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THE STABILIZATION OF PROTEIN-CONTAINING TEXTILES AND THE RESULTING PRODUCTS

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This invention relates to the treatment of protein-containing textile materials and to the products thereof. It relates to a process of treating protein-containing textile materials, 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 emulsions 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, render the latter substantially shrink-proof. Another object is to provide a process for shrink-proofing and felt-proofing protein-containing textiles through the use of the aforesaid emulsions. It is an object to shrink-proof and felt-proof the textiles without adversely affecting such other properties of the textile as wearing qualities or softness to the touch. 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 the stabilization of wool-containing textile materials, 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 and other synthetic fibers which are produced from casein, soybeans, collagen, et cetera. The terms "textile" and "textile materials" are used herein to include filaments, fibers, yarns, threads 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 cotton, linen, rayon or nylon.

The process of stabilizing the textile materials comprises impregnating them with an aqueous emulsion of the kind described in detail below and then heating the textiles at a temperature which is at least as high as 240° 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 emulsion. 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.

The emulsions which are employed in this process are made by emulsifying a mixture of copolymerizable monomeric esters and then copolymerizing the materials while they are in the emulsified form. The copolymerizable mixtures invariably contain at least one of each of these two kinds of essential components: (1) ureidoethyl acrylate, $\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{NHCONH}_2$, and ureidoethyl methacrylate, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{NHCONH}_2$, and (2) alkyl esters of acrylic and methacrylic acids which

have the general formula $\text{CH}_2=\text{CR}-\text{COOR}'$ in which R is a hydrogen atom (in which case the esters are those of acrylic acid) or a methyl group (in which case the esters are those of methacrylic acid) and in which R' is a straight- or branched-chain alkyl group of one to eight carbon atoms. Examples of the alkyl group which are represented by R' in the above formula include methyl, ethyl, propyl, isopropyl, n-butyl, sec.-butyl, tert.-butyl, n-octyl and 2-ethylhexyl groups as well as the isomers of these radicals. It should be pointed out that a softer hand is obtained when the alkyl group of the acrylic or methacrylic acid ester is a straight chain group.

The amount of ureidoethyl acrylate or ureidoethyl methacrylate in the copolymerizable mixtures should be from 2% to 10% and preferably from 3% to 8%—based on the total weight of the copolymerizable materials in the monomeric mixture.

Although it is preferred to prepare the emulsions from mixtures of one ureidoethyl ester from the first group above and one alkyl ester from the second group, mixtures can be used—and frequently are used—which contains both of the ureidoethyl esters and one, two, or even more of the alkyl esters.

It should also be pointed out that the emulsions containing the alkyl esters of methacrylic acid ordinarily impart a harsher "hand" or feel to the treated wool-containing textile than do the emulsions which contain the corresponding alkyl esters of acrylic acid.

The emulsions which are employed in the process of this invention are prepared by agitating a copolymerizable mixture of the two kinds of monomeric ingredients in an aqueous solution of an emulsifying or dispersing agent and an activator for the copolymerization. A wide variety of emulsifying agents including the well recognized cationic, anionic, and non-ionic surface-active agents can be used. An emulsifying agent of the non-ionic type is, however, strongly recommended. The mixture is copolymerized at a temperature from 0° C. to 100° C., and preferably from about 10° C. to about 50° C., in the presence of a catalyst system of the redox type. Such catalytic 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 and hydrosulfites 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 emulsion of copolymer comprises agitating an aqueous suspension of a mixture of the copolymerizable monomers and redox catalytic combination at room temperature without the application of heat and allowing the heat which is generated in the exothermic polymerization reaction to carry the temperature up to about 50° C. The amount of catalyst can vary but for purposes of efficiency from 0.01% to 1.0%, based on the weight of the monomers, of the peroxidic agent and the same or lesser proportions of the reducing agent are recommended. In this way it is possible to prepare emulsions which contain as little as 1% and as much as 60% of the resinous copolymer on a weight basis. It is, however, more convenient and practical—and hence preferred—to produce emulsions which contain about 15–35% resins solids.

The emulsion 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 impregnated by the emulsion. This can be done at any de-

sired temperature up to the boiling point of the emulsion. Ordinarily the textile is padded at room temperature with an emulsion which has been adjusted to a resin-content of about 1% to 20%. The material being treated must pick up or take up and then retain sufficient emulsion to provide from 1% to about 20%—and preferably from 3% to 12%—of the copolymer, based on the weight of the dry textile.

