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PROCESS FOR DURABLY SECURING FABRIC IN A DESIRED CONFIGURATION

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ABSTRACT OF THE DISCLOSURE

Washable, durable press keratinous fiber-containing fabrics are prepared by the steps of subjecting the fabric to a polymeric external stabilization operation, treating the stabilized fabric with a reducing agent, securing the fabric in a desired configuration, and subjecting the fabric to the action of an aldehyde or reactive ketone to set the fabric in the selected configuration.

This invention relates to keratinous fiber-containing fabrics which have a propensity to durably conform to a preselected configuration, and more specifically, to wool fabrics having creases which are durable to home laundering operations.

Garments containing creases which are durable to home laundering operations are known to the art. Garments prepared from cellulosic fiber-containing fabrics having home laundry durable creases set therein have recently found wide acceptance in the textile industry. Cellulosic garments of the aforementioned types and the methods for their preparation are set forth in U.S. Patent No. 2,974,432. A satisfactory process for the preparation of durable creases in wool fabrics which will withstand home laundering operations, however, has not heretofore been found. The problems which are inherent in preparing wool fabrics which are durable to home laundering operations are readily apparent, that is to say, the propensity of wool fabrics to shrink as well as the fact that harsh stabilizing techniques will destroy the hand and other aesthetic properties which are responsible for making wool a premium fabric. A certain amount of success has been achieved by setting blends of thermoplastic fibers and wool fibers by means of pressing the fabric at temperatures near the melting point of the thermoplastic fiber. While such a process will produce a crease which has a certain degree of durability to home laundering operations, the setting operation destroys the desirable hand and surface effects of the fabric.

It is therefore an object of this invention to provide a process for the preparation of a keratinous fiber-containing fabric having a propensity to durably conform to a preselected configuration, the preselected configuration being durable to home laundering operations.

It is another object of this invention to provide a process for the preparation of an all-wool keratinous fiber-containing fabric having a propensity to durably conform to a preselected configuration, the preselected configuraton being durable to home laundering operations.

It is still another object of this invention to provide a keratinous fiber-containing fabric which has a propensity to durably conform to a preselected configuration, the preselected configuration being durable to home laundering operations.

In accordance with this invention, it has now been discovered that a keratinous fiber-containing fabric having a preselected configuration which is durable to home laundering operations may be obtained by means of a multistep process involving external stabilization of the keratious fiber, internal reformation of the keratinous fiber and permanent setting of the internally reformed keratinous fiber in its final configuration. The preselected configurations which are contemplated herein are pleats, creases and texturing effects such as pebble textures and the like.

The external setting of the keratinous fiber is preferably accomplished by means of a chemical reagent which is capable of reacting with keratin so as to produce new linkages. It should be understood, however, that the external stabilization of the keratinous fiber may also be accomplished by means of coating the fibers with a nonreactive coating compositions so as to secure the fibers in the desired configuration by means of the mechanical forces exerted by the coating. While the preferred external setting medium is a medium of the type which produces new chemical bonds by reacting with a keratin fiber, the only prerequisite for this type of reagent is that at least some of the new chemical bonds be formed on the surface of the keratinous fiber, that is to say chemical bonds may be formed internally and externally but at least some bonds must be formed on the surface of the fiber. Systems which have been found to be especially suitable for the external stabilization of this invention are interfacial polymerization such as polyhexamethylene sebacate interfacial polymerization, treatments with reactive terpolymers based on vinyl type monomers, treatments with polyepoxide-polyamine compositions, treatments with acid colloidal dispersions of melamine formaldehyde, treatments with reactive polyurethanes and treatments with emulsions of certain acrylic esters such as, for instance, polymethylmethacrylate, polyethylmethacrylate, polypropylmethacrylate, and polybutylmethacrylate.

The most preferred external stabilizing agents for purposes of this invention are isocyanate reaction products. Among the isocyanate reaction products which may be employed are isocyanate reaction products selected from two general catagories, the first of which is a urethane prepared from a polyfunctional isocyanate and a polymeric polyhydroxy compound and the second of which is the reaction product of a polyfunctional isocyanate and polymeric polyfunctional compound selected from the group consisting of polyesters, polyamides, polyepoxides and reaction products of phenol and alkanol oxides, formaldehyde resins, hydrogenation products of olefin-carbon monoxide copolymers and polyepihalohydrins. It should be understood that the isocyanate reaction products may be applied to the fabric as a single solution in pre-polymer form or in separate two-step applications forming the isocyanate on the fabric in situ.

By "pre-polymer" herein is meant the reaction products of the polyfunctional isocyanate and the preselected second polymeric compound carried to an extent below which a gel is produced which is insoluble in one of the organic solvents for each of the two reaction compounds and particularly the chlorinated hydrocarbons.

Among the suitable isocyanates that may be used in accordance with this invention are included aryl diisocyanates such as a 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, p-phenylene diisocyanate, 1,5-naphthylene diisocyanate, m-phenylene diisocyanate, diphenyl-4,4'-diisocyanate, azobenzene-4,4'-diisocyanate, diphenylsulphone - 4,4' - diisocyanate, 1-isopropylbenzene-3, 5-diisocyanate, 1 - methyