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STABILIZATION OF PROTEIN-FIBER-CONTAINING TEXTILES

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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 a process for shrink-proofing and felt-proofing textiles containing scale-surfaced protein fibers, whether of natural or artificial origin, through the use of aqueous dispersions of resins. It is an object to shrink-proof and felt-proof the textiles without adversely affecting such other properties of the textile as wearing qualities and tensile strength.

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 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 yarns, threads, and plied yarns as such or in woven, knitted, 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.

The process of treating the textile materials in accordance with the invention comprises impregnating them with an aqueous dispersion of a polyester-aminoplast condensation product 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 condensate in the dispersion and at the same time further condensation takes place between the molecules of the condensate assuring complete infusibility and insolubility in the impregnant. The condensate appears to be chemically bound to the textile and not merely deposited as a dry coating on the fibers. As a result, the resinous condensate 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 marked reduction in the shrinking and felting properties of wool-containing textiles can be obtained by the application thereto of an aqueous dispersion containing, dispersed therein at a concentration such as to apply from 0.7% to 8% on the fabric weight of a polyester-aminoplast condensation product which has excellent curing qualities, produces films of good adhesion and hardness, and yet is self-dispersible in aqueous systems. The

condensation product used for the present invention may be generally characterized as the coreaction product of at least two components (A) and (B) as follows:

(A) A special polyester having an average molecular weight of about 800 to 1500 containing hydroxyl groups available for condensation with the aminoplast and free carboxyl groups available for neutralization by means of ammonia, an amine, or a quaternary ammonium compound, and

(B) An aminoplast soluble in such organic solvents as butanol, isopropanol and monoalkyl ethers of diethylene glycol in which the alkyl group is methyl, ethyl, or the like.

COMPONENT A

Component A is a special low molecular weight polyester containing hydroxyl groups adapted to enable its coreaction with the aminoplast (Component B) and some carboxyl groups for neutralization. The acid number of Component A should be between about 90 and about 100. This polyester is formed by first condensing a dibasic aliphatic acid having from 5 to 10 carbon atoms with a polyol or a mixture thereof containing at least 25 mole percent of a polyol having three or more hydroxyl groups therein. For example, the polyol may contain up to 75 mole percent by weight of a diol, such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, and trimethylene glycol, 1,3-butane-diol, 1,4-butane-diol, and 1,5-pentane-diol. Examples of the polyols containing more than two hydroxyl groups that may be used include glycerine, sorbitol, pentaerythritol, inositol, tetramethylolcyclohexanol, di- and poly-pentaerythritol, and so forth, but tri-methylolethane is preferred. Preferably, the proportion of diol is not over 50 mole percent of the entire polyol component, and, of course, the diol may be completely absent.

The aliphatic dicarboxylic acid that is used may be adipic acid, succinic acid, glutaric acid, sebacic acid or the like. Preferably it contains from 5 to 8 carbon atoms, but it may contain 4 to 18 carbon atoms.

The polyol and dibasic aliphatic acid are mixed in the proportion of 1.2 to 1.8 moles of polyol to each mole of acid, preferably 1.2 to 1.5 moles of polyol being used for each mole of acid. The mixture is heated to a temperature within the range of about 200° to 260° C. either in the presence of an inert gas, such as carbon dioxide, nitrogen, argon, helium, when atmospheric or higher pressures are employed. If desired, a reduced pressure may be present during the reaction to remove the water formed on esterification and to favor a shift in the equilibrium toward the esterification product. Pressures of 20 to 50 mm. or more absolute pressure may be used. Optionally, an esterification catalyst may be used, such as 0.1 to 1% of sulfuric acid, toluene-sulfonic acid, zinc chloride, or phosphorus pentoxide. Such catalyst, however, is not necessary. The reaction is carried out until the acid number is reduced to a value of 10 or less. Preferably, the acid number is reduced to a value of less than 5.

The polyester obtained has terminal hydroxyl groups and also some hydroxyl groups at intervals along the polyester molecule.

Instead of using the free dibasic acid itself as one of the starting materials in this esterification reaction, there may be used the lower alkyl diesters of the dibasic acids, such as the dimethyl or diethyl esters. Reaction in this case involves an ester interchange and sometimes has the advantage of yielding a product having less color. In this procedure, the alcohol liberated is boiled off.

Optionally, the polyester may be modified with a fatty acid having 8 to 30 carbon atoms, such as lauric acid, stearic acid, oleic acid, linoleic acid, linolenic acid, palmitic acid, and ricinoleic acid. The modification may

be effected by directly reacting the fatty acid with the polyol or with the hydroxyl-containing polyester; alternatively, the same result may be effected by transesterification, in which case an ester of the fatty acid, such as an ester thereof with glycerol, is reacted with the polyol or the hydroxyl-containing polyester in the presence of a suitable catalyst, such as an alkali metal alkoxide. There should be used from 1 to 3 moles of polyol or polyol mixture to each mole of the fatty acid (or the equivalent thereof in the case of an ester thereof when transesterification is employed); preferably there is used from about 1.2 to 1.5 moles of polyol to each mole of acid or equivalent of ester. When modification with a fatty acid is resorted to, it is preferable to react the mono-basic fatty acid or its ester (in the case of transesterification) with the polyol or a part of it before the polyol is reacted with the dibasic acid. Thus, when a modified polyester is desired, the fatty acid or ester thereof, such as a fat or oil, is first mixed with the polyol or polyol mixture and the esterification or transesterification with the monobasic fatty acid is carried out under the same conditions as stated hereinabove in respect to the esterification with a dibasic acid. Thus, the temperature may be from 200° to 260° C.; the pressure from 20 mm. absolute up to atmospheric or higher, an inert gas being used preferably at atmospheric or higher pressures. Optionally, an esterification or transesterification catalyst may be used as before. The reaction is continued until the acid number reaches a value of 10 or less. Preferably, it is continued until the acid number reaches a value of less than 1. It is desirable that the monobasic acid be completely bound up in the ester product, and to this end the most desirable condition is attained when the acid number approaches or reaches a value of zero. The esterification product obtained from the polyol and monobasic acid is then mixed with the dibasic acid and any additional amount of polyol needed to bring the proportion of polyol used in the entire condensation reaction to a proportion of between 1.2 to 1.8 moles of polyol to one mole of the dibasic acid. This esterification reaction is continued at the same conditions as stated hereinabove in describing the preparation of the simple polyester unmodified with monobasic acid. As in the previous case, the reaction is continued until the acid number of the product is reduced to a value of 10 or less and preferably to a value of less than 5. The oil-modified polyester in this instance has some of its hydroxyl groups esterified with monoacyl radicals derived from the fatty acid. Of course, a mixture of fatty acids may be employed instead of a single one and similarly a mixture of dibasic acids may be employed instead of a single one whether an oil-modified polyester or an unmodified polyester is to be prepared up to this point.

The unmodified or oil-modified polyester thus prepared is then reacted with o-phthalic acid or o-phthalic acid containing lower alkyl substituents in the benzene ring, such as methyl, ethyl, propyl, or butyl substituents or with the anhydrides thereof. The use of the anhydrides are preferred because of their solubility in the polyester at this stage and the ease of reaction of one carboxylic group thereof, apparently without appreciable reaction of both such groups which would lead to cross-linking, water-insolubility, and gelation. Any other polycarboxylic acid, such as isophthalic acid or terephthalic acid, has not been found satisfactory in this phase of the preparation of the polyester, either because of insolubility and lack of reactivity therein, or, in some instances, because of rapid cross-linking to a water-insoluble, gel stage. The amount of the phthalic acid or its derivative or anhydride used is in the proportion of 2 to 3.5 moles for every 3 moles of the polyol. When the polyol consists entirely of one containing 3 hydroxyl units, it is preferred to use approximately 2 moles of the phthalic acid for 3 moles of the polyol. The reaction with the phthalic acid is believed to provide terminal carboxyphenyl groups on the polyester molecules. The reaction of the mixture of phthalic acid with the unmodified or oil-modified polyester may be effected at a temperature of 150° to 170° C. for a period of 1 to 2 hours. The reaction is continued until the acid number is reduced to 100 but is stopped before the acid number is reduced appreciably below 90. When the desired acid number within the range of 90 to 100 is reached, the reaction mixture is cooled to a temperature below 60° C. and preferably down to 20° or 30° C. to stop the esterification reaction. The reaction product thereby obtained provides Component A for reaction as will be described hereinbelow.

COMPONENT B

Component B consists of an alkylated polymethylol nitrogen compound obtained by the reaction of formaldehyde or substances yielding formaldehyde and certain alcohols on a nitrogen compound selected from the group consisting of urea, thiourea, N,N'-ethyleneurea (imidazolidinone-2), and triazines including guanamines, such as acetoguanamine and benzoguanamine, melamine and substituted melamines. The alkylation should be that resulting from an alcohol having from 3 to 6 carbon atoms, such as isopropanol, n-propanol, butanol, pentanol, hexanol, or cyclohexanol, so that the aminoplast will be soluble in such solvents as butanol, isopropanol, pentanol and the like. Examples of the substituted melamines include N,N-dialkylmelamines in which the alkyl group has from 1 to 4 carbon atoms, e.g. methyl, ethyl, propyl, isopropyl, and n-butyl, also N,N'-dialkylmelamines in which the alkyl group may be any of those just stated, N-monoalkylmelamines in which the alkyl group may be any of those just stated. The preparation of the alkylated polymethylol nitrogen-containing compound is in itself no part of the present invention since these condensation products are well known and available commercially.

I. Condensation product obtained by coreaction of Components A and B

The condensation product of Components A and B may be obtained by reacting a mixture of them in organic solvents at a concentration of 50 to 90% solids; for example, Component A may be dissolved in xylene, benzene, toluene, ketones, such as dioxane or methylethyl ketone, or in monoalkyl ethers of ethylene glycol, such as the monobutyl ether, butanol or mixtures of such solvents. Similarly, the aminoplast (Component B) may be dissolved in butanol or a mixture of butanol and xylene or in any other mixture of the various solvents just mentioned. Component A and Component B are reacted in proportions of about 40 to 60 parts by weight of Component A to about 60 to 40 parts by weight of Component B. Preferably, the concentration of the reactants in the organic solvent, and consequently of the reaction product therein, is maintained as high as possible consistent with manipulability which depends upon the viscosity. The reaction of the mixture is effected in the organic solvent solution at a temperature of 50° to 120° C., and preferably at a temperature of 70° to 90° C., at atmospheric pressure. The reaction is carried out until a sample to which an amine (such as 10% of triethylamine on weight of condensate solids) is added is soluble in water. Generally, the reaction is accompanied by an advance in viscosity of about 3 to 10 poises when measured at 60% solids concentration in any particular organic solvent at room temperature.

The reaction product is cooled below 60° C., such as to 25° to 55° C., and then it is neutralized or at least partially neutralized with ammonia, an amine, or a quaternary ammonium compound. If desired, a small proportion of the neutralizing component may be a fixed base, such as potassium or sodium hydroxide, or carbonates. However, it is preferred to use as the entire neu-

tralizing agent either ammonia, a volatile amine or a quaternary ammonium compound or a mixture of 2 or 3 of such materials. When ammonia is the neutralizing agent, it is generally introduced as an aqueous solution. Preferably the ammonia is rather concentrated when it is desired to store or ship the product in order to save bulk. However, the ammonia may be sufficiently dilute to directly produce an aqueous solution or dispersion of the condensation product of the present invention having the desired solids concentration for direct application to the textile. When an amine or a quaternary ammonium compound is used as the neutralizing agent, it may be added without adding water so that the neutralized condensation product of the invention is essentially anhydrous but is capable of practically unlimited dilution with water without being coagulated. Such amines as monoethylamine, triethylamine, dimethylamine, trimethylamine, and morpholine are quite suitable as neutralizing agents. Also quaternary ammonium compounds, such as choline, trimethylbenzylammonium chloride, octadecylbenzyldimethylammonium chloride, methylpyridinium chloride, may be used for neutralization. As in the case of the amines, they may be used without the addition of water so that the product is obtained as a substantially anhydrous solution which is dilutable with water to practically unlimited extent. If desired, the amines or the quaternary ammonium compounds may be introduced as aqueous solutions and, in the case of ammonia, a dilution may be such as to provide the concentration of the condensation product desired for application. On the other hand, the substantially anhydrous products obtained by neutralization by an amine or a quaternary ammonium compound may be stored or shipped in that concentrated form and then diluted with water for application at the point of its destined use.

COMPONENT C

Component C, when used, may be any of the common alkyd resins including oil-modified alkyd resins. For example, simple alkyds that may be used may be those obtained by condensing a dicarboxylic acid, such as o-phthalic, terephthalic, isophthalic, pyromellitic, succinic, glutaric, adipic or sebacic acids, with a polyhydric alcohol, such as ethylene glycol, diethylene glycol, glycerol, pentaerythritol, sorbitol, inositol, trimethylolethane, tetramethylolcyclohexanol, di- and poly-pentaerythritol. Preferably the polyhydric alcohol component from which the alkyd is derived comprises at least 25% by weight of at least one alcohol containing at least three hydroxyl groups in order to provide an excess of hydroxyl groups available for reaction with the aminoplast (Component B). If desired, there may be used as a part of the dicarboxylic acid component one or more ethylenically unsaturated acids, such as maleic acid, fumaric acid, or the polycarboxylic acid compounds obtained by interacting maleic anhydride with abietic acid, ricinoleic or eleostearic acids. The unsaturated dicarboxylic acid may amount to fifty percent of the total dicarboxylic acid used, but is preferably not over 25% of such total.

The alkyds may be modified with a higher monobasic aliphatic acid having 12 to 30 carbon atoms, such as a fatty acid or fatty acid mixture derived from drying, semi-drying, or non-drying oils or fats in which the fatty acid has from 12 to 30 carbon atoms and up. The modifying fatty acid may be lauric acid, myristic acid, coconut oil fatty acids, palm oil fatty acids, palmitic acid, oleic acid, stearic acid, linolenic acid, or fatty acids obtained by hydrogenation of fish, animal, or vegetable oils or fats.

In preparing the alkyd, the glycerol or other polyhydric alcohol or mixture thereof may first be partially esterified with the monoacid or mixture thereof, and the resulting partial ester may then be reacted with the dicarboxylic acid, such as phthalic acid. Alternatively, the dicarboxylic acid, the polyhydric alcohol and the monocarboxylic acid may be mixed together and reacted simultaneously. It is preferred to use alkyds modified with essentially saturated, non-drying fatty acids to assure freedom from yellowing and embrittlement on ageing. Preferred alkyds may be obtained from 39 to 50% phthalic acid, 20 to 30% glycerol, and 30 to 35% coconut fatty acids. The preparation of the alkyd is in itself no part of the present invention, since conventional oil-modified alkyds may be used.

