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COAPPLICATION OF SOFTENERS WITH AN ACID HALIDE CONTAINING POLYMERIC SHRINK-PROOFING AGENT TO TEXTILE FIBERS

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ABSTRACT OF THE DISCLOSURE

A composition comprising an acid halide copolymer shrinkage-resisting agent, a polyether or polysiloxane softener and a solvent, the process of applying the composition to polymeric fibers and subsequently heat treating the fibers, and a polymeric substrate coated with the shrinkage-resisting agent and the softener.

BACKGROUND OF THE INVENTION

This invention concerns the use of special chemical agents for improving the tactile aesthetics of a fabric product. Commonly called "hand" or "feel," and perhaps best expressed by the word "softness," this quality of any fabric is of great importance economically in obtaining customer acceptance of clothing and other textile articles. Certain shrink-proofing agents may leave a "boardy" or unacceptable "feel" to fabric products unless efficient agents are used to improve this quality. The softening agents of this invention remarkedly improve the softness or "feel" of fabric products without deleterious effects on either the aesthetics of the material or on its practical qualities, such as durability and warmth.

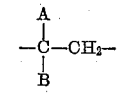
In particular, the tendency of wool to shrink upon washing has long been a bar to its wider use, and many methods have been used to improve its resistance to shrinking. Shrinking of wool textiles by laundering and drying includes relaxation shrinkage and felting shrinkage.

Relaxation shrinkage results from relaxation of stresses imposed on the garment structure during manufacture. Such shrinkage is nonprogressive, is not unique to wool, and it cannot be prevented by any known shrink-proofing treatment. Felting shrinkage, on the other hand, is a phenomenon restricted to wool and it is progressive. Felting is associated with the fact that wool fibers are highly elastic in the wet state and exhibit a directional friction effect due to the presence of scales on the fiber surface. The morphology of the scales is such that the co-efficient of friction of the wool fiber is higher in the tip to root direction than vice versa. Because of the directional friction effect wool fibers, during agitation in the wet state tend to move rootwards only, thus resulting in inextricable entanglement.

A new and efficient process which improves the dimensional stability of textiles is described in U.S. Patent No 3,310,428. However, while shrink-resistance is greatly improved by this process, the quality of "hand" or "feel" in the resulting product is poorer than it was before the treatment, particularly when the process is applied to finished articles such as sweaters. It is to this problem, the improvement of the "hand" of the treated textiles, that this invention provides a solution.

SUMMARY OF THE INVENTION

A solution of an acid halide comprising (a) at least 50 mole percent of ethylenically unsaturated units having the formula:

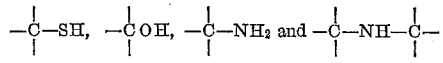


where A is selected from the group consisting of hydrogen, C_1 to C_8 alkyl, C_1 to C_8 alkoxy, aryl, chloride, bromine, carboalkoxy such that the unit is an acrylate or methacrylate, acyloxy such that the unit is a vinyl ester, cyano, aldo such that the monomer is acrolein or substituted acrolein, and B is seletced from the group consisting of hydrogen, methyl, chlorine or bromine, and (b) from 0.1 to 50 mole percent of alpha, beta-ethylenically unsaturated carboxylic acid halide units having 3 to 8 carbon atoms, and from about 1 to 3 times the weight of said copolymer of a polymeric oxygen containing organic compound immiscible with said copolymer, and a chlorinated solvent having no reactive hydrogen atoms.

DESCRIPTION OF THE INVENTION

The term "hand" is a commonly used expression in the textile trade. A discussion of its meaning and its relation to softeners is contained in the article "An Assessment of the Relationships Between Softener Level and People's Appreciation of Fabric 'Hand'," American Dyestuff Reporter, Jan. 3, 1966, (pages 30–39). The desirability of dimensional stability or shrink resistance in textile fabric is generally accepted. U.S. Patent 3,310,428, describes a new and improved process which increases the dimensional stability of textile fabric. While the use of this process does not cause excessive stiffening of fabric such as is caused by some thermosetting resin treatments, some deficiency of the "hand" or "feel" of the fabric usually accompanies it.

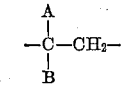
Textile fibers which may be treated effectively according to the subject invention are any fibers which contain reactive groups selected from the class consisting of groups having formulas:



It is apparent that the textile fibers employed in the present invention comprise polymeric materials containing mercapto groups, hydroxyl groups, primary and secondary amine groups and amide groups. A relatively large class of materials containing these functional groups are naturally occurring polymeric materials. The present invention is particularly applicable to such proteinaceous polymers as wool and other types of hair, leather, and silk. The present invention is also applicable to cellulosic fibers such as cotton and all synthetic polymeric fibers which contain the necessary functional groups. Blends of fibers may also be treated.

The textile fibers may be treated in the form of yarn, of woven or knitted fabrics, or fabricated garments such as shirts, dresses, sweaters, socks, and the like.

The shrink-proofing agent employed in the present fiber treating process is a copolymer comprising (1) ethylenically unsaturated units having the formula:



where A is hydrogen, C_1 to C_8 alkyl, C_1 to C_8 alkoxy, aryl, chlorine, bromine, carboalkoxy such that the monomer is an acrylate or methacrylate, acyloxy such that the monomer is a vinyl ester, cyano, aldo such that the monomer is acrolein or substituted acrolein, and B is hydrogen, methyl, chlorine or bromine and (2) alpha, beta-ethylenically unsaturated carboxylic acid halide units having 3 to 8 carbon atoms. The alpha, beta-ethylenically unsaturated carboxylic acid halide units are present in the copolymer to the extent of at least 0.1 mole percent and can be as high as 50 mole percent. The preferred concentration of the acid halide component of the copolymer is from 0.2 to 20 mole percent. The ethylenically unsaturated units of the copolymer may be supplied by a single monomer or at least by two different monomers and such units will be present in the copolymer in the amount of at least 50 mole percent based upon the total moles of units polymerized to form the polymer. The degree of polymerization of the acid halide copolymer should be at least 75 to 100 to ensure that the copolymer is a solid at use temperatures which are usually below 125° F.

Direct polymerization of ethylenically unsaturated acid halides does not result in the formation of polymeric materials which are suitable for use as shrinkage resistant agents in the invention process. The acid halide groups in the polymeric agent are obtained by the polymerization of an alpha, beta-ethylenically unsaturated acid containing preferably 3 to 8 carbon atoms which is then converted to the acid halide. Examples of such acids are acrylic, methacrylic, itaconic, maleic, crotonic, fumaric, glutaconic, and cinnamic acid. In the case of the polycarboxylic acids, one of the acid groups can be esterified.

The preferred monomers for supplying the ethylenically unsaturated units of the copolymers are alpha olefins such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-butene, styrene, and the like. The scope of the acid copolymers suitable for conversion to polymeric acid halides for use in the invention process is illustrated by the following examples: Copolymers of ethylene/acrylic acid, ethylene/methacrylic acid, ethylene/itaconic acid, ethylene/methyl hydrogen maleate, ethylene/maleic acid, styrene/methacrylic acid, methyl methacrylate/methacrylic acid, ethylene/acrylic acid/methyl methacrylate, ethylene/methacrylic acid/ethyl acrylate, ethylene/itaconic acid/methyl methacrylate, ethylene/methyl hydrogen maleate/ethyl acrylate, ethylene/methacrylic acid/vinyl acetate, ethylene/propylene/acrylic acid, ethylene/styrene/acrylic acid, ethylene/methacrylic acid/acrylonitrile and ethylene/vinyl chloride/acrylic acid.

The preparation of the copolymers from which the acid halide copolymers are derived is well known; for example, methods for the preparation of ethylene/carboxylic acid copolymers are given in USP 2,646,425. In general, the copolymers are formed by direct copolymerization of the monomers employing a free radical catalyst, such as a peroxide, or Friedel Crafts and related ionic catalysts. The polymerization is generally carried out in the presence of an inert solvent but may also be carried out in bulk when the monomers are liquid at polymerization conditions. The acid halide copolymers employed in the invention process are obtained from the acid copolymers by treating with a halogenating agent such as carbonyl chloride, thionyl chloride, phosphorous trichloride and phosphorous pentachloride and the equivalent bromine and fluorine compounds. The halogen substitution is usually carried out in an organic solvent for the copolymer, preferably a halogen containing solvent such as carbon tetrachloride, perchloroethylene, trichloroethylene. Although it is possible to have a complete conversion of the acid to the acid halide, satisfactory products for use in the invention process may be obtained at lower conversions. Although the acid halide may be a chloride, a bromide, a fluoride, or an iodide, it is preferred to employ the chloride because the chlorination reaction of the acid copolymer is readily achieved and controlled, and because the chloride is the most economical.

The following statement sets forth a method for the conversion of an acid copolymer to the corresponding acid chloride product:

One pound of ethylene/vinyl acetate/methacrylic acid copolymer, 69.9 parts of ethylene per 23.2 parts of vinyl acetate per 6.9 parts of methacrylic acid having a melt index of 480, was added to 3 gallons of carbon tetrachloride at a temperature between 50° and 60° C. One hundred and fifty grams of phosphorous pentachloride were dissolved on a steam bath in 1½ gallons of carbon tetrachloride. This solution was added to the ethylene terpolymer slurry. The mixture was placed in a five gallon glass-lined stirred kettle fitted with a condenser and a nitrogen inlet. The temperature was maintained at 60° C. for 2 hours with agitation while a slow nitrogen purge was maintained on the kettle. Hydrogen chloride gas was trapped off from the reactor. The temperature was then raised to 70° C. for 5 hours. All polymer was in solution. The solution was then added to 30 gallons of acetone with vigorous stirring to precipitate the polymer. The polymer was collected on a filter, washed several times with acetone by redispersing the polymer in acetone and dried in a vacuum at room temperature. Complete conversion of acid to acid chloride was indicated by infrared scan, and no loss in vinyl acetate was detected. Polymer was readily soluble in xylene at room temperature.

The preferred softeners to be used according to this invention are polymeric oxygen containing organic compounds of the polyether type such as polytetramethylene glycols, polyethylene glycols, polypropylene glycols and polybutylene glycols and polysiloxanes. Certain species of all of these generic types of polymers meet the standards imposed by the requirements of the invention, namely they must be mutually soluble with the polymeric shrink-proofing agent in certain inert organic solvents, and they must be immiscible with the polymeric shrink-proofing agent itself.

The solvent used to produce a solution of the polymeric acid halide shrink-proofing agent and the softening agent is a chlorinated solvent having no reactive hydrogen atoms and preferably having a boiling point near the boiling point of water or steam distilling at this temperature and being nonflammable. By steam distilling is meant a flashing off from the fiber of solvents having a B.P. 160° F.; the vaporizing, with steam, of solvents having a B.P. above 212° F.; and the flashing off or vaporizing, with steam, of solvents having a B.P. between 160° F. and 212° F., depending on said water temperature. Representatives of such a solvent are perchloroethylene, trichloroethylene, carbon tetrachloride, methyl chloroform.

The solution of the copolymer containing acid halide units and the softening agents is applied to the fiber (1) by padding, wherein a dip into a solution bath is followed by passage through squeeze rolls, (2) by spraying one or both surfaces of the fabric, or (3) by dipping followed by centrifuging to remove the excess solution. The padding and spraying application methods may be operated continuously and are preferred for woven or knitted piece goods. The dipping and centrifuging procedure is suitable for sweaters, socks, yarns in skein form. The solution may also be applied in a package or rawstock dyeing machine where the solution is pumped through a package of yarn or rawstock (loose fibers). In this case, the solvent may be removed by suction and the cure subsequently effected by application of heat at 80° C. to 130° C. Alternatively, the impregnated fiber may be removed from the dyeing machine for the heat cure in another piece of equipment. The copolymer solution may be applied by "electrostatic spraying"—a method that may be preferred for non-uniformly shaped objects.

The fiber may be treated at any of several stages of

processing, e.g. (1) fibers before spinning (2) spun yarn; (3) fabric (a) after carbonizing, (b) after bleaching, (c) after dyeing, (d) before dyeing or (e) after printing; (4) knit fabrics, (5) knit garments and (6) sewn garments may also be so treated.

The amount of copolymer that is applied to the fiber depends upon whether the fabric is to be made resistant to shrinkage during such mill processing operations as bleaching, scouring, and dyeing or is to have resistance to shrinkage during laundering. To prevent shrinkage during one or two machine launderings a concentration of at least 1.2% based on the weight of the fabric of the polymeric acid chloride is required. To withstand 5 or more launderings without shrinkage, a concentration of 1.8% to 2% is recommended. Amounts of up to 5% may be used in special cases where the tendency to shrink is hard to overcome and the fabric hand and cost of application are secondary considerations. Shrinkage of the fibers during mill processing is generally prevented with from 0.5 to 1% of the copolymer, but higher amounts will be used under severe conditions of wet processing. Enough solution of a given solution concentration is picked up by the fiber to provide the above amounts of shrink-proofing agent. A wet pick-up of 50 to 150% by weight is usually attained. The softening agent is used in an amount 1 to 3 times the weight of the shrink-proofing agent.

The mechanism by which acid halide containing polymers impart dimensional stability to textile materials is believed to be mainly due to extensive intramolecular cross-linking induced by water present in the fabric. This mechanism is illustrated using chlorine by the following equations:

(1) $\text{Resin-}\overset{\overset{O}{\|}}{C}\text{-Cl} + H_2O \rightleftarrows \text{Resin-}\overset{\overset{O}{\|}}{C}\text{-OH} + HCl$

$$\text{Resin-}\overset{\overset{O}{\|}}{C}\text{-Cl} + \text{Resin-}\overset{\overset{O}{\|}}{C}\text{-OH} \rightleftarrows \text{Resin-}\overset{\overset{O}{\|}}{C}\text{-O-}\overset{\overset{O}{\|}}{C}\text{-Resin} + HCl$$

A secondary mechanism which may contribute to dimensional stability of the textile materials is the reaction of the resin with portions of the materials containing an active hydrogen atom, such as amino, hydroxy and mercapto groups. This mechanism is illustrated by the following equation:

(3) $\text{Resin}\text{—}\overset{\overset{O}{\|}}{C}\text{—Cl} + \text{HA-protein} \rightarrow \text{Resin}\text{—}\overset{\overset{O}{\|}}{C}\text{—A-protein} + HCl$

where A=N, S or O.

The mechanism by which the dimensional stabilization of the textile material is achieved is believed to involve: (a) chemical bonding of the resin to the fiber (Equation 3), and (b) encapsulation or sheathing of individual wool fibers resulting from intramolecular cross-linking of the resin itself (Equations 1 and 2). It is felt that fiber-to-fiber bonding, particularly at high added-on levels of resin, may be responsible for the relative harshness of "boardy" feel of fabrics so treated.

The use of conventional paraffinic softeners in co-application with the acid halide containing resins results in adverse effects on dimensional stability. This is probably due to the chemical similarity between such softeners and the shrink-proofing agent, whose nature is largely paraffinic. Softeners of this type appear to function as extenders for the resin after the common solvent is removed. The resulting dilution effect, coupled with the rather high viscosities of most softeners, appears to impair the ability of the resin to undergo effective cross-linking. The hydrophobic nature of paraffins seems to further hamper the process of cross-linking by preventing or reducing the access of water to the reactive sites of the acid halide containing resin. These arguments are supported by the fact that shrink-proofing is generally improved whenever samples are cured under humid conditions and elevated temperatures. The latter factor, of course, affects the viscosities of resin softener mixtures and thus the frequency of intramolecular collisions that lead to the cross-linking of resin molecules.

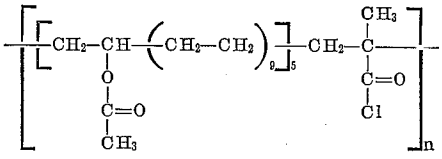
It appears, therefore, necessary to fined softeners which are soluble in the solvents usually used for resin application but immiscible with the acid chloride containing resin. Coapplication on fibers under the above provision, followed by evaporation of the solvent, results in deposition of discrete phases of resin and softeners so that cross-linking within the former is not hampered by the latter. The competition of the two incompatible chemicals for the same areas reduces the extent of fiber-to-fiber bonding resulting when the shrink-proofing agent is applied alone. It is also desirable that the softener does not exhaust significantly on the fiber, so that mixtures with the shrink-proofing agent can be used repeatedly without any appreciable change in their composition.

To explain the action of the softener types revealed by this invention, it is necessary to visualize the action of the shrink-proofing agent without softener as resulting in a more or less continuous phase of resin polymer, concurrent with, and coating the fibers. If a deficiency of the resin is present, dimensional stability will not be ensured. If too much resin is present, a "boardiness" or harsh hand will result. The recommended type softeners will first of all compete with the shrink-proofing agent for sites in the fiber, thus lessening the rigid character of the resin-polymer phase. Subsequent removal of some of the softener by washing will leave a "net" of shrink-proofing resin, which will effectively maintain dimensional stability, but which, nevertheless, will afford a fluidity and ease of deformation accounting for the excellent "hand" or "feel" of the material. Residual softener will contribute to the softness of the material due to its lubricating quality.

The essential nature of this invention is embodied in the requirement that the softening agent be immiscible with the acid halide containing resin employed for the shrink-proofing function. While not limited to specific chemical types, the nature of the softener used will normally be lubricative, as are most conventional textile softening agents.

Among the chemical types of softening agent which meet the two requirements of (1) mutual solubility with the acid halide containing shrink-proofing resin in the same solvent and (2) immiscibility with the resin itself, are certain polyethers such as polytetramethylene glycols, polyethylene glycols, polypropylene glycols and polybutylene glycols and polysiloxanes.

The following examples are representative embodiments of this invention. All percents are by weight unless otherwise specified. The shrink-proofing agent used in the examples was



Example 1

A number of woolen swatches (Carleton, style 178) were treated in perchloroethylene solutions containing 0.75% of a polymeric acid-chloride containing shrink-proofing agent and 1.5% of softener. The swatches were extracted to about 200% wet pick-up (about 1.5% shrink-proofing agent and 3% softener), air dried and cured at 100° C. for about 10 minutes. The "hand" or "feel" of all swatches on which softener has been co-applied was excellent, and markedly superior to that of samples treated with shrink-proofing agent alone. Properties after

3 standard home washes are summarized in the following table:

TABLE I.—EFFECT OF CO-APPLIED SOFTENERS ON SHRINK PROOFING

Sample	Softener	Percent shrinkage after three washes: Warp, percent	Fill, percent
A	None	3.0	2.5
B	Polyethylene glycol (ave. mol. wt. —550).	3.5	2.5
C [1]	Polyethylene glycol (ave. mol. wt. —660).	3.5	3.0
D	Silicone oil	5.0	3.5
Untreated fabric		18.0	11.0
Relaxation shrinkage		6.0	2.5

[1] Trichloroethylene was used as solvent.

In the above examples, the total shrinkage of the treated swatches after 3 washes was much less than that of the untreated swatches, and about the same as the relaxation shrinkage inherent in the type of fabric tested.

Example 2

The following solutions were prepared:

TABLE II

(A) 1.5% shrink-proofing agent+3% polypropylene glycol 400 in perchloroethylene
(B) 1.5% shrink-proofing agent+3% polypropylene glycol 1200 in perchloroethylene
(C) 1.5% shrink-proofing agent+3% polypropylene glycol 2000 in perchloroethylene

Each solution was used to treat 2 woolen swatches (Carleton, style 178) to 100% wet pick-up by soaking the swatches in the solution and wringing out the excess. One swatch from each solution was marked with a subscript x and air dried at room temperature, then cured in an oven at 100° C. for 5 minutes. The other swatches were air dried and cured in the 100° C. oven for a total of 8 minutes.

