United States Patent Office

3,100,674

Patented Aug. 13, 1963

3,100,674

PROCESS FOR SHRINK-PROOFING PROTEINACEOUS TEXTILE MATERIALS AND THE PRODUCT THEREFROM

Fred H. Steiger, Philadelphia, and Hugo A. Alps, Huntingdon Valley, Pa., assignors to Rohm & Haas Company, Philadelphia, Pa., a corporation of Delaware

No Drawing. Filed Dec. 8, 1959, Ser. No. 858,028

5 Claims. (Cl. 8—127.6)

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

An object of this invention is to apply certain aqueous dispersions of resins to protein-containing woven and knitted textile materials which, after heating, markedly reduce the tendency of the materials to shink or render them substantially shrink-proof. Another object is to provide a process for shrink-proofing of textile materials formed of interlocked yarns 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 the textiles without adversely affecting such other properties of the textile as wearing qualities, tensile strength, dye-fastness qualities, 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 woven and knitted textile materials such as those made of or containing silk, mohair, fur, Aralac and other synthetic fibers which are produced from casein, soybeans, zein, collagen, et cetera, and especially scale-surfaced protein fibers of either natural or artificial origin. 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 shrinking. In many cases such reduction in shrinking tendencies has been obtained at the sacrifice of some other desirable property of the material. Some treatments damage the fiber, reduce or completely inhibit the capacity of the textile material to be dyed with acid dyestuffs, 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. Some treatments reduce the wash-fastness of dyed fabrics.

The process of treating the woven and knitted textile materials in accordance with the invention comprises impregnating them with an aqueous dispersion of a water-insoluble linear emulsion copolymer 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 especially with chlorinated hydrocarbons.

In accordance with the present invention, it has been found that certain polymers are capable of improving the abrasion resistance of the protein-containing textiles and are highly effective for the stabilization of textiles comprising at least 40% by weight of scale-surfaced protein fibers, such as wool. More particularly, it has been discovered that certain linear addition copolymers containing N-methylolamide groups with or without other coreactive groups, in certain proportions, when applied to protein-containing woven and knitted textile fabrics and cured by heating at elevated temperatures, impart resistance to normal laundering operations such as may be performed with modern detergents of the type represented by Tide, All, and Fab, as well as resistance to dry-cleaning by chlorinated hydrocarbons such as carbon tetrachloride. By "coreactive" is meant groups which react with the N-methylolamide groups.

The linear addition copolymers applied in accordance with the present invention are water-insoluble copolymers of a mixture of copolymerizable monoethylenically unsaturated molecules comprising (A) 0.5 to 6% (preferably 1 to 4%) by weight of N-methylolacrylamide, N-methylolmethacrylamide, or of a mixture thereof, which compounds may be represented by the generic formula

$$H_2C{=}\underset{\displaystyle CONHCH_2OH}{\underset{|}{C}}{-}(CH_2)_{n-1}H \qquad (I)$$

in which n is an integer having a value of 1 to 2, and (B) zero to 6% by weight of a monomer which contains a group coreactive with the N-methylolamide group. The copolymers should have an apparent second order transition temperature, T_i, which is not over 0° C. The molecular weight may be from 100,000 to 10,000,000. The T_i value referred to herein is the transition temperature or inflection temperature which is found by plotting the modulus of rigidity against temperature. A convenient method for determining modulus of rigidity is described by I. Williamson, British Plastics 23, 87–90, 102 (September 1950). The T_i value here used is that determined at 300 kg./cm.^{2}.

The coreactive monomers are those which contain reactive hydrogen atoms in amide groups (—$CONH_2$), amino groups (—NH_2), hydroxyl groups (—OH), and carboxyl or carboxylate groups (—COOH). Examples include acrylic acid, methacrylic acid, itaconic acid, acrylamide, methacrylamide, β-hydroxyethyl acrylate or methacrylate, N-β-hydroxyethyl-acrylamide or -methacrylamide, β-hydroxypropyl acrylate or methacrylate, N-β-hydroxypropyl-acrylamide or -methacrylamide, β-hydroxyethyl or β-hydroxypropyl vinyl ether or vinyl sulfide, and B-aminoethyl vinyl ether or β-aminoethyl acrylate. The nitrogen atoms of the amide and amino groups may be secondary atoms, i.e., they may have only one hydrogen atom attached thereto, as in N-(β-(α-methacryloxy-acetamido)ethyl)-N,N'-ethyleneurea or β-(N-t-butylamino)ethyl methacrylate, but it is preferred that the nitrogen atoms are primary atoms because of the greater reactivity thereof. The amide groups embrace ureido groups as in ureidoethyl acrylate or methacrylate, or in ureidoethyl vinyl ether or sulfide.

Besides the N-methylolamide, and coreactive monomer when present, the copolymer comprises units which may be obtained from one or more esters of the formula

$$H_2C=\underset{\displaystyle COOR}{\underset{|}{C}}-(CH_2)_{n-1}H \qquad \text{(II)}$$

wherein n is an integer having a value of 1 to 2, R is an alkyl group having 1 to 18 carbon atoms when n is 1 and 4 to 18 carbon atoms when n is 2. Examples of the latter esters are butyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate, t-octyl acrylate and methacrylate, and octadecyl acrylate and methacrylate. When monomers, such as acrylonitrile, methyl methacrylate, vinyl acetate, and styrene, which produce homopolymers having high T_i values are used, the proportion of any such monomer used in the copolymer is limited to that which will produce, with the other monomers used in the particular copolymer, such as ethyl acrylate, methyl acrylate, butyl acrylate, or octyl acrylate or methacrylate, a T_i value of 0° C. or less.

The N-methylolamide of Formula I may be used in greater amounts than the 6% upper limit mentioned and the coreactive monomer may be used in greater amounts than the 6% upper limit mentioned above, but generally the total of N-methylolamide units and of units coreactive therewith should not exceed 25% by weight and the optimum results are obtained when these monomers are used in the ranges heretofore given. Higher proportions of the compound of Formula I tend to make the product excessively stiff and higher proportions of the coreactive compound tend to reduce the wash-resistance of the products. The preferred copolymers are those employing N-methylolacrylamide. In general, these copolymers are twice as efficient for a given content of the monomer of Formula I, other components and all conditions being the same, as the copolymers obtained from N-methylolmethacrylamide.

It is noteworthy that the application of acrylamide or methacrylamide copolymers in conjunction with free formaldehyde, other conditions being the same, does not produce products having the laundering-resistance and dry-cleaning resistance obtained with the copolymers of the present invention.

The N-methylolamide copolymers may be produced by conventional emulsion polymerization procedures employing a suitable emulsifier such as a non-ionic, cationic, or an anionic emulsifier or mixtures of a non-ionic with a cationic or an anionic emulsifier in conjunction with a free-radical initiator which may, if desired, be a component of any of the well-known redox systems. Examples of emulsifiers that may be used include sodium lauryl sulfate, t-octylphenoxypolyethoxyethanols containing from about 10 to 50 oxyethylene units per molecule, and lauryl pyridinium chloride. The amount of emulsifier may range from about ½% to 6% on the weight of monomers. Any free-radical initiator such as azodiisobutyronitrile, t-butyl hydroperoxide, and ammonium or potassium persulfates may be employed. The proportion of initiator may be from 0.1% to 2% on the weight of monomers.

The polymers used in the present invention may also be graft or block copolymers wherein one or more, but not all, of the monomers are first polymerized and then one or more other monomers are copolymerized with the first polymer obtained. Thus, methacrylamide or N-methylolacrylamide may first be homopolymerized or copolymerized with one or more, but less than all, of the comonomers to be introduced into the ultimate copolymer, and then the last monomer or monomers are added to the system and copolymerized or grafted on to the first homopolymer or copolymer formed. The same procedure may be used in reverse order to graft the methacrylamide or N-methylolacrylamide on to a previously-formed homopolymer or copolymer of other monomeric units. Again, a plurality of monomeric units may be introduced in succession and the methacrylamide or N-methylolacrylamide may be introduced at the beginning, at any intermediate stage, or at the end as desired.

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, with a given N-methylolamide monomer, 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 N-methylolamide 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. The textile material should 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 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 dispersion to provide from 1 to about 20%, and preferably from 3% to 10% of the copolymer, based on the weight of the dry stabilized 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 500° 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 to 15 minutes) to about 310° F. (for about 5 to 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 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.

The aqueous dispersions of the copolymers of the monomers of Formula I, especially those with alkyl acrylates or methacrylates mentioned above, are generally colorless, non-toxic, non-irritating, and free of any disagreeable odor, before, during, and after application to the fabric. They are easily applied, involve no fire hazard, and require no solvent recovery system. They do not alter the color of the wool, whether dyed or not. The finished fabrics are generally not deleteriously altered, and are frequently improved, in respect to their resistance to deterioration on exposure to sunlight, heat, and normal ageing conditions.

In some cases, it may be advantageous to add an acid or acidic substance 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. There may also be used acidic substances or salts that are substantially neutral at ordinary temperature but liberate acid on heating during the curing stage, such as ammonium phosphate, ammonium thiocyanate, hydrochloric or other acid salts of a hydroxy aliphatic amine including 2-methyl-2-amino-1-propanol, 2-methyl-2-amino - 1,3 - propanediol, tris(hydroxymethyl)aminomethane, 2-phenyl-2-amino-1-propanol, 2-methyl-2-amino-1-pentanol, 2-aminobutanol, triethanolamine, 2-amino-2-ethyl-1-butanol, also ammonium chloride, pyridine hydrochloride, benzyldimethylamine oxalate. For this purpose from 0.1% to 2% acid or acidic substance, based on the weight of the pad liquor, is suggested.

As stated hereinabove, the products obtained employing the aqueous dispersion of the N-methylolamide-containing copolymers of the present invention have good resistance to laundering and dry-cleaning when the copolymer is used as the sole stabilizing agent and is cured in the manner stated hereinabove. Such products are also free of any tendency to become discolored on chlorination and ironing. However, for some purposes, particularly where chlorination and/or ironing are not encountered, the copolymer of the present invention may be employed in conjunction with a thermosetting resin condensate such as an aminoplast or polyepoxide. The amount of such condensate that may be included in the binder compositions may be as high as 20% by weight of the copolymer, a proportion of 3 to 10% being preferred when such condensate is used.

The aminoplast condensates which may be employed are the low molecular weight or monomeric reaction products of formaldehyde with 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'-diethoxyethyl-urea, 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, dimethoxymethylmonomethylolmelamine. Preferably, the extent of condensation of these resin-forming aminoplast condensates is such that they are still soluble in water or self-dispersible therein to a colloidal condition.

The epoxy thermosetting resin-forming condensates may be either water-soluble or self-dispersible in water. The water-soluble types may be any of those having the Formulas III, IV, V, and VI:

$$\underset{\diagdown O \diagup}{H_2C{-}CH}CH_2O(CH_2CH(OH)CH_2O)_xCH_2\underset{\diagdown O \diagup}{CH{-}CH_2} \qquad \text{(III)}$$

where X is a number having an average value of 1 to 3;

$$\underset{\diagdown O \diagup}{H_2C{-}CH}CH_2O(CH_2)_yOCH_2\underset{\diagdown O \diagup}{CH{-}CH_2} \qquad \text{(IV)}$$

where y is a number having an average value of 2 to 4; and

$$\underset{\diagdown O \diagup}{H_2C{-}CH}CH_2O(C_mH_{2m}O)_zCH_2\underset{\diagdown O \diagup}{CH{-}CH_2} \qquad \text{(V)}$$

where m is an integer having a value of 2 to 4, and z is a number having an average value of 1 to 5.

The water-insoluble but self-dispersible condensates containing epoxide groups include the compounds of Formula IV above wherein y has an average value of 5 to 10 and also compounds of Formula VI:

$$\underset{\diagdown O \diagup}{H_2C{-}CH}CH_2O(\phi C(CH_3)_2\phi O)_pCH_2\underset{\diagdown O \diagup}{CH{-}CH_2} \qquad \text{(VI)}$$

where ϕ is the p-phenylene group, and p is a number having an average value of 1 to 3.

The use of such auxiliary substances is not necessary to produce effective stabilization in a practical manner. However, in some instances, their use enhances the stabilization obtainable or enables stabilization to be effected at less expense.

While the stabilizing copolymer composition may be preferentially applied, if desired, to portions of the wool fabric, it is characteristic of the compositions of the present invention that, if such preferential treatment is not desired, substantially uniform distribution may be obtained because of the reduced tendency of the compositions after initial distribution throughout the body of the fibrous product to migrate to the surfaces thereof during drying.

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 shrinkproof. 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. They also retain dyeability with acid dyestuffs and are resistant to loss of stabilization when subjected to hot acid baths during dyeing.

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, 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 to 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 woolen flannel 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

An aqueous dispersion containing 45% by weight of an emulsion copolymer of about 0.8% of acrylamide, 98% of ethyl acrylate, and 1.2% of N-methylolacrylamide was prepared by emulsion copolymerization. The resin dispersion was diluted to a 5% concentration of the resin content and ½% of ammonium chloride was added and applied to a wool flannel as described above. Above 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 3½% of the weight of the fabric. The shrinkage of the treated fabric after the five-hour wash described hereinabove was 3%. The untreated control shrank 36% after such a wash.

Similar results are obtained by application in the same way of a copolymer of 98% of ethyl acrylate and 2% of N-methylolacrylamide.

