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PROCESS FOR STABILIZATION OF PROTEIN TEXTILES WITH 4-VINYL PYRIDINE COPOLYMERS AND PRODUCTS PRODUCED THEREFROM

Benjamin B. Kine and Nathaniel A. Matlin, Levittown, Pa., assignors to Rohm & Haas Company, Philadelphia, Pa., a corporation of Delaware

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This invention relates to the treatment of protein-containing textile materials and to the products thereof. It relates more particularly to a process of treating textile materials comprising scale-surfaced protein fibers, such as wool and wool-containing fabric, whereby the textile materials are stabilized against shrinking and felting.

An object of this invention is to provide aqueous dispersions of resins which are so stable that they can be stored and shipped, and which, when they are applied to protein-containing textile materials and are then heated, markedly reduce the tendency of the materials to shrink or render them substantially shrink-proof. Another object is to provide a process for shrink-proofing and felt-proofing textiles containing scale-surfaced protein fibers, whether of natural or artificial origin, through the use of the aforesaid dispersions. It is an object to shrink-proof and felt-proof the textiles without adversely affecting such other properties of the textile as wearing qualities, tensile strength, or hand. Still another object is to produce protein-containing textile materials, particularly woolen fabrics, which have a much reduced tendency to shrink and which also retain the desirable characteristics which are associated with woolen fabrics.

While this invention is principally concerned with improvements of, and more particularly the reduction of shrinkage and/or complete stabilization of textile materials of proteinaceous types, and while the invention is described primarily in terms of wool-containing textiles, the invention embraces the treatment of other protein-containing textile materials, such as those made of or containing silk, mohair, fur, Aralac (casein) and other synthetic fibers which are produced from casein, soybeans, collagen, et cetera, and especially scale-surfaced protein fibers of either natural or artificial origin. The terms "textile" and "textile materials" are used herein to include filaments, fibers, yarns, threads, plied yarns, rovings, and slivers as such or in woven, knitted, felted or otherwise formed fabrics, sheets, cloths and the like. Such textile materials may contain only one kind of proteinaceous fiber or a mixture of such fibers with other natural or synthetic fibers such as of cotton, linen, rayon, nylon, or polymers of acrylonitrile.

A number of different methods have been proposed for the treatment of textile materials formed of or containing wool or other protein fibers in order to prevent or decrease felting and shrinking. In many cases, such reduction in felting and shrinking tendencies has been obtained at the sacrifice of some other desirable property of the material. Some treatments damage the fiber and reduce the wearing qualities while others impart an undesirable harshness to the fabric. Other treatments are not permanently effective and may even cause an ultimate increase in shrinkage. Still other shrink-proofing methods are difficult to apply with uniformity and create hazards to the workers involved in their applications.

Certain polymers of the linear type have also been recommended, such as those containing isocyanate groups

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and certain esters of acrylic or methacrylic acid, such as the glycidyl esters thereof. The types of polymers of this class that have been found effective for reducing the shrinkage and felting of protein-containing textiles have so far been of rather limited scope. It has been found that many polymers of this type, which are quite similar to those which are effective, have no effect or have so little effect as to be of no practical value. For example, polymers or copolymers of glyceryl methacrylate,



are of this character.

The process of treating the textile materials in accordance with the invention comprises impregnating them with an aqueous dispersion of the kind described in detail below and then heating the textiles at a temperature which is at least as high as 212° F., but which is lower than the charring point of the textile. During the treatment of the textiles in this way a chemical reaction is believed to take place between the proteinaceous portion of the textile and the copolymer in the dispersion. The copolymer appears to be chemically bound to the textile and not merely deposited as a dry coating on the fibers. As a result, the resinous copolymer is not leached or removed from the textile during subsequent wet-washing or dry-cleaning operations.

In accordance with the present invention, it has been found that the application to textiles containing proteinaceous fibers or filaments of an aqueous dispersion of a water-insoluble linear copolymer of at least 3% by weight of 4-vinyl pyridine with at least one other copolymerizable monoethylenically unsaturated monomer improves the abrasion resistance of the textiles and is highly effective for the reduction of shrinkage and felting and/or for the substantially complete stabilization against washing or laundering of textiles comprising scale-surfaced protein fibers, such as wool.

It has been found that 4-vinyl pyridine is unique among the various vinyl pyridines in forming copolymers which are capable of reducing shrinkage and felting of fabrics containing scale-surfaced protein fibers or filaments, such as wool. Similar insoluble copolymers of 2-vinyl pyridine, 2-methyl-5-vinyl pyridine and 5-methyl-2-vinyl pyridine have been found to have little or no effect in reducing shrinkage of wool fabrics.

The copolymers must not be water-soluble. The upper limit of the 4-vinyl pyridine component in the copolymer molecule depends on the nature of the comonomer or comonomers in the particular copolymer. When the comonomer is of a highly insoluble type, a larger proportion, such as up to 70% of the 4-vinyl pyridine, may be combined in the copolymer. The 4-vinyl pyridine may be copolymerized with a mixture of comonomers, one of solubilizing type and the other of insolubilizing type in which event the proportion of 4-vinyl pyridine must be reduced in direct proportion to the amount of solubilizing comonomer introduced. For most purposes, copolymers containing from 3 to 30% by weight of 4-vinyl pyridine with at least one insolubilizing comonomer are quite practical from the standpoints of cost and controlling properties in the treated textile, such as hand.

Other polymerizable compounds containing a single ethylenically unsaturated group that may be copolymerized with the 4-vinyl pyridine to produce binary, ternary, etc. copolymers include the esters of acrylic acid or methacrylic acid with monohydric alcohols such as methyl, ethyl, butyl, octyl, dodecyl, cyclohexyl, cyanoethyl, benzyl, phenylethyl, and the like; diesters of itaconic acid and the above alcohols; esters of maleic, fumaric or citraconic acids, and the above alcohols; vinyl esters of carboxylic acids such as acetic, propionic,

butyric, and the like; vinyloxyalkyl esters such as vinyl-oxyethyl acetate, etc.; vinyl ethers such as ethyl vinyl ether, butyl vinyl ether, octyl vinyl ether; methacrylonitrile or acrylonitrile; acrylamide, or methacrylamide, and N-alkyl-substituted amides of these types; vinyl-toluene, vinyl-naphthalenes, such as 4-chloro-1-vinylnaphthalene, vinyl chloride, vinyl bromide, vinylidene chloride, vinylidene fluoride, vinylidene cyanide, 1-chloro-1-fluoroethylene, ethylene, and styrene.

The emulsifiers or dispersing agents that may be used for preparing the monomeric emulsions before copolymerization or dispersions of the polymer after polymerization include those of anionic and non-ionic types. In some cases, it is preferable to use a mixture of anionic and non-ionic emulsifying and dispersing agents. Suitable anionic agents include the sulfates of higher fatty alcohols and their alkali metal salts, such as sodium lauryl sulfate; aryl and/or alkyl substituted phenol sulfonates; sulfonated alkyl phenoxyethoxyethanols having from 1 to 5 oxyethylene units per molecule; sulfonated higher alkyl succinates, such as di-t-octyl sodium sulfosuccinate; suitable non-ionic agents, such as alkyl-phenoxyethoxyethanols having alkyl groups of about seven to eighteen carbon atoms and 6 to 60 or more oxyethylene units, such as heptylphenoxyethoxyethanols, octylphenoxyethoxyethanols, methyloctylphenoxyethoxyethanols, nonylphenoxyethoxyethoxyethanols, dodecylphenoxyethoxyethoxyethanols, and the like; polyethoxyethanol derivatives of methylene linked alkyl phenols; sulfur-containing agents such as those made by condensing 6 to 60 or more moles of ethylene oxide with nonyl, dodecyl, tetradecyl, t-dodecyl, and the like mercaptans or with alkylthiophenols having alkyl groups of six to fifteen carbon atoms; ethylene oxide derivatives of long-chained carboxylic acids, such as lauric, myristic, palmitic, oleic, and the like or mixtures of acids such as found in tall oil containing 6 to 60 oxyethylene units per molecule; analogous ethylene oxide condensates of long-chained alcohols, such as octyl, decyl, lauryl, or cetyl alcohols, ethylene oxide derivatives of etherified or esterified polyhydroxy compounds having a hydrophobic hydrocarbon chain, such as sorbitan monostearate containing 6 to 60 oxyethylene units, etc.; also ethylene oxide condensates of long-chain or branched-chain amines, such as dodecylamine, hexadecylamine, and octadecylamine, containing 6 to 60 oxyethylene groups, block copolymers of ethylene oxide and propylene oxide comprising a hydrophobic propylene oxide section combined with one or more hydrophilic ethylene oxide sections.