The impregnated textile material must then be heated at a temperature of 240° F. or higher—preferably at a temperature from 240° F. to about 310° F.—in order to effect cure; that is, to effect chemical reaction between the textile and the copolymer, and to impart dimensional stability to the former. Drying of the emulsion-treated textile and the heat-treatment which effects the chemical reaction can be carried out in one step, or the textile can be 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 is not a long period and is usually measured in minutes—about two to fifteen minutes. The most satisfactory time of heating for any particular combination of emulsion 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.

It has been found to be advantageous to add an acid to the emulsion with which the textile is treated because the acid serves to accelerate the reaction between the resin and the textile and brings about the stabilization 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 of formaldehyde—or materials which are equivalents of formaldehyde such as glyoxal or formals—in conjunction with the emulsions enhances the stabilization of woolen textiles. While formaldehyde has been employed successfully as an added component of the emulsions, most satisfactory results have been obtained by applying a solution of formaldehyde after the textile has been treated with the emulsion. The advantage of using formaldehyde is especially evident on extended laundering of the textile.

The thus-treated textiles are characterized by dimensional stability. Thus, they are substantially shrink-proof. And they do not stiffen, degrade or discolor on aging or on exposure to ultraviolet light as do comparable textiles which have been treated, for example, with latices of butadiene copolymers.

The following examples serve to illustrate this invention.

Example I

The following components were placed in a 500-ml. flask equipped with a mechanical agitator and thermometer:

95.5 g. ethyl acrylate
4.5 g. ureidoethyl methacrylate
288 g. water
8.6 g. non-ionic dispersing agent (a 70% aqueous solution of a tert.-octylphenoxypolyethoxyethanol)

The contents of the flask was cooled to 15° C. and there were added 0.12 gram of ammonium persulfate and 0.16 gram of sodium hydrosulfite. The mixture was agitated, and over a period of about 20 minutes the temperature rose to 40° C. Agitation was continued for 30 minutes while the resultant emulsion cooled to room temperature.

The effectiveness of this emulsion and of the other emulsions exemplified below in stabilizing wool was de-

termined by impregnating measured pieces of flannel with the emulsions, 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 Botany woolen flannel (Style #405; 2/2 right hand 45° twill, 55 x 44; S-twist in ends, Z in picks; scoured, carbonized, neutralized and peroxide-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 emulsion 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 thus-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 10 gallons of water and 70 grams of soap (Ivory). 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 experimental error in tests of this kind is about $\pm 2\%$.

The above emulsion was diluted to a 5% resin-content and test pieces of flannel were prepared therefrom in the following ways:

A. Test pieces were padded through the above emulsion. The pick-up was 3.5% resin (dry resin on dry flannel). Test pieces were dried 10 minutes at 240° F. and cured 10 minutes at 300° F.

B. Test pieces were padded through the emulsion containing 1% added oxalic acid. The pick-up was 3.5% and the drying period was 15 minutes at 240° F.

C. The treatment with the emulsion was the same as in B above but the heating period was only 10 minutes at 240° F., followed by curing for 10 minutes at 300° F.

D. Here again the treatment with the emulsion was the same as in B above. The pieces were dried 10 minutes at 240° F. and were then additionally padded through a 1% solution of formaldehyde followed by drying for 10 minutes at 240° F. and curing for 10 minutes at 300° F.

E. The pieces were treated with the emulsion according to the process of A above. Later they were given a treatment with 1% formaldehyde and were finally dried at 240° F. for 10 minutes.

The results of the wash tests are given in the following table wherein the numbers at the top of the columns indicate the number of minutes of washing and the other numbers represent the percentage of shrinkage:

Specimen	15 min.	30 min.	45 min.	60 min.	90 min.	120 min.
	Percent	Percent	Percent	Percent	Percent	Percent
A.....	0	0	0	0	4	10
B.....	0	0	3	3	11	25
C.....	0	0	0	0	0	0
D.....	0	0	0	0	0	2
E.....	0	0	0	0	1	6
Blank.....	6	16	28	34	45	48

It is apparent from the above that an acid catalyst or an after-padding with formaldehyde enhances the resistance to shrinkage. It is further evident that the curing at 300° F. is extremely beneficial.