The alkyd of which Component C is constituted is essentially a water-insoluble product that is soluble in organic solvents, such as butanol, pentanol, the monoethyl ether of ethylene glycol and the like and has an average molecular weight of about 2000 to about 10,000. Such alkyds have excellent film-forming qualities but are not adapted to be applied from aqueous systems in the production of coatings or other materials.

II. Condensation product obtained by coreaction of Components A, B, and C

The condensation product of Components A, B, and C is obtained by first reacting the aminoplast (Component B) with the alkyd (Component C). They may be reacted in organic solvents at a concentration of 50 to 80% solids; for example, Component C may be dissolved in xylene, benzene, toluene, ketones, such as dioxane or methylethyl ketone, or in monobutyl ether of ethylene glycol, butanol or mixtures of such solvents. Similarly, the aminoplast (Component B) may be dissolved in butanol or a mixture of butanol and xylene or in any other mixture of the various solvents just mentioned. Component B and Component C are reacted in proportions of about 20 to 30 parts by weight of Component C to about 20 to 30 parts by weight of Component B. The reaction of the mixture is effected in the organic solvent solution at a temperatore of 60° to 120° C., and preferably at a temperature of 70° to 90° C., at atmospheric pressure. The reaction is carried out until an advance in viscosity of at least 3 poises is obtained when measured at 60% solids concentration in any particular organic solvent at room temperature.

The organic solvent solution of the reaction product of B and C is then mixed with the polyester Component A whether unmodified or oil-modified in proportions of about 40 to 60 parts by weight of Component A, preferably about 50 parts thereof, to 50 parts by weight of the reaction product of B and C. Component A may be added to the reaction product of B and C as such or it may be dissolved first in an organic solvent, such as toluene, xylene, benzene, or monoalkyl ethers of ethylene glycol, such as the monobutyl ether thereof, at concentrations of 50 to 90% solids, preferably as high as possible consistent with the working of viscous medium. The reaction is effected in the organic solvent solution at 50 to 80% solids content at a temperature of about 60° C. for about one-half hour. Preferably, the concentration of the reactants in the organic solvent, and consequently of the reaction product therein, is maintained as high as possible consistent with manipulability which depends upon the viscosity. This reaction is continued for a time sufficient to raise the viscosity at least 2 poises when measured at 60% solids concentration in an organic solvent at room temperature.

The reaction product is cooled below 60° C., such as to 25° to 55° C., and then it is neutralized or at least partially neutralized with ammonia, an amine, or a quaternary ammonium compound. If desired, a small proportion of the neutralizing component may be a fixed base, such as potassium or sodium hydroxide, or carbonates. However, it is preferred to use as the entire neutralizing agent either ammonia, a volatile amine or a quaternary ammonium compound or a mixture of two or three of such materials. When ammonia is the neutralizing agent, it is generally introduced as an aqueous solution. Preferably the ammonia is rather concentrated when it is desired to store or ship the product in

order to save bulk. However, the ammonia may be sufficiently dilute to directly produce an aqueous solution or dispersion of the condensation product of the present invention having the desired solids concentration for direct application. When an amine or a quaternary ammonium is used as the neutralizing agent, it may be added without adding water so that the neutralized condensation product of the invention is essentially anhydrous but is capable of practically unlimited dilution with water without being coagulated. Such amines as monoethylamine, triethylamine, dimethylamine, trimethylamine, and morpholine are quite suitable as neutralizing agents. Also, quaternary ammonium compounds, such as choline, trimethylbenzylammonium chloride, octadecylbenzyldimethylammonium chloride, and methylpyridinium chloride, may be used for neutralization. As in the case of the amines, they may be used without the addition of water so that the product is obtained as a substantially anhydrous solution which is dilutable with water to practically unlimited extent. If desired, the amines or the quaternary ammonium compounds may be introduced as aqueous solutions and, in the case of ammonia, a dilution may be such as to provide concentration of the condensation product desired for application. On the other hand, the substantially anhydrous products obtained by neutralization by an amine or a quaternary ammonium compound may be stored or shipped in that concentrated form and then diluted with water for application at the point of its destined use.

The proportion of the condensate that is applied to the fabric may vary from 0.7 to 8% by weight of the fabric, a proportion of 2.5 to 5% being preferred. The concentration of the aqueous dispersion may be varied accordingly depending on pick-up. When about 50 to 60% pick-up is employed, the concentration will be from 1.5 to 15% and preferably from about 5 to 10%. 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 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 the dispersion.

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 temperatures, 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 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 condensate and possibly the textile. In any event, the heating sets the condensate on the textile, and especially 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 condensate, 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 dispersion 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 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.

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 resin solids. 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 wool fabrics 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 the invention and parts and percentages are by weight unless otherwise indicated:

PREPARATION OF CONDENSATES

I. Component A

EXAMPLE A

Into a reaction vessel, there are introduced 292 grams of adipic acid (2.0 moles) and 360 grams of trimethylolethane (3 moles). Heat and reduced pressure are applied and the batch held at 230° C. until the acid number value falls below 4.0. The reaction mixture is then cooled to ca. 160° C., vented and 296.0 grams of o-phthalic anhydride (2.0 moles) is charged. The mixture is heated to 150° to 160° C. at atmospheric pressure and held at this temperature until the acid number of the batch falls to ca. 100. At this point, full cooling is applied to the batch and sufficient xylol is charged to adjust the solids content of the batch to ca. 85%.

EXAMPLE B

The procedure of Example A is repeated replacing the adipic acid with 404.0 grams of sebacic acid (2 moles) and the polyol with 332.0 grams of glycerine (3.6 moles).

EXAMPLE C

The procedure of Example A is repeated replacing the adipic acid with 236.0 grams of succinic acid (2 moles) and the polyol with 437.0 grams of sorbitol (2.4 moles).

EXAMPLE D

The procedure of Example A is repeated replacing the adipic acid with 264.0 grams of glutaric acid (2 moles) and the polyol with 340.0 grams of pentaerythritol (2.5 moles).

EXAMPLE E

The procedure of Example A is repeated replacing the polyol with a mixture of 233.0 grams of diethylene glycol

(2.2 moles) and 96.0 grams of trimethylolethane (0.8 mole).

EXAMPLE F

200 grams (1.0 mole) of lauric acid and 156.0 grams (1.3 moles) of trimethylolethane are heated under reduced pressure (total pressure=ca. 30 mm. Hg) to a temperature of 230° C. The mixture is held at this temperature until the acid number of the batch (mg. KOH reqd. to neutralize 1.0 gram) falls below 1.0. The system is then cooled to below 170° C., vented and 292.0 grams of adipic acid (2.0 moles) and 204.0 grams of trimethylolethane (1.7 moles) are charged. Heat and reduced pressure are re-applied and the batch again held at 230° C. until the acid number value falls below 4.0. The reaction mixture is then cooled to ca. 160° C., vented and 296.0 grams of o-phthalic anhydride (2.0 moles) is charged. The mixture is heated to 150° C. to 160° C. at atmospheric pressure and held at this temperature until the acid number of the batch falls to ca. 100. At this point, full cooling is applied to the batch and sufficient xylol is charged to adjust the solids content of the batch to ca. 85%.

EXAMPLE G

The procedure of Example F is followed substituting 364.0 grams of sebacic acid (1.8 moles) for the adipic acid.

EXAMPLE H

The procedure of Example F is followed substituting 138.0 grams of diethylene glycol (1.3 moles) for the first charge of trimethylolethane.

EXAMPLE I

The procedure of Example F is followed substituting 264.0 grams of glutaric acid (2 moles) for the adipic acid and 120.0 grams of glycerol (1.3 moles) for the first charge of trimethylolethane.

EXAMPLE J

The procedure of Example F is followed substituting 427.0 grams of stearic acid (1.5 moles) for the lauric acid.

EXAMPLE K

Charge 444 grams of soybean oil to a reaction vessel along with 120 grams of trimethylolethane (1.0 mole). Heat is applied to the mixture and nitrogen gas is sparged through the batch continuously throughout the reaction. At 130 C., 1.0 gram of a 25° solution of sodium methylate in methanol is added to the batch. The heating is continued. At 165° C., 0.5 gram of triphenylphosphite is charged to the batch. Heating is continued to a batch temperature of 230° to 240° C. The mixture is held in this temperature range about five minutes until a clear "pill" is obtained in cooled droplets from a rod dipped into the mixture. The mixture is then cooled to approximately 180° C., at which point there is charged 438 grams (3 moles) of adipic acid and also another 360 grams (3 moles) of the trimethylolethane, and heating is once more resumed. The batch is heated to 260° and held at this temperature until the acid number drops to less than 2.0. Then the batch is cooled to 170° C. and 444 grams (3 moles) of phthalic anhydride are charged. Heating is again resumed. The batch is heated to 150° to 160° C. until the acid number drops to 90° to 100° C., at which point the reaction is probably complete and full cooling is applied. At a temperature of 110° C., the batch is diluted to about 85% solids with 300 grams of xylol.

EXAMPLE L

The procedure of Example K is repeated substituting 444.0 grams of coconut oil for the soybean oil.

II. Condensates formed of Components A and B

EXAMPLE M

A mixture of 100 grams of a 60% solution in xylene of a butylated polymethylolmelamine and 100 grams of the polyester product of Example A is stirred at room temperature for about one-half hour to insure reasonably thorough mixing before any heat is applied. The mixture is then heated to 55° to 60° C. and held in this range for one-half hour. At the end of this time, reaction is stopped by applying cooling to the batch and adding an amount of concentrated 28% aqueous NH_3 or triethylamine (100%) equal to 20% of the weight of polyester solids present.

EXAMPLE N

The procedure of Example M is followed substituting 120 grams of the polyester of Example F for the polyester of Example A therein.

EXAMPLE O

The procedure of Example N is repeated in successive runs substituting for the polyester there used 120 grams of each of the polyesters of Examples B to E and G to L.

EXAMPLE P

The procedure of Example N is followed except that 120 grams of the polyester of Example K is substituted for the polyester of Example F.