Particularly valuable dispersions are obtained by emulsifying a mixture of 4-vinyl pyridine and one or more monomeric esters of acrylic, methacrylic, or itaconic acid or mixtures of these acids in water and polymerizing the mixture while it is in the emulsified form. The monomeric esters which have proven to be most satisfactory are the alkyl esters in which the alkyl group contains one to eight carbon atoms and which are exemplified by the following: methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, isoamyl, tert-amyl, hexyl, heptyl, n-octyl, and 2-ethylhexyl acrylates, methacrylates, and itaconates. To impart alcohol-compatibility, a portion of the ester component may be hydrolyzed to the free acid and converted to the ammonium, sodium, potassium, or lithium salt by means of the corresponding hydroxide. Hydrolysis may be sufficient to produce from as little as 1/2% by weight of carboxyl-containing (—COOH) monomeric units in the copolymer to as much as 5% to 10% of carboxylic acid units in the copolymer, but generally 1% to 2% is preferred.

Hydrolysis of the 4-vinyl pyridine/ester copolymer may be effected by either acid or alkaline treatments. Preferably, the copolymer is treated with an aqueous

solution of an alkali metal hydroxide, such as sodium hydroxide, lithium hydroxide, or potassium hydroxide of about 1/2 to 1 normal or higher concentration, until from 1/2 to 4% by weight of acrylic acid is introduced into the copolymer by the hydrolysis. This may be effected at room temperature up to 50° C. for periods of time from 1/2 to several hours, depending on the temperature and the concentration of the caustic hydroxide solution. Instead of relying on hydrolysis to introduce the carboxyl groups, the appropriate amount of acrylic acid, methacrylic acid, itaconic acid or other polymerizable acid, such as maleic, fumaric and citraconic, may be directly introduced into the emulsified mixture of monomers so that it is copolymerized with the 4-vinyl pyridine and other monomer in the desired proportion.

The polymerizable emulsions can be prepared at temperatures from 0° C. to about 100° C., but intermediate temperatures are much preferred. Thus, when the preferred copolymers with esters are made with the esters in which the alkyl group contains one to four carbon atoms, a temperature from about 10° C. to about 60° C. is employed, whereas a higher temperature, e. g., 30° C. to 80° C., is recommended when esters containing five to eight carbon atoms in the alkyl group are copolymerized. Peroxidic free-radical catalysts, particularly catalytic systems of the redox type, are recommended. Such systems, as is well known, are combinations of oxidizing agents and reducing agents such as a combination of potassium persulfate and sodium metabisulfite. Other suitable peroxidic agents include the "per-salts" such as the alkali metal and ammonium persulfates and perborates, hydrogen peroxide, organic hydroperoxides such as tert-butyl hydroperoxide and cumene hydroperoxide, and esters such as tert-butyl perbenzoate. Other reducing agents include water-soluble thiosulfates, hydrosulfites, tertiary amines, such as triethanolamine, and the salts, such as the sulfates, of metals which are capable of existing in more than one valence state, such as cobalt, iron, nickel, and copper. The most convenient method of preparing the dispersion of copolymers comprises agitating an aqueous suspension or emulsion of a mixture of copolymerizable monomers and a redox catalytic combination at room temperature without the application of external heat. The amount of catalyst can vary but for purposes of efficiency from 0.01% to 3.0%, based on the weight of the monomers, of the peroxidic agent and the same or lower proportions of the reducing agent are recommended. In this way, it is possible to prepare dispersions which contain as little as 1% and as much as 60% or even more of the resinous copolymer on a weight basis. It is, however, more practical, and hence preferred, to produce dispersions which contain about 30–50% resin-solids.

The proportion of the copolymer that is applied to the fabric may vary widely, such as from 1% to 20%, by weight of the fabric, a proportion of 1 1/2% to 7 1/2% being preferred. The hand or feel of the fabric may be varied widely depending on the comonomer or comonomers selected. Thus, a softer and more lubricious hand may be imparted by copolymerizing the 4-vinyl pyridine with a comonomer that introduces a long-chain fatty group into the copolymer. For example, the 4-vinyl pyridine may be copolymerized with acrylic, methacrylic, or itaconic esters of alcohols containing from 1 to 18 carbon atoms, the longer the chain of the alcohol, the more lubricious the hand.

The dispersion is deposited on the textile material by such means as exhausting, spraying, padding, or dipping. What is required is that the textile material be saturated and impregnated by the dispersion. This can be done at any desired temperature short of the boiling point of the dispersion. Ordinarily the textile is passed at room temperature with a dispersion which has been adjusted to a resin-content of about 1% to 25%. The material

being treated must pick up or take up and then retain sufficient dispersions to provide from 1% to about 20%, and preferably from 1½% to 7½% of the copolymer, based on the weight of the dry textile.

The impregnated textile material must then be heated at a temperature between 212° F. and 700° F. for a period of about ten seconds to 30 minutes, the higher the temperature, the shorter the period required. In any event the time and temperature should not be such as to damage the fabric. Preferably this heating is effected at a temperature from 240° F. (for about 10–15 minutes) to about 310° F. (for about 5–10 minutes), and it is believed that it effects some chemical reaction involving the polymer and possibly the textile. In any event, the heating sets the polymer on the textile, and in the case of wool, reduces shrinkage and/or imparts full dimensional stability thereto. Drying of the treated textile and the heat-treatment which effects the chemical reaction can be carried out simultaneously or concurrently in one step, or the textile can be substantially or completely dried at a conveniently lower temperature and then heated later at the higher temperature. As will be evident to those skilled in the art, the optimal length of the heating period depends on the particular temperature which is employed, on the particular copolymer, and on the quantity thereof which is on the textile. But in any case, the heat-treatment does not require a long period and is usually measured in minutes, generally one to thirty minutes and preferably about five to fifteen minutes. The most satisfactory time of heating for any particular combination of dispersions and textile is readily determined by heating pieces of the impregnated textile for varying lengths of time at a given temperature and then measuring the resultant stabilization of the individual pieces by means of a wet-washing test.

In some cases, it may be advantageous to add an acid to the dispersion with which the textile is treated to accelerate the reaction and to bring about the stabilization or reduction in shrinkage in a shorter period of time at a given temperature or at a lower temperature in a given time. Strong acids such as formic, oxalic, sulfuric, and phosphoric acids are recommended. For this purpose, from 1% to 2% acid, based on the weight of the pad liquor, is suggested. It has also been found that the use in conjunction with the dispersions of such acid catalyst with an auxiliary reactive substance, such as formaldehyde, or materials which are equivalents of formaldehyde, such as glyoxal or formals, or mixtures of formaldehyde or the like with aminoplast-forming compounds, or low-molecular weight, water-soluble, reaction products, preferably of formaldehyde or the like with such compounds, enhances the stabilization of woolen or proteinaceous textiles. While such auxiliary reactive substances and the acid catalyst may be employed as an added component of the dispersions, they may also be employed by applying a solution of the auxiliary reactive substance and the acid catalyst after the textile has been treated with the dispersion. The use of the auxiliary reactive substance is advantageous in some cases where it becomes especially evident on extended laundering of the textile. Also in combination fabrics, such as those containing fibers or yarns of silk or cellulosic type, such as cotton or rayon, as well as fibers or yarns of proteinaceous types, such as wool, including as an example woolen garments sewn together with cotton threads, the use of the auxiliary reactive substance serves to reduce shrinkage of or completely stabilize the first-mentioned fabric components while the linear polymer dispersion acts similarly upon the proteinaceous or woolen components.