Example II

In the same manner as described in Example I above, an emulsion was made from a mixture of 92.5 parts of ethyl acrylate and 7.5 parts of ureidoethyl methacrylate. This emulsion was applied to flannel in the following two ways:

A. Test pieces were padded through the emulsion containing 1% oxalic acid. They had a pick-up of 5% resin-solids. They were then dried for 10 minutes at 240° F. and cured for 10 minutes at 300° F.

B. Here the pieces were treated by process A, immedi-

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ately above, and were then after-padded with a 1% solution of formaldehyde and were then heated 10 minutes at 240° F. and 10 minutes at 300° F.

It is noteworthy that none of the test pieces, whether prepared by method A or B, shrank at all during 120 minutes of washing. After 240 minutes of washing, the product of method A had shrunk 12% but the product of method B remained virtually unchanged.

Example III

The procedure of Example I was followed in the preparation of emulsions of several other copolymers. The emulsions were applied to flannel and tested for their effect on shrinkage. Invariably the shrinkage was reduced when as little as 1% resin-solids was applied and the treated fabric was heated above 240° F.

Particularly good results were obtained by using emulsions containing copolymers of ureidoethyl methacrylate with the alkyl esters of acrylic acid in which the alkyl group contained four to eight carbon atoms. Such emulsions had very little if any effect on the handle but did have outstanding stabilizing effects.

For reasons of efficiency and economy the process of this invention is directed to the use of compositions containing the copolymerized ureidoethyl esters of acrylic and methacrylic acids. It should, however, be pointed out that woollen textiles can also be stabilized by the use of emulsions which contain other copolymerized ureido esters such as ureidopropyl, ureidoheptyl and ureidooctyl acrylates and methacrylates, all of which are more hydrophobic than the ureidoethyl esters.

I claim:

1. A process for treating protein-containing textile material to reduce the shrinking tendencies thereof, which comprises impregnating said textile material with an aqueous emulsion of a copolymer of a mixture containing on a weight basis (1) from 2% to 10% of a member of the class consisting of ureidoethyl acrylate and ureidoethyl methacrylate and (2) from 90% to 98% of a member of the class consisting of alkyl esters of acrylic and methacrylic acids in which the alkyl groups contain one to eight carbon atoms, drying, and heating the thus-treated textile material at a temperature which is at least 240° F. but is below the charring point of said textile material.

2. A process for treating wool-containing textile material to reduce the shrinking tendencies thereof, which comprises impregnating said textile material with an aqueous emulsion of a copolymer of a mixture containing on a weight basis (1) from 2% to 10% of a member of the class consisting of ureidoethyl acrylate and ureidoethyl methacrylate and (2) from 90% to 98% of a member of the class consisting of alkyl esters of acrylic and methacrylic acids in which the alkyl groups contain one to eight carbon atoms, retaining by said textile material such an amount of emulsion as to provide from 1% to 20% of said copolymer based on the dry weight of said textile material, drying, and heating the thus-treated textile material at a temperature which is at least 240° F. but is below the charring point of said textile material.

3. A process for treating wool-containing textile material to reduce the shrinking tendencies thereof, which comprises impregnating said textile material with an aqueous emulsion of a copolymer of a mixture containing on a weight basis (1) from 2% to 10% of a member of the class consisting of ureidoethyl acrylate and ureidoethyl methacrylate and (2) from 90% to 98% of a member of the class consisting of alkyl esters of acrylic and methacrylic acids in which the alkyl groups contain one to eight carbon atoms, retaining by said textile material such an amount of emulsion as to provide from 3% to 12% of said copolymer based on the dry weight of said textile material, drying, and heating the thus-treated textile material at a temperature from 240° F. to 310° F.

4. A process for treating wool-containing textile material to reduce the shrinking tendencies thereof, which com-

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prises impregnating said textile material with an aqueous emulsion of a copolymer of a mixture containing on a weight basis (1) from 3% to 8% of ureidoethyl methacrylate and (2) from 92% to 97% of butyl acrylate, the amount of said emulsion which is retained by said textile material being such as to deposit in said textile material from 1% to 20% of said copolymer based on the dry weight of said textile, drying, and heating the thus-treated textile material at a temperature which is at least 240° F. but is below the charring point of said textile material.

5. A process for treating wool-containing textile material to reduce the shrinking tendencies thereof, which comprises impregnating said textile material with an aqueous emulsion of a copolymer of a mixture containing on a weight basis (1) from 3% to 8% of ureidoethyl methacrylate and (2) from 92% to 97% of n-butyl acrylate, the amount of said emulsion which is retained by said textile material being such as to deposit in said textile material from 3% to 12% of said copolymer based on the dry weight of said textile, drying, and heating the thus-treated textile material at a temperature from 240° F. to about 310° F.