All swatches were subjected to 3 home washes (medium fill, normal cycle, 30 g. of laundry detergent, hot wash-warm rinse, 14 minute cycle). After every washing, samples were tumble dried at about 70° to 80° C. and the percent shrinkage was determined. The "hand" or "feel" of the samples was also judged.

TABLE III.—POLYPROPYLENE GLYCOLS AS SOFTENERS

Sample	Percent total shrinkage after— 1st wash: Warp	Fill	2nd wash: Warp	Fill	3rd wash: Warp	Fill	"Hand" or "Feel"
A_x	6.0	2.5	6.0	2.5	6.0	2.5	Good.
A	6.0	3.0	6.0	1.5	6.5	3.0	Do.
B_x	5.0	1.5	5.5	0.0	5.5	1.5	Do.
B	6.0	2.0	5.5	1.5	5.5	1.5	Do.
C_x	6.0	2.0	5.5	0.0	6.0	1.5	Excellent.
C	6.0	1.5	5.5	0.0	6.0	1.5	Do.
Control (Untreated).	15.0	5.0	16.5	6.5	21.0	10.0	

Example 3

Solutions were prepared of 1.5% shrink-proofing agent and 2.5% of the following softeners in trichloroethylene as solvent:

TABLE IV

	Ave. mol. wt.
(A) Polyethylene glycol	600
(B) Polyethylene glycol	1500
(C) Isooctyl phenyl polyethoxy ethanol	----
(D) Nonylphenoxypoly(ethyleneoxy)ethanol	720
(E) Nonylphenoxypoly(ethyleneoxy)ethanol	630

Three woolen swatches (Carleton, style 178) were treated with solution A to about 100% wet pick-up of the solution, then dried and cured for 5 minutes at 100° C. Each of the other solutions was used to treat three swatches in the same manner. The "hand" or "feel" of all treated swatches was much improved over that of the swatches containing no softener.

One swatch of each type was subjected to five home washes, and the percent shrinkage determined.

TABLE V.—PERCENT TOTAL SHRINKAGE

Sample	After 1st Wash: Warp	Fill	After 3rd Wash: Warp	Fill	After 5th Wash: Warp	Fill
A	5.0	1.5	6.5	2.0	6.5	2.0
B	5.5	1.5	6.5	2.0	6.5	2.5
C	6.0	2.0	6.0	3.0	6.0	3.0
D	5.5	2.0	6.0	2.5	6.0	3.0
E	6.0	2.5	6.5	2.5	6.5	2.5
Untreated	15.0	7.5	20.0	12.0	26.0	16.0

Example 4

The following solutions were prepared from a copolymer made with 85% ethylene and 16% methacrylyl chloride.

TABLE VI

(A) 1.5% copolymer in trichloroethylene
(B) 1.5% copolymer in tetrachloroethylene
(C) Same as (A), but including 2.5% polyethylene glycol (ave. mol. wt. —550)
(D) Same as (B), but including 3.0% polypropylene glycol (ave. mol. wt. —2000)
(E) 3.0% copolymer plus 5% polytetramethylene glycol in trichloroethylene (ave. mol. wt. —1000)
(F) 3.0% copolymer plus 5% polyethylene glycol in trichloroethylene (ave. mol. wt. —1500)

The woolen swatches (Carleton, style 178) were treated with solution A to 100% wet pick-up, then air dried and cured at 100° C. for about 7 minutes. Similarly, two swatches were treated with solution B, two with solution C and two with solution D. With solutions E and F, the swatches were wrung out to about 50% wet pick-up, tumble dried at 70°–80° C. then cured for 7 minutes at 100°–105° C.