Examples of the aminoplast-forming compounds include urea, thiourea, biuret, or other homologs or derivatives thereof, such as N,N'-ethyleneurea, N,N'-ethyleneurea, N,N'-dimethylurea, N,N'-diethylurea, N,N'-dimethoxymethylurea, N,N'-dimethoxymethylurea, N,N'-diethoxymethylurea, tetramethoxymethylurea, tetraethoxymethyl-

urea. Similar reaction products of formaldehyde with triazines, such as melamine may also be employed, such as N,N'-dimethylmelamine and alcohol-modified melamine-formaldehyde thermosetting resin condensates, e. g., of methyl and ethyl alcohols, for example, dimethoxymethyl-monomethylolmelamine.

The treated textiles are characterized by greater resistance to abrasion and/or reduced shrinkage and, in many cases, fully practical dimensional stability against laundering, by which is meant that they are substantially shrink-proof. They do not stiffen, degrade or discolor on ageing or on exposure to ultraviolet light as do comparable textiles which have been treated, for example, with latices of butadiene copolymers.

The effectiveness of the dispersions exemplified below in stabilizing wool was determined by impregnating measured pieces of flannel with them, drying, and heating the impregnated pieces of flannel at a temperature of 240° F. or higher, laundering the pieces in hot water, then drying them and measuring the shrinkage. In these tests pieces of woolen flannel (2/2 right hand 45° twill, 55 x 44; S-twist in warp ends, Z-twist in the filling; scoured, carbonized, neutralized and bleached) were used. All pieces were 10 inches square, with axes along the yarn systems. The pieces of flannel were padded with a pad liquor of the resin dispersion which was so adjusted in solids-content as to provide the desired amount of resins-solids (1%–20% based on the weight of the dry flannel) at a pick-up of about 75%; that is, when the flannel contained the emulsion in an amount equal to about 75% of the weight of the dry flannel. The treated specimens were dried and heated and cured at a temperature of at least 240° F. The specimens were washed, together with untreated pieces of flannel, in a Cascade wheel washer containing 70 grams of soap (Ivory) in 10 gallons of water for five hours. In all cases the load in the washer was made up to three pounds with cotton toweling and the temperature was maintained at 140° F. The values of shrinkage are given as percentage reduction in the initial area after taking into account any inherent residual shrinkage in the initial fabric that may be present as a result of previous drying under tension and is removable by simply wetting and drying. In other words, the shrinkage values hereinbelow are obtained by subtracting relaxation shrinkage from the actual shrinkage measured.

The following examples serve to illustrate this invention:

Example 1

A dispersion of a copolymer was prepared by emulsifying 90 parts by weight of n-butyl acrylate with 10 parts by weight of 4-vinyl pyridine in about 300 parts by weight of water with about 6 parts by weight of an ethylene oxide condensation product of an octyl phenol containing between 30 and 50 oxyethylene units per molecule. To the emulsified monomers 0.3% by weight (on the total weight of monomers) of ammonium persulfate, 1.0% of triethanolamine, and 0.06% of sodium hydrosulfite were added to catalyze the copolymerization which was carried out for a period of seventeen minutes. During this period the temperature rose from 20° C. to 46° C.

The resin dispersion was diluted to a 13.5% concentration of the resin (copolymer) content and applied to a wool flannel as described above. After drying 10 minutes at 240° F., followed by curing for 10 minutes at 300° F., it was found that the proportion of copolymer applied to the fabric was about 10.0% of the weight of the fabric. The shrinkage of the treated fabric after the five-hour wash described hereinabove was zero.