EXAMPLE Q

The procedure of Example M is repeated except that 100 grams of a 50% solution of a butylated dimethylolurea is substituted for the melamine resin.

EXAMPLE R

The procedure of Example M is repeated except that 100 grams of a 45% solution of N,N'-diisopropoxymethyl-imidazolidinone-2 is substituted for the melamine resin.

EXAMPLE S

The procedure of Example N is repeated substituting 100 grams of a 60% solution in xylene of a butylated polymethylol-N,N-dimethylmelamine.

III. Condensates formed of Components A, B, and C

EXAMPLE T

A mixture of 100 grams of a 60% solution in xylene of a butylated polymethylolmelamine and 100 grams of a 60% solution in xylene of a coconut oil-modified glycerol-phthalic acid alkyd resin is heated with agitation to 70° to 80° C. at atmospheric pressure. The mixture is held at this temperature with continuous agitation until the viscosity of the batch advanced about 15 poises from its original viscosity (when measured at 25° C. and at a 60% concentration). The reaction is then stopped by cooling the batch to room temperature. During the cooling, there is gradually added 100 grams of the polyester product of Example A.

The entire mixture is stirred at room temperature for ca. ½ hour to insure reasonably thorough mixing before any heat is applied. The mixture is then heated to 55° to 60° C. and held in this range for one-half hour. At the end of this time, reaction is stopped by applying cooling to the batch and adding an amount of concentrated aqueous NH_3 (ca. 28%) or triethylamine (100%) equal to 20% of the weight of polyester solids present.

EXAMPLE U

The procedure of Example T is followed substituting 120 grams of the polyester of Example F for the polyester of Example A therein used.

The coreaction product obtained is neutralized with triethylamine.

EXAMPLE V

The procedure of Example U is repeated in successive runs substituting for the polyester there used 120 grams of each of the polyesters of Examples B to E and G to L.

EXAMPLE W

The procedure of Example U is followed except that 120 grams of the polyester of Example K is substituted for the polyester of Example F and 100 grams of a 60%

solution in xylene of a linseed oil-modified glycerol phthalate is substituted for the alkyd solution there used.

EXAMPLE X

The procedure of Example T is repeated except that 100 grams of a 50% solution of a butylated dimethylolurea is substituted for the melamine resin.

EXAMPLE Y

The procedure of Example T is repeated except that 100 grams of a 45% solution of N,N'-diisopropoxymethyl-imidazolidinone-2 is substituted for the melamine resin.

EXAMPLE Z

The procedure of Example U is repeated substituting 100 grams of a 60% solution in xylene of a butylated polymethylol-N,N-dimethylmelamine.

IV. Stabilization of fabrics

EXAMPLE 1

(*a*) A wool flannel as described above is impregnated with an aqueous dispersion obtained from the ammonia-neutralized product of Example P diluted with water to a 5% solids concentration at a wet pick-up of about 50% on the weight of the fibers. Heating for 10 minutes at 250° F. dries and cures the condensate on the fabric. The fabric carries 2.5% of the condensate and after the five-hour wash shows a shrinkage of 2%. The untreated control fabric shows 42% shrinkage.

(*b*) The same procedure using a concentration of 10% applies 5% condensate and the fabric obtained has zero shrinkage.

EXAMPLE 2

(*a*) A wool flannel as described above is impregnated with an aqueous dlispersion obtained from the ammonia-neutralized product of Example T diluted to 5% solids concentration. Heating for 10 minutes at 250° F. dries and cures the condensate on the fabric. The fabric carries 2.5% of the condensate and after the five-hour wash shows a shrinkage of 16%. The untreated control fabric shows 45% shrinkage.

(*b*) The same procedure using a concentration of 10% applies 5% condensate and the fabric obtained has 4% shrinkage.

EXAMPLE 3

(*a*) By separately repeating the procedure of Example 1(*a*) with each of the condensates of Examples M, N, O, Q, R, and S with a knitted woolen fabric, which untreated shows a shrinkage of 63%, shrinkages in the treated fabrics are obtained which range from 3 to 12%.

(*b*) By separately repeating the procedure of Example 1(*b*) with each of the condensates of Examples M, N, O, Q, R, and S with a knitted woolen fabric, which untreated shows a shrinkage of 63%, shrinkages in the treated fabrics are obtained which range from zero to 4%.

EXAMPLE 4

(*a*) The procedure of Example 2(*a*) is repeated separately with a fabric as defined in Example 2(*a*) using the condensates of Examples U, V, W, X, Y, and Z. The untreated fabric shows a shrinkage of 53%. The treated fabrics show shrinkages in the range of 5% to 15%.

(*b*) By repeating the procedure of part (*a*) hereof with dispersions containing 10% of the respective condensates, the treated fabrics show shrinkages in the range from 1 to 5%.

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.