All of the samples containing softeners had significantly better "hand" and felt much softer than samples A and B, where no softener was used.

All swatches were subjected to five home washes using laundry detergent (normal setting, medium load, hot wash, warm rinse) and finally tumble dried at 70°–80° C. There was no significant difference in shrinkage among the swatches, as indicated by the results tabulated below.

TABLE VII.—PERCENT TOTAL SHRINKAGE

Sample	After 1st Wash: Warp	Fill	After 3rd Wash: Warp	Fill	After 5th Wash: Warp	Fill
A	4.0	0.0	5.5	0.0	6.0	2.0
B	3.0	1.0	5.0	1.5	5.0	1.5
C	3.5	1.0	5.0	1.5	5.5	2.0
D	4.5	0.5	6.0	2.0	6.5	2.0
E	4.0	1.5	6.5	1.5	6.5	1.5
F	4.0	1.0	5.5	1.5	6.0	2.0
Untreated	13.0	8.0	39.0	12.0	25.0	16.0

Relaxation shrinkage.—After wetting with water containing 1% isooctyl phenyl polyethoxyethanol for about one hour, followed by a cold water rinse, shrinkage was 5.5% in the warp and 1.5% in the fill.

Example 5

A number of tests were made to determine the usefulness of various solvents in the process involving co-

application of 1.5% shrink-proofing agent and various textile softeners in various solvents as follows:

TABLE VIII.—1.5% SHRINK-PROOFING AGENT +

Softener	Solvent
A 3% polyethylene glycol (ave. mol. wt. —750)	Carbon tetrachloride.
B 2.5% polyethylene glycol (ave. mol. wt. —550)	Benzene.
C 2.5% polypropylene glycol (ave. mol. wt. —2025).	1:1:1 trichloromethane.
D 3% polymethylene glycol (ave. mol. wt. —1010).	Chloroform.
E 3% silicone oil	Cyclohexane.
F 2.5% polypropylene glycol (ave. mol. wt. —1200).	Hexane.
G 2.5% octylphenoxy poly (ethyleneoxy) ethanol (ave. mol. wt. —770).	Chloroform.
H 3.0% polymethylene glycol (ave. mol. wt. —2000).	1:1:1 trichloroethane.
I 3.0% polyethylene glycol (ave. mol. wt. —750)	Chloroform.
J 2.5% polypropylene glycol (ave. mol. wt. —2000).	Benzene.
K 2.5% isooctylphenylpolyethoxy ethanol (ave. mol. wt. about 650).	Chloroform.
L 3.0% polypropylene glycol (ave. mol. wt. —1200).	Carbon tetrachloride.

Two swatches (Carleton, style 178) were treated with solution A, two with solution B and so on for each of the twelve solutions to about 100% wet pick-up. One swatch from each set was air dried at room temperature, the other tumble dried at 70°–80° C. All swatches were cured at 100°–150° C. for about 7 minutes. All were significantly softer than swatches treated in perchloroethylene with shrink-proofing agent alone. Swatches A, B, F and J were the best. After five home washes the following data were obtained:

TABLE IX

	Percent total shrinkage (Warp and Fill)		
	After 1st Wash	After 3rd Wash	After 5th Wash
A	9.5 x 0.0	6.0 x 1.5	6.5 x 2.0
B	4.5 x 1.0	6.0 x 2.0	6.5 x 2.0
C	5.0 x 0.0	5.5 x 1.5	6.0 x 1.5
D	3.5 x 1.0	4.5 x 1.5	5.5 x 2.0
E	5.0 x 1.0	5.5 x 2.0	6.5 x 2.5
F	3.5 x 1.5	5.0 x 2.0	5.5 x 2.0
G	5.5 x 1.5	6.0 x 2.0	6.5 x 2.5
H	3.0 x 1.5	5.0 x 2.0	6.0 x 2.5
I	4.0 x 1.5	5.0 x 2.0	6.0 x 2.5
J	5.0 x 0.5	6.0 x 1.5	6.0 x 2.5
K	5.5 x 1.5	6.5 x 1.5	7.5 x 2.0
L	5.0 x 0.5	6.0 x 1.5	0.5 x 2.0
Untreated	13.0 x 6.0	21.0 x 12.0	26.0 x 16.0

It is to be understood that the preceding examples are representative and that said examples may be varied within the scope of the total specification, as understood by one skilled in the art, to produce essentially the same results.

