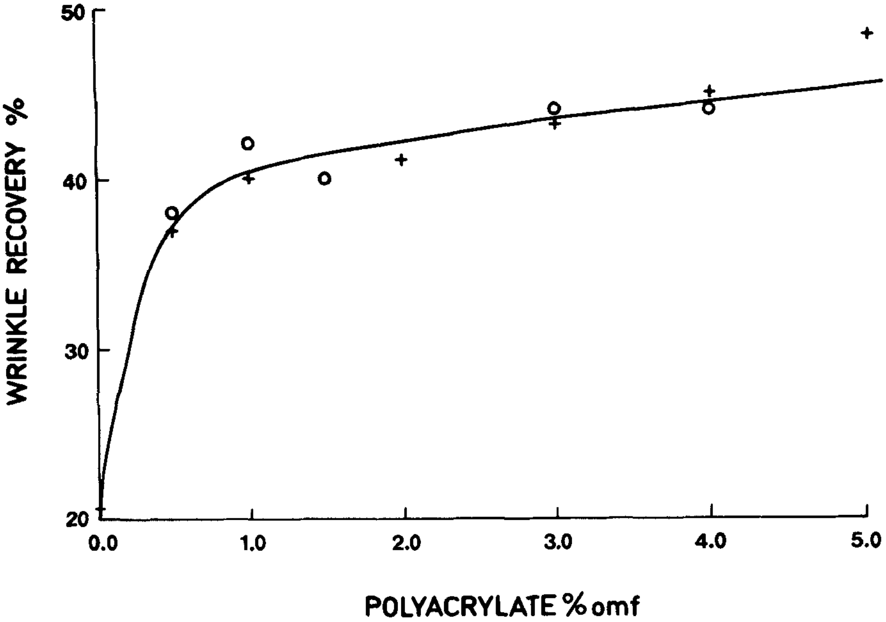

FIG. 7. Variation of wrinkle recovery of cotton fabric with level of polyacrylate applied by padding (○) and exhaustion (+).

their greater surface irregularity. The electron micrographs of treated cotton (Fig. 8) suggest that individual fibers are encapsulated, an indication of complete wetting. By contrast, the polymer film appears to form a small but finite contact angle on the more hydrophobic wool fibers. Incomplete coating of nylon is also evident.

CONCLUSION

A thermosetting textile finishing composition consisting of a chemically stable blend of an epoxy-functional polyacrylate emulsion and polyethylenimine has been applied to wool, cotton, and nylon fabrics by padding and exhaustion. Exhaust application depended on the role of high molecular weight PEI in the controlled destabilization of the polyacrylate emulsion by means of either pH variation or a temperature increase in the presence of suitable surfactants. PEI is an efficient cross-linking agent for the polymer, and the resulting finishes exhibited excellent durability on the hydrophobic surface of wool fibers. These treatments impart shrink-resist properties to wool and improved wrinkle-recovery properties to nylon and cotton fabrics.

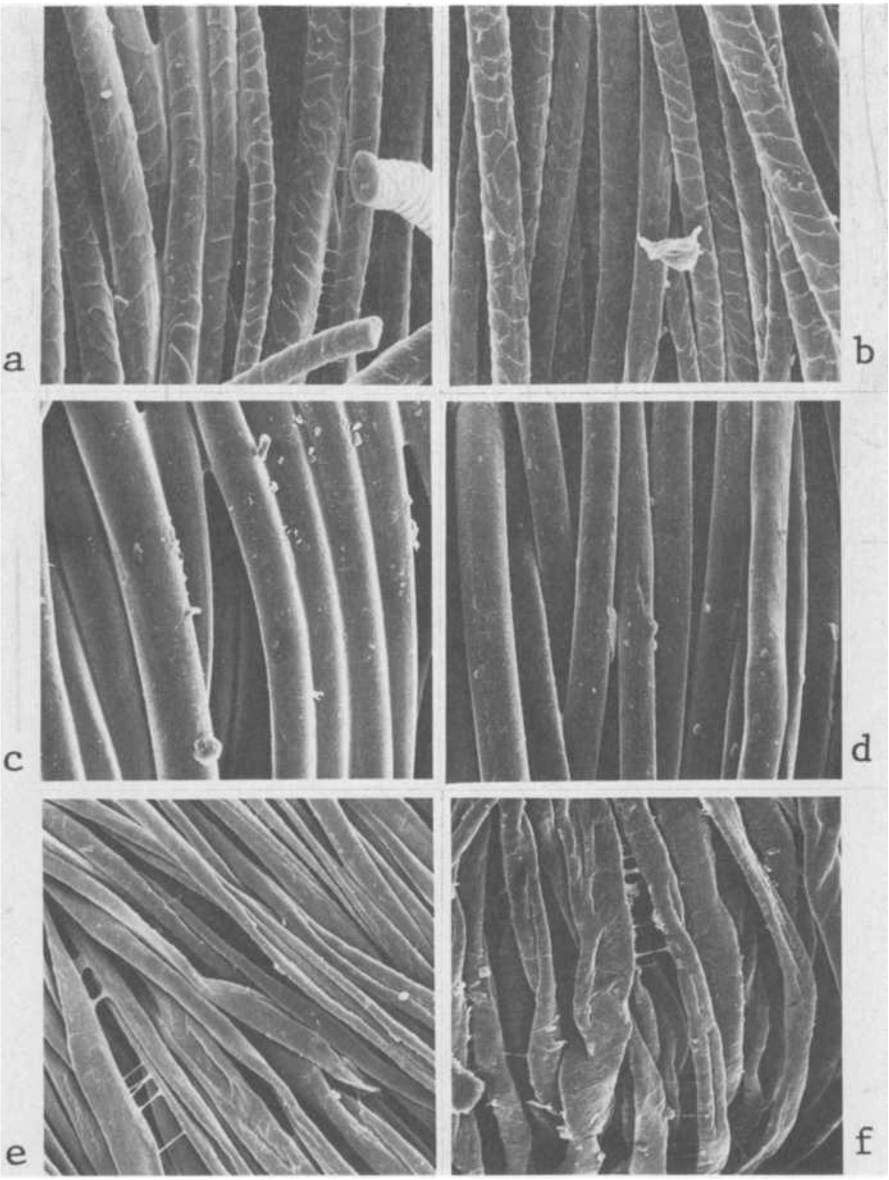

FIG. 8. Scanning electron micrographs of wool (a, b), nylon (c, d), and cotton (e, f) fabrics treated with polyacrylate [1% omf, except for (b): 3% omf] by pad application (a, c, e) and exhaust application (b, d, f).

The improved textile properties imparted to various fabrics reflect the frequency of interfiber bonds formed by the polymer. The efficiency of interfiber bond formation in wool and nylon was greater in pad treatments, whereas on cotton the results of exhaust and pad treatments were comparable.

The substantivity of this polymer treatment on wool fibers contrasts with the poor performance of commercial acrylic latices, and suggests that it may also adhere better to other hydrophobic fibers.

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