I claim:

1. As an article of manufacture, a textile material containing protein fibers modified by 0.7 to 8% by weight of an insoluble product obtained by the heating of an impregnant thereon comprising a salt of a member selected from the group consisting of ammonium hydroxide, volatile amines, and quaternary ammonium hydroxides with a condensation product of 40 to 60 parts by weight of an organic solvent-soluble (C_3–C_6) alkylated condensate of formaldehyde with a compound selected from the group consisting of urea, thiourea, imidazolidinone-2, acetoguanamine, benzoguanamine, melamine, and mono- and di-(C_1–C_4)alkylmelamines with 40 to 60 parts by weight of a polyester having an average molecular weight of about 800 to 1500 containing hydroxyl groups, free carboxyl groups, and an acid number between about 90 and about 100, the polyester being a condensation product of an aromatic member selected from the group consisting of o-phthalic acid, o-phthalic acid containing lower alkyl substituents in the ring and their anhydrides with a condensation product selected from the group consisting of (*a*) polyesters having an acid value of not over 10 and obtained from the condensation of a mixture of at least one dibasic aliphatic acid having 5 to 10 carbon atoms with a polyol material containing at least 25 mole percent of at least one polyol containing at least three hydroxyl groups, the proportions in the mixture being in the range of 1.2 to 1.8 moles of polyol to each mole of acid, and (*b*) polyesters as obtained in (*a*) but modified by condensation with a fatty acid having 8 to 30 carbon atoms; the proportion of the aromatic member to the total polyol materials being in the range of 2 to 3.5 moles of the former for each 3 moles of the latter.

2. An article of manufacture as defined in claim 1 in which said polyol consists entirely of one or more polyols having at least three hydroxyl groups.

3. An article of manufacture as defined in claim 1 in which said polyol is trimethylolethane.

4. An article of manufacture as defined in claim 1 in which said polyol is pentaerythritol.

5. An article of manufacture as defined in claim 1 in which said polyol is glycerol.

6. An article of manufacture as defined in claim 1 in which said polyol is trimethylolethane and the dibasic aliphatic acid is adipic acid.

7. An article of maufacture as defined in claim 1 in which said polyol is trimethylolethane and the dibasic aliphatic acid is sebacic acid.

8. An article of manufacture as defined in claim 1 in which said polyol is trimethylolethane and the dibasic aliphatic acid is adipic acid and the polyester is modified by lauric acid.

9. An article of manufacture as defined in claim 1 in which said polyol is trimethyolethane and the dibasic aliphatic acid is adipic acid and the polyester is modified by the acid of soybean oil.

10. An article as defined in claim 1 in which the textile material contains wool fibers.

11. As an article of manufacture, a textile material containing protein fibers modified by 0.7 to 8% by weight of an insoluble product obtained by the heating of an impregnant thereon comprising a salt of a member selected from the group consisting of ammonium hydroxide, volatile amines, and quaternary ammonium hydroxides with the condensation product of 50 parts by weight of the reaction product of an alkyd and an organic solvent-soluble (C_3–C_6)alkylated condensate of formaldehyde with a compound selected from the group consisting of urea, thiourea, imidazolidinone-2, acetoguanamine, benzoguanamine, melamine, and mono- and di-(C_1–C_4)alkylmelamines with 40 to 60 parts by weight of a polyester having an average molecular weight of about 800 to 1500 containing hydroxyl groups, free carboxyl groups, and an acid number between about 90 and about 100.

12. As an article of manufacture, a textile material containing protein fibers modified by 0.7 to 8% by weight of an insoluble product obtained by the heating of an impregnant thereon comprising a salt of a member selected from the group consisting of ammonium hydroxide, volatile amines, and quaternary ammonium hydroxides with a condensation product of (A) a polyester having an average molecular weight of about 800 to 1500

containing hydroxyl groups, free carboxyl groups, and an acid number between about 90 and about 100, the polyester being a condensation product of an aromatic member selected from the group consisting of o-phthalic acid, o-phthalic acid containing lower alkyl substituents in the ring and their anhydrides with a condensation product selected from the group consisting of (*a*) polyesters having an acid value of not over 10 and obtained from the condensation of a mixture of at least one dibasic aliphatic acid having 5 to 10 carbon atoms with a polyol material containing at least 25 mole percent of at least one polyol containing at least three hydroxyl groups, the proportions in the mixture being in the range of 1.2 to 1.8 moles of polyol to each mole of acid, and (*b*) polyesters as obtained in (*a*) but modified by condensation with a fatty acid having 8 to 30 carbon atoms; the proportion of the aromatic member to the total polyol material being in the range of 2 to 3.5 moles of the former for each 3 moles of the latter, (B) an organic solvent-soluble (C_3–C_6)alkylated condensate of formaldehyde with a compound selected from the group consisting of urea, thiourea, imidazolidinone-2, acetoguanamine, benzoguanamine, melamine, and mono- and di-(C_1–C_4)alkylmelamines, and (C) an alkyd.

13. An article of manufacture as defined in claim 12 in which the condensation product is formed of 40 to 60 parts of Component A for each 50 parts of the condensation product of Components B and C and the latter condensation product is formed of about 20 to 30 parts of B to 20 to 30 parts of C.