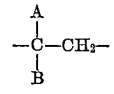
As many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof, except as defined in the appended claims.

I claim:

1. As a composition of matter a solution comprising

(1) a copolymer consisting essentially of

(a) at least 50 mole percent of ethylenically unsaturated units having the formula



where A is selected from the group consisting of hydrogen, C_1 to C_8 alkyl, C_1 to C_8 alkoxy, aryl, chloride, bromine, carboalkoxy such that the unit is an acrylate or methacrylate, acyloxy such that the unit is a vinyl ester, cyano, aldo such that the monomer is acrolein or substituted acrolein, and B is selected from the group consisting of hydrogen, methyl, chlorine or bromine, and

(b) from 0.1 to 50 mole percent of alpha, beta-ethylenically unsaturated carboxylic acid halide units having 3 to 8 carbon atoms, and

(2) from about 1 to 3 times the weight of said copolymer of a polymeric oxygen containing organic compound selected from the group consisting of polyalkylene glycols having from 1 to about 5 carbon atoms per monomeric unit and alkyl C_{6-10} phenoxypoly (ethyleneoxy) ethanols which compound is immiscible with said copolymer, and

(3) a chlorinated hydrocarbon solvent of 1 to 2 carbon atoms having no reactive hydrogen atoms.

2. The composition of claim **1** in which the polymeric oxygen containing organic compound is selected from the group consisting of polytetramethylene glycols, polyethylene glycols and polypropylene glycols.

3. The composition of claim **2** in which the chlorinated solvent is selected from the group consisting of perchloroethylene, trichloroethylene, carbon tetrachloride and methyl chloroform.

4. The process of imparting softness and shrinkage resistance to polymeric fibers which comprises

(1) applying the composition of claim **1** to said polymeric fibers, and

(2) subsequently raising the temperature of said polymeric fiber to a temperature of from 80° to 130° C. to evaporate the solvent and to fix the acid polymer on the fiber.

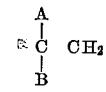
5. The process of claim **4** in which the polymeric fiber contains basic groups selected from the class consisting of groups having the formula —CSH, —COH, —CNH_2, and C—NH—C—.

6. The process of claim **4** in which the polymeric fiber is wool.

7. A composite comprising a polymeric substrate containing basic groups selected from the class consisting of groups having the formula —CSH, —COH, —CNH_2, —C—NH—C— and a coating on said substrate comprising

(1) a copolymer consisting essentially of

(a) at least 50 mole percent of ethylenically unsaturated units having the formula:



where A is selected from the group consisting of hydrogen, C_1 to C_8 alkyl, C_1 to C_8 alkoxy, aryl, chloride, bromine, carboalkoxy such that the unit is an acrylate or methacrylate, acyloxy such that the unit is a vinyl ester, cyano, aldo such that the monomer is acrolein or substituted acrolein, and B is selected from the group consisting of hydrogen, methyl, chlorine or bromine, and

(b) from 0.1 to 50 mole percent of alpha, beta-ethylenically unsaturated carboxylic acid chloride units having 3 to 8 carbon atoms, and

(2) from about 1 to 3 times the weight of said copolymer of a polymeric oxygen containing organic compound selected from the group consisting of polyalkylene glycols having from 1 to about 5 carbon atoms per monomeric unit and alkyl C_{6-10} phenoxypoly (ethyleneoxy) ethanols, which compound is immiscible with said copolymer, and in which at least 0.1 mole percent of the units of the coating polymer is reacted with the substrate through

the acid halide group to form linkages selected from the class consisting of ester amide linkages.

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117—138.8, 139.5, 141; 260—33.8