Example 2

The procedure of Example 1 was followed except that after drying the fabric at 240° C., it was passed through an aqueous solution containing 1% sulfuric acid and 1% formaldehyde and then dried 10 minutes at 240° C. and cured for a period of 10 minutes at 300° F. The result-

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ing fabric showed no shrinkage after the five-hour wash test. Whereas the hand obtained in Example 1 was about as soft as that of the initial fabric, the formaldehyde treatment reduced the softness of the hand only slightly as compared to the product of Example 1.

Example 3

The procedure of Example 1 was followed except that the dispersion was diluted to 2½% copolymer concentration before application so that 1½% was taken up by the fabric. The fabric showed 2% shrinkage on completion of the five-hour wash test.

Example 4

The procedure of Example 3 was followed except that after drying the fabric at 240° F., it was passed through a 3% aqueous solution of dimethoxymethylurea and cured for a period of 10 minutes at 300° F. The fabric showed no shrinkage as a result of the five-hour wash test.

Example 5

The procedure of Example 1 was followed with a copolymer obtained by emulsion polymerization of 94.5% n-butyl acrylate, 0.5% methacrylic acid, and 5% 4-vinyl pyridine and neutralization with ammonium hydroxide. The treated fabric showed no shrinkage on completion of the five-hour wash test.

Example 6

A terpolymer of 92.6% n-butyl acrylate, 5% 4-vinyl pyridine and 2.4% of methyl acrylate was prepared as in Example 1 and then hydrolyzed by treatment with one-normal sodium hydroxide at room temperature until the equivalent of 2% of acrylic acid units was produced in the copolymer. The aqueous dispersion of the sodium salt of the hydrolyzed polymer was diluted to a concentration of 5% copolymer and applied to the textile as in Example 1. The textile picked up 3% and after drying 10 minutes at 250° F., it showed no shrinkage on completion of the five-hour wash test.

Example 7

The procedure of Example 1 is followed with a copolymer of 85% diethyl itaconate and 15% of 4-vinyl pyridine. The fabric shows no shrinkage on completion of the wash test.

Example 8

The procedure of Example 1 is followed with a copolymer of 75% of n-octyl acrylate with 25% of 4-vinyl pyridine. The fabric exhibits no shrinkage as a result of the five-hour wash test.

It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined in the appended claims.

We claim:

1. A process for treating protein textile materials to reduce the shrinkage thereof comprising impregnating a protein textile material with an aqueous dispersion containing 1 to 20% of a water-insoluble, linear copolymer of 3 to 70% by weight of 4-vinyl pyridine and 97 to 30% respectively of comonomeric material consisting of at least one member selected from the group consisting of (1) esters of an acid selected from the group consisting of acrylic, methacrylic, itaconic, maleic, fumaric, and citraconic acids and a monohydric alcohol selected from the group consisting of acyclic alkanols having 1 to 18 carbon atoms, cyclohexanol, cyanoethanol, benzyl alcohol, and phenylethyl alcohol, (2) vinyl esters of fatty acids having 2 to 4 carbon atoms, (3) vinyloxyethyl acetate, (4) alkyl vinyl ethers in which the alkyl group has 2 to 8 carbon atoms, methacrylonitrile, acrylonitrile, acrylamide, methacrylamide, vinyltoluene, 4-chloro-1-vinylnaphthalene, vinyl bromide, vinyl chloride, vinylidene chloride, vinylidene fluoride, vinylidene cyanide, 1-chloro-

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1-fluoroethylene, ethylene, and styrene, at least sufficient of the comonomeric material being of water-insolubilizing character to render the copolymer water-insoluble, and subsequently heating the impregnated textile to a temperature of 212° to 700° F. until the fabric shows substantial reduction of shrinkage on laundering.

2. A process for treating protein textile materials to reduce the shrinkage thereof comprising impregnating a protein textile material with an aqueous dispersion containing 1 to 20% of a water-insoluble, linear copolymer of 3 to 70% by weight of 4-vinyl pyridine and 97 to 30% respectively of at least one ester of acrylic acid and an acyclic alkanol having 1 to 18 carbon atoms, and subsequently heating the impregnated textile to a temperature of 212° to 700° F. until the fabric shows substantial reduction of shrinkage on laundering.

3. A process for treating protein textile materials to reduce the shrinkage thereof comprising impregnating a protein textile material with an aqueous dispersion containing 1 to 20% of a water-insoluble, linear copolymer of 3 to 70% by weight of 4-vinyl pyridine, about ½% to 5% of methacrylic acid, and 96½ to 30% respectively of at least one ester of acrylic acid with an acyclic alkanol having 1 to 18 carbon atoms, and subsequently heating the impregnated textile to a temperature of 212° to 700° F. until the fabric shows substantial reduction of shrinkage on laundering.

4. A process for treating protein textile materials to reduce the shrinkage thereof comprising impregnating a protein textile material with an aqueous dispersion containing 1 to 20% of a water-insoluble, linear copolymer of 3 to 70% by weight of 4-vinyl pyridine, about ½% to 5% of acrylic acid, and 96½ to 30% respectively of at least one ester of acrylic acid with an acyclic alkanol having 1 to 18 carbon atoms, and subsequently heating the impregnated textile to a temperature of 212° to 700° F. until the fabric shows substantial reduction of shrinkage on laundering.

5. A process for treating protein textile materials to reduce the shrinkage thereof comprising impregnating a protein textile material with an aqueous dispersion containing 1 to 20% of a water-insoluble, linear copolymer of 3 to 70% by weight of 4-vinyl pyridine, about ½ to 5% of itaconic acid, and 96½ to 30% respectively of at least one ester of acrylic acid with an acyclic alkanol having 1 to 18 carbon atoms, and subsequently heating the impregnated textile to a temperature of 212° to 700° F. until the fabric shows substantial reduction of shrinkage on laundering.

6. The process as defined in claim 1 in which the copolymer comprises 5% 4-vinyl pyridine and 95% n-butyl acrylate.

7. The process as defined in claim 1 in which the copolymer comprises about 5% 4-vinyl pyridine, about ½% methacrylic acid, and about 94.5% n-butyl acrylate.

8. The process as defined in claim 1 in which the copolymer comprises about 5% 4-vinyl pyridine, about 2% acrylic acid, and about 93% n-butyl acrylate.

9. The process as defined in claim 1 in which the copolymer comprises 15% 4-vinyl pyridine and 85% diethyl itaconate.

10. The process as defined in claim 1 in which the copolymer comprises 25% 4-vinyl pyridine and 75% n-octyl acrylate.

11. As an article of manufacture, a textile material containing protein fibers stabilized against shrinkage on laundering, said material being the product of the process of claim 1.

12. As an article of manufacture, a textile material containing protein fibers stabilized against shrinkage on laundering, said material being the product of the process of claim 2.

13. As an article of manufacture, a textile material containing wool fibers stabilized against shrinkage on

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laundrying, said material being the product of the process of claim 1.

14. As an article of manufacture, a textile material containing wool fibers stabilized against shrinkage on laundrying, said material being the product of the process of claim 2.

15. As an article of manufacture, a textile material containing wool fibers stabilized against shrinkage on laundrying, said material being the product of the process of claim 3.

16. As an article of manufacture, a textile material containing wool fibers stabilized against shrinkage on laundrying, said material being the product of the process of claim 6.

17. As an article of manufacture, a textile material containing wool fibers stabilized against shrinkage on laundrying, said material being the product of the process of claim 7.

18. As an article of manufacture, a textile material containing wool fibers stabilized against shrinkage on laundrying, said material being the product of the process of claim 8.

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19. As an article of manufacture, a textile material containing wool fibers stabilized against shrinkage on laundrying, said material being the product of the process of claim 9.

20. As an article of manufacture, a textile material containing wool fibers stabilized against shrinkage on laundrying, said material being the product of the process of claim 10.

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