14. As an article of manufacture, a textile material containing protein fibers modified by 0.7 to 8% by weight of an insoluble product obtained by the heating of an impregnant thereon comprising a salt of a member selected from the group consisting of ammonium hydroxide, volatile amines, and quaternary ammonium hydroxides with a condensation product of 50 parts by weight of the reaction product of an alkyd and an organic solvent-soluble (C_3–C_6)alkylated condensate of formaldehyde with a compound selected from the group consisting of urea, thiourea, imidazolidinone-2, acetoguanamine, benzoguanamine, melamine, and mono- and di-(C_1–C_4)alkylmelamines with 40 to 60 parts by weight of a polyester having an average molecular weight of about 800 to 1500 containing hydroxyl groups, free carboxyl groups, and an acid number between about 90 and about 100, the polyester being a condensation product of an aromatic member selected from the group consisting of o-phthalic acid, o-phthalic acid containing lower alkyl substituents in the ring and their anhydrides with a condensation product selected from the group consisting of (*a*) polyesters having an acid value of not over 10 and obtained from the condensation of a mixture of at least one dibasic aliphatic acid having 5 to 10 carbon atoms with a polyol material containing at least 25 mole percent of at least one polyol containing at least three hydroxyl groups, the proportions in the mixture being in the range of 1.2 to 1.8 moles of polyol to each mole of acid, and (*b*) polyesters as obtained in (*a*) but modified by condensation with a fatty acid having 8 to 30 carbon atoms; the proportion of the aromatic member to the total polyol material being in the range of 2 to 3.5 moles of the former for each 3 moles of the latter.

15. An article of manufacture as defined in claim 14 in which the salt is a quaternary ammonium salt.

16. An article of manufacture as defined in claim 14 in which the salt is an ammonium salt.

17. An article of manufacture as defined in claim 14 in which the salt is an amine salt.

18. An article of manufacture as defined in claim 14 in which the salt is a triethylamine salt.

19. An article of manufacture as defined in claim 18 in which the polyol is trimethylolethane and the dibasic aliphatic acid is adipic acid and the polyester is modified by lauric acid.

20. An article of manufacture as defined in claim 19 in which the aminoplast is a butylated polymethylol-melamine and the alkyd is a coconut oil-modified glycerol phthalate.

21. An article of manufacture as defined in claim 18 in which the polyol is trimethylolethane, the dibasic acid is adipic acid, the polyester is modified by soybean oil acids, the alkyd is a linseed oil-modified glycerol phthalate, and the aminoplast is a butylated polymethylol-melamine.

22. A process for treating proteinaceous textile materials to reduce the shrinkage thereof comprising impregnating such a material with an aqueous dispersion containing about 1.5 to 15% by weight of a salt of a member selected from the group consisting of ammonium hydroxide, volatile amines, and quaternary ammonium hydroxides with a condensation product of 40 to 60 parts by weight of an organic solvent-soluble (C_3–C_6)alkylated condensate of formaldehyde with a compound selected from the group consisting of urea, thiourea, imidazolidinone-2, acetoguanamine, benzoguanamine, melamine, and mono- and di-(C_1–C_4)alkylmelamines with 40 to 60 parts by weight of a polyester having an average molecular weight of about 800 to 1500 containing hydroxyl groups, free carboxyl groups, and an acid number between about 90 and about 100, the polyester being a condensation product of an aromatic member selected from the group consisting of o-phthalic acid, o-phthalic acid containing lower alkyl substituents in the ring and their anhydrides with a condensation product selected from the group consisting of (*a*) polyesters having an acid value of not over 10 and obtained from the condensation of a mixture of at least one dibasic aliphatic acid having 5 to 10 carbon atoms with a polyol material containing at least 25 mole percent of at least one polyol containing at least three hydroxyl groups, the proportions in the mixture being in the range of 1.2 to 1.8 moles of polyol to each mole of acid, and (*b*) polyesters as obtained in (*a*) but modified by condensation with a fatty acid having 8 to 30 carbon atoms; the proportion of the aromatic member to the total polyol material being in the range of 2 to 3.5 moles of the former for each 3 moles of the latter, drying and heating the treated textile at a temperature of 212° to 700° F. for a period of about 5 seconds to about 30 minutes but insufficient to damage the fabric.

23. A process as defined in claim 22 in which the textile material contains wool fibers.

24. A process for treating proteinaceous textile materials to reduce the shrinkage thereof comprising impregnating such a material with an aqueous dispersion containing about 1.5 to 15% by weight of a salt of a member selected from the group consisting of ammonium hydroxide, volatile amines, and quaternary ammonium hydroxides with the condensation product of 50 parts by weight of the reaction product of an alkyd and an organic solvent-soluble (C_3–C_6)alkylated condensate of formaldehyde with a compound selected from the group consisting of urea, thiourea, imidazolidinone-2, acetoguanamine, benzoguanamine, melamine, and mono- and di-(C_1–C_4)alkylmelamines with 40 to 60 parts by weight of a polyester having an average molecular weight of about 800 to 1500 containing hydroxyl groups, free carboxyl groups, and an acid number between about 90 and about 100, drying and heating the treated textile at a temperature of 212° to 700° F. for a period of about 5 seconds to about 30 minutes but insufficient to damage the fabric.

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