Example 2

(*a*) An aqueous dispersion containing 46% by weight of an emulsion copolymer of about 1.7% of acrylamide, 47.9% of ethyl acrylate, 48.0% of 2-ethylhexyl acrylate, and 2.4% of N-methylolacrylamide was prepared by emulsion copolymerization. The resin dispersion was diluted to a 6% concentration of the resin content. Then 0.5% ammonium chloride and 0.1% of t-octylphenoxypolyethoxyethanol having an average of about ten oxyethylene units per molecule were added and applied to an unbleached wool flannel as described above. After drying 10 minutes at 210° F., followed by curing for 10 minutes at 300° F., it was found that the proportion of copolymer applied to the fabric was about 5% of the weight of the fabric. The shrinkage of the treated fabric after the five-hour wash described hereinabove was 3%. The untreated control shrank 61% after such a wash.

(*b*) Similar results were obtained when the fabric treated with the copolymer was simultaneously dried and cured at 250° F. for 25 minutes instead of as described hereinabove.

(*c*) Similar results were also obtained when the fabric treated with the copolymer was simultaneously dried and cured at 300° F. for seven minutes instead of as described hereinabove.

Example 3

Results similar to those obtained in Example 2(*a*) were obtained by application in the same way of a copolymer of 1.7% of acrylamide, 95.9% ethyl acrylate, and 2.4% of N-methylolacrylamide.

Example 4

Results similar to those obtained in Example 2(*a*) were obtained by application in the same way of 7% of the weight of the fabric of a copolymer of about 96% of ethyl acrylate and 4% of N-methylolmethacrylamide.

Example 5

The procedure of Example 2 was repeated with good reduction of shrinkage, using an emulsion copolymer of 46% of ethyl acrylate, 48% of butyl acrylate, and 6% of N-methylolmethacrylamide.

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. As an article of manufacture, a textile material comprising interlocked yarns of proteinaceous fibers modified by reaction with 1 to 20% by weight of a water-insoluble linear addition copolymer of 0.5 to 6% by weight of an N-methylolamide of an acid of the formula

$$H_2C=\underset{\substack{|\\ COOH}}{C}-(CH_2)_{n-1}H$$

and at least one ester of the formula

$$H_2C=\underset{\substack{|\\ COOR}}{C}-(CH_2)_{n-1}H$$

in which formulas n is an integer having a value of 1 to 2, and R is an alkyl group having 1 to 18 carbon atoms when n is 1 and 4 to 18 carbon atoms when n is 2.

2. As an article of manufacture, a textile material comprising interlocked yarns of proteinaceous fibers modified by reaction with 1 to 20% by weight of a water-insoluble linear addition copolymer of ethyl acrylate and 0.5 to 6% by weight of N-methylolacrylamide.

3. As an article of manufacture, a textile material comprising interlocked yarns of proteinaceous fibers modified by reaction with 1 to 20% by weight of a water-insoluble linear addition copolymer of 0.5 to 6% by weight of an N-methylolamide of an acid of the formula

$$H_2C=\underset{\substack{|\\ COOH}}{C}-(CH_2)_{n-1}H$$

up to 6% by weight of a monomer having a group coreactive with the N-methylolamide, and at least one ester of the formula

$$H_2C=\underset{\substack{|\\ COOR}}{C}-(CH_2)_{n-1}H$$

in which formulas n is an integer having a value of 1 to 2, and R is an alkyl group having 1 to 18 carbon atoms when n is 1 and 4 to 18 carbon atoms when n is 2.

4. As an article of manufacture, a textile material comprising interlocked yarns of proteinaceous fibers modified by reaction with 1 to 20% by weight of a water-insoluble linear addition copolymer of 0.5 to 6% by weight of N-methylolacrylamide, up to 6% by weight of acrylamide, and ethyl acrylate.

5. A process for treating proteinaceous woven and knitted textile materials to reduce the shrinkage thereof comprising treating such a material with an aqueous dispersion of a water-insoluble linear addition polymer exclusively of monoethylenically unsaturated molecules comprising from 1 to 20% by weight of a water-insoluble linear addition copolymer of 0.5 to 6% by weight of an N-methylolamide of an acid of the formula

$$H_2C=\underset{\substack{|\\ COOH}}{C}-(CH_2)_{n-1}H$$

and at least one ester of the formula

$$H_2C=\underset{\substack{|\\ COOR}}{C}-(CH_2)_{n-1}H$$

in which formulas n is an integer having a value of 1 to 2, and R is an alkyl group having 1 to 18 carbon atoms when n is 1 and 4 to 18 carbon atoms when n is 2, and then drying and heating the textile at a temperature of at least 212° F.

References Cited in the file of this patent

UNITED STATES PATENTS

2,447,539	Rust	Aug. 24, 1948
2,447,540	Rust	Aug. 24, 1948
2,719,072	Kine	Sept. 27, 1955
2,780,567	Kine et al.	Feb. 5, 1957
2,827,359	Kine et al.	Mar. 18, 1958
2,937,920	Pasternak	May 24, 1960