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STABILIZATION OF PROTEIN-CONTAINING TEXTILES WITH NITROGEN CONTAINING POLYMERS

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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 the 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 qualtities while other 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 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, $CH_2=C(CH_3)COOCH_2CH(OH)CH_2OH$, 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 polymers of certain ethers, amides and esters which contain an amino group on the monomeric units of the polymer are capable of improving the abrasion resistance of protein-containing textiles and are highly effective for the stabilization of textiles comprising scale-surfaced protein fibers, such as wool. More specifically, it has been found that marked reduction in the shrinking and felting properties of wool-containing textiles can be obtained by the application thereto of an aqueous dispersion of a water-insoluble linear polymer of monoethylenically unsaturated molecules comprising at least 3% by weight of a monomeric compound having the following general formula:

$$CH_2=\underset{\displaystyle R}{\overset{|}{C}}-A-R'-N(R^2)_2$$

where R is H and CH_3, R^2 is selected from the group consisting of H and saturated aliphatic hydrocarbon groups having from 1 to 10 carbon atoms,

A is $-O-$, $-\overset{\displaystyle O}{\overset{\|}{C}}-O-$, $-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle R^2}{\overset{|}{N}}-$

and R' is a straight or branched chain alkylene group having from 2 to 10 carbon atoms. Members R^2 may be identical or different groups in its several occurrences in any particular compound.

A preferred group is that of amines having the formula

$$CH_2=CH-O-(CH_2)_x-NH_2$$

where x may be 2 to 10 but is preferably 2 to 5, the efficiency generally being a maximum when x is 2.

Examples of these monomers are:

N-(γ-dimethylamino)propyl methacrylamide
N-(β-dimethylamino)ethyl acrylamide
N-(β-dimethylamino)ethyl methacrylamide
10-aminodecyl vinyl ether
8-aminooctyl vinyl ether
Diethylaminohexyl methacrylate
Diethylaminoethyl vinyl ether
5-aminopentyl vinyl ether
3-aminopropyl vinyl ether
2-aminoethyl vinyl ether
2-aminobutyl vinyl ether
4-aminobutyl vinyl ether
2-aminoethyl vinyl ether
Dimethylaminoethyl methacrylate
Dimethylaminoethyl vinyl ether
N-(3,5,5-trimethylhexyl)aminoethyl vinyl ether
N-cyclohexylaminoethyl vinyl ether
t-Butylaminoethyl acrylate

2-(1,1,3,3-tetramethylbutylamino)ethyl methacrylate
N-t-butylaminoethyl vinyl ether
N-methylaminoethyl vinyl ether
N-2-ethylhexylaminoethyl vinyl ether
N-t-octylaminoethyl vinyl ether

The polymers must not be water-soluble. Where the amine-containing monomer that is polymerized is of such character that a homopolymer produced therefrom is appreciably water-soluble, it is necessary to copolymerize such a monomer with at least one other copolymerizable monoethylenically unsaturated monomer which is of a character that will render the final copolymer insoluble in water. Many of the amine-containing monomers have such a large proportion of hydrophobic groups in their molecule that homopolymers thereof will necessarily be water-insoluble and, in such cases, a homopolymer can be applied to the fabrics for accomplishing the purpose of the invention. Frequently, however, it is preferable from the cost standpoint, and for controlling properties, such as hand, to copolymerize the amine monomer with a cheaper and more readily available comonomer. Preferred compositions of the invention are, therefore, those copolymers of from 3 to 30% of the amine-containing monomer or of a mixture of such monomers, the balance of the copolymer being formed of other less expensive comonomers.

Other polymerizable compounds containing a single ethylenically unsaturated group that may be copolymerized with the amine-containing monomer to produce binary, ternary, etc. copolymers include the esters of an alphamethylene monocarboxylic acid, such as acrylic acid or methacrylic acid, with monohydric alchols 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 with the above alcohols; vinyl esters of carboxylic acids such as acetic, propionic, butyric, and the like; vinyloxyalkyl esters such as vinyloxyethyl 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-vinyl naphthalene, 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 are preferably of the non-ionic type and include the following: alkylphenoxypolyethoxyethanols having alkyl groups of about seven to eighteen carbon atoms and 6 to 60 or more oxyethylene units, such as heptylphenoxypolyethoxyethanols, octylphenoxypolyethoxyethanols, methyloctylphenoxypolyethoxyethanols, nonylphenoxypolyethoxyethanols, dodecylphenoxypolyethoxyethanols, 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 resin dispersions are obtained by emulsifying a mixture of (*a*) one or more of the amine-containing monomers above and (*b*) 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.

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 meta-bisulfite. Other suitable peroxidic agents include the "persalts" 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 dispersions 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 polymer that is applied to the fabric may vary widely, such as from 1 to 20% by weight of the fabric, a proportion of 3 to 10% being preferred. The hand or feel of the fabric may be varied widely depending on the polymer selected. Thus polymers of amines which contain, in the place of R′ in the formula above, a long-chain alkylene group between the terminal amine group and the ether oxygen will generally have a softer hand than those with a shorter alkylene chain. The same applies when sulfide or ester monomers are employed. The variation in hand may be controlled by the selection of the comonomer as well. Thus, for a given monomer containing terminal amine groups, a softer and more lubricous hand may be imparted by copolymerizing with a comonomer of such character that it introduces a long-chain fatty group into the copolymer. For example, the amine-group-containing monomer 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 lubricous the hand.

The dispersion is deposited on the textile material by such means as exhausting, spraying, or dipping. What is required is that the textile material be saturated and im-

pregnated by the dispersion. This can be done at any desired temperature short of the boiling point of the dispersion. Ordinarily the textile is padded 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 3% 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 400° F. for a period of about one-half minute to 30 minutes, the higher the temperature, the shorter the period required. A flash cure at temperatures above 400° F. even up to 700° F. for short periods of five to ten seconds may be employed. 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'-diethoxyethylurea, tetramethoxymethylurea, tetraethoxyethylurea. 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 ends, Z in picks; 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 95 parts by weight of n-butyl acrylate with 5 parts by weight of 2-aminoethyl vinyl ether 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 of ammonium persulfate, 0.06% of sodium hydrosulfite, and 1% triethanolamine were added to catalyze the copolymerization which was carried out for a period of about fifteen minutes during which the temperature rose from 20° C. to 45° 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% 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° F., it was passed through a 1% solution of formaldehyde and then dried 10 minutes at 240° C. and cured for a period of 10 minutes at 300° F. The resulting fabric showed no shrinkage after the five-hour wash test. Whereas the hand obtained in Example 1 was softer than 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

A similar dispersion was prepared of a copolymer of 95 parts by weight of n-butyl acrylate with 5 parts by weight of 3-aminopropyl vinyl ether. The procedure of Example 1 was followed and the shrinkage after a five-hour wash was found to be 5% as compared to a 63% shrinkage of a control fabric after only two hours washing with other conditions remaining the same.

Example 4

The procedure of Example 2 was followed with the copolymer of Example 3. The resulting formaldehyde-treated 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 of 90% isopropyl acrylate and 10% t-butylaminoethyl acrylate. The fabric showed no shrinkage after the five-hour wash test.

Example 6

The procedure of Example I was followed with an aqueous dispersion of a copolymer of 95% n-butyl acrylate with 5% of 5-aminopentyl vinyl ether. The treated fabric exhibited 10% shrinkage after the five-hour wash as compared with the 63% shrinkage on the two-hour wash of the control and had an extremely soft hand both before and after the wash.

Example 7

The procedure of Example 2 was followed with the copolymer of Example 6. The formaldehyde treatment altered the hand only slightly and the shrinking was reduced to zero after the five-hour wash.

Example 8

The procedure of Example 1 was followed with an aqueous dispersion of a copolymer of 85% s-butyl acrylate with 15% of 3-aminopropyl vinyl ether. After the five-hour wash test, the fabric exhibited only 5% shrinkage.

Example 9

The procedure of Example 2 was followed with the copolymer of Example 8 and the resulting fabric showed no shrinkage after the five-hour wash test.

Example 10

The procedure of Example 1 was followed with an aqueous dispersion of a copolymer of 95% t-butyl acrylate and 5% of dimethylaminoethyl methacrylate. The fabric obtained showed a shrinkage of zero after the five-hour wash test. Both before and after the wash, it had a hand which was somewhat fuller than the initial fabric.

Example 11

The procedure of Example 1 was followed with a copolymer of 90% by weight of 2-ethylhexyl acrylate with 10% by weight of 5-aminopentyl vinyl ether. The fabric showed 3% shrinkage after a five-hour wash and both before and after the wash, it had an extremely soft hand.

Example 12

The procedure of Example 1 was followed with a copolymer of 92% by weight of diethyl itaconate with 8% of 8-aminooctyl vinyl ether. The fabric obtained showed a shrinkage of 4% after the five-hour wash and it was characterized by an extremely soft lubricous hand.

Example 13

The procedure of Example 1 was followed with an aqueous dispersion diluted to 20% resin-content of a copolymer of 97% of ethyl acrylate with 3% of β-aminoethyl vinyl ether. The fabric after the five-hour wash test showed a shrinkage of 3%.

Example 14

The procedure of Example 1 was followed with an aqueous dispersion containing 6% by weight of a copolymer of 80% n-butyl acrylate with 20% of dimethylaminoethyl methacrylate. The fabric obtained showed a shrinkage of zero after a five-hour wash.

Example 15

The procedure of Example 1 was followed with an aqueous dispersion of a copolymer of 95% n-butyl acrylate and 5% N-cyclohexylaminoethyl vinyl ether. The fabric showed a shrinkage of zero on completion of the five-hour wash.

Example 16

The procedure of Example 1 was followed with a copolymer of 20% of vinyl acetate with 70% ethyl acrylate and 10% of dimethylaminoethyl vinyl ether. The treated fabric showed 8% shrinkage after the five-hour wash test.

Example 17

The procedure of Example 2 was followed with the aqueous dispersion of Example 16. The formaldehyde after-treated fabric showed no shrinkage as a result of the five-hour wash test.

Example 18

The procedure of Example 16 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 19

The procedure of Example 1 was followed with a copolymer of 95% of n-butyl acrylate with 5% of N-(γ-dimethylamino)-propyl methacrylamide. The treated fabric showed no shrinkage after the five-hour wash test.

Example 20

The procedure of Example 1 was followed except that only 3.5% of the copolymer was applied to the fabric. The fabric after drying and curing showed 2% shrinkage on completion of the five-hour wash test.

Example 21

The procedure of Example 1 was followed except that only 2% of the coplymer was applied to the fabric. The fabric after drying and curing showed 5% shrinkage on completion of the five-hour wash test.

Example 22

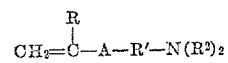
The procedure of Example 21 was followed except that ½% by weight of dimethoxymethyl-monomethylolmelamine is included in the copolymer dispersion before application to the fabric. The fabric showed 1% shrinkage on completion of the five-hour wash test.

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 wool textile materials to re-

duce the shrinkage thereof comprising impregnating a wool textile material with an aqueous dispersion of a water-insoluble linear addition copolymer of 3 to 30% by weight of a monomer having the formula

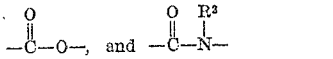


where

R is selected from the group consisting of H and CH_3,

R^2 is selected from the group consisting of H and monovalent saturated aliphatic hydrocarbon groups having from 1 to 10 carbon atoms,

A is selected from the group consisting of —O—,



and

R′ is selected from the class consisting of straight and branched chain alkylene groups having from 2 to 10 carbon atoms,

and 70 to 97% by weight of at least one monomer selected from the group consisting of esters of a monohydric alcohol having 1 to 18 carbon atoms with an acid of the group consisting of acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, and citraconic acid, vinyl acetate, vinyloxyethyl acetate, vinyl alkyl ethers having 1 to 8 carbon atoms in the alkyl group, methacrylonitrile, acrylonitrile, acrylamide, methacrylamide, vinyltoluene, and styrene, the amount of copolymer deposited on the textile by such impregnation being about 3 to 10% by weight of the textile, and subsequently heating the impregnated textile to a temperature of 212° F. to 400° F. to set the polymer on the textile.

2. As an article of manufacture, a textile material comprising wool fibers modified by 3 to 10% by weight, based on the weight of fibers, of a water-insoluble addition copolymer as defined in claim 1, said textile material being a product obtained by the process of claim 1.

3. As an article of manufacture, a textile material comprising wool fibers modified by 3 to 10% by weight of a deposit from a water-insoluble, linear addition polymer of monoethylenically unsaturated molecules comprising 3 to 30% of N-cyclohexylaminoethyl vinyl ether, said textile material being a product obtained by the process of claim 1.

4. The process of claim 1 in which the polymer is a copolymer of N-cyclohexylaminoethyl vinyl ether with butyl acrylate.

5. As an article of manufacture, a textile material comprising wool fibers modified by 3 to 10% by weight of a deposit from a water-insoluble, linear addition polymer of monoethylenically unsaturated molecules comprising 3 to 30% of dimethylaminoethyl methacrylate, said textile material being a product obtained by the process of claim 1.

6. The process of claim 1 in which the polymer is a copolymer of dimethylaminoethyl methacrylate with butyl acrylate.

7. The process for treating wool textile materials to reduce the shrinkage thereof comprising impregnating a wool textile material with an aqueous dispersion of a water-insoluble linear addition copolymer of 3 to 30% by weight of a monomer having the formula

$$CH_2=CH—O—(CH_2)_x—NH_2$$

where x is an integer having a value from 2 to 10, and 70 to 97% by weight of at least one monomer selected from the group consisting of esters of a monohydric alcohol having 1 to 18 carbon atoms with an acid of the group consisting of acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, and citraconic acid, vinyl acetate, vinyloxyethyl acetate, vinyl alkyl ethers having 1 to 8 carbon atoms in the alkyl group, methacrylonitrile, acrylonitrile, acrylamide, methacrylamide, vinyltoluene, and styrene, the amount of copolymer deposited on the textile by such impregnation being about 3 to 10% by weight of the textile, and subsequently heating the impregnated textile to a temperature of 212° F. to 400° F. to set the polymer on the textile.

8. As an article of manufacture, a textile material comprising wool fibers modified by 3 to 10% by weight of a water-insoluble addition copolymer as defined in claim 7, said textile material being a product obtained by the process of claim 7.

9. As an article of manufacture, a textile material comprising wool fibers modified by 3 to 10% by weight of a deposit from a water-insoluble, linear addition polymer of monoethylenically unsaturated molecules comprising 3 to 30% of 2-aminoethyl vinyl ether, said textile material being a product obtained by the process of claim 7.

10. The process of claim 7 in which the polymer is a copolymer of 2-aminoethyl vinyl ether with butyl acrylate.

11. As an article of manufacture, a textile material comprising wool fibers modified by 3 to 10% by weight of a deposit from a water-insoluble, linear addition polymer of monoethylenically unsaturated molecules comprising 3 to 30% of 3-aminopropyl vinyl ether, said textile material being a product obtained by the process of claim 7.

12. The process of claim 7 in which the polymer is a copolymer of 3-aminopropyl vinyl ether with butyl acrylate.

13. As an article of manufacture, a textile material comprising wool fibers modified by 3 to 10% by weight of a deposit from a water-insoluble, linear addition polymer of monoethylenically unsaturated molecules comprising 3 to 30% of 5-aminopentyl vinyl ether, said textile material being a product obtained by the process of claim 7.

14. The process of claim 7 in which the polymer is a copolymer of 5-aminopentyl vinyl ether with butyl acrylate.

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