6. A process for treating wool-containing textile material to reduce the shrinking tendencies thereof, which comprises impregnating said textile material with an aqueous emulsion of a copolymer of a mixture containing on a weight basis (1) from 3% to 8% of ureidoethyl methacrylate and (2) from 92% to 97% of octyl acrylate, the amount of said emulsion which is retained by said textile material being such as to deposit in said textile material from 3% to 12% of said copolymer based on the dry weight of said textile, drying, and heating the thus-treated textile material at a temperature which is at least 240° F. but is below the charring point of said textile material.

7. A process for treating wool-containing textile material to reduce the shrinking tendencies thereof, which comprises impregnating said textile material with an aqueous emulsion of a copolymer of a mixture containing on a weight basis (1) from 3% to 8% of ureidoethyl acrylate and (2) from 92% to 97% of butyl acrylate, the amount of said emulsion which is retained by said textile material being such as to deposit in said textile material from 3% to 12% of said copolymer based on the dry weight of said textile, drying, and heating the thus-treated textile material at a temperature which is at least 240° F. but is below the charring point of said textile material.

8. A process for treating wool-containing textile material to reduce the shrinking tendencies thereof, which comprises impregnating said textile material with an aqueous emulsion of a copolymer of a mixture containing on a weight basis (1) from 3% to 8% of ureidoethyl acrylate and (2) from 92% to 97% of octyl acrylate, the amount of said emulsion which is retained by said textile material being such as to deposit in said textile material from 3% to 12% of said copolymer based on the dry weight of said textile, drying, and heating the thus-treated textile material at a temperature from 240° F. to about 310° F.

9. A protein-containing textile material which is resistant to shrinkage and carries deposited therein a cured copolymer of a mixture containing on a weight basis (1) from 2% to 10% of a member of the class consisting of ureidoethyl acrylate and ureidoethyl methacrylate and (2) from 90% to 98% of a member of the class consisting of alkyl esters of acrylic and methacrylic acids in which the alkyl groups contain one to eight carbon atoms.

10. A protein-containing textile material which is resistant to shrinkage and carries deposited therein from 1% to 20%, on the dry weight of the textile material, of a cured copolymer of a mixture containing on a weight basis (1) from 2% to 10% of a member of the class consisting of ureidoethyl acrylate and ureidoethyl methacrylate and (2) from 90% to 98% of a member of the

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class consisting of alkyl esters of acrylic and methacrylic acids in which the alkyl groups contain one to eight carbon atoms.

11. A wool-containing textile material which is resistant to shrinkage and carries deposited therein from 1% to 20%, on the dry weight of the textile material, of a cured copolymer of a mixture containing on a weight basis (1) from 3% to 8% of ureidoethyl methacrylate and (2) from 92% to 97% of butyl acrylate.

12. A wool-containing textile material which is resistant to shrinkage and carries deposited therein from 1% to 20%, on the dry weight of the textile material, of a cured copolymer of a mixture containing on a weight basis (1) from 3% to 8% of ureidoethyl acrylate and (2) from 92% to 97% of butyl acrylate.

13. A wool-containing textile material which is resistant to shrinkage and carries deposited therein from 1% to 20%, on the dry weight of the textile material, of a cured copolymer of a mixture containing on a weight basis (1) from 3% to 8% of ureidoethyl methacrylate and (2) from 92% to 97% of octyl acrylate.

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14. A wool-containing textile material which is resistant to shrinkage and carries deposited therein from 1% to 20%, on the dry weight of the textile material, of a cured copolymer of a mixture containing on a weight basis (1) from 3% to 8% of ureidoethyl acrylate and (2) from 92% to 97% of octyl acrylate.

15. A wool-containing textile material which is resistant to shrinkage and carries deposited therein from 1% to 20%, on the dry weight of the textile material, of a cured copolymer of a mixture containing on a weight basis (1) from 3% to 8% of ureidoethyl methacrylate and (2) from 92% to 97% of ethyl acrylate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,313,742	Engelmann	Mar. 16, 1943
2,355,265	Bock	Aug. 8, 1944
2,499,653	Kropa	Mar. 7, 1950
2,606,810	Erickson	Aug. 12, 1952
2,661,313	Folkers	Dec. 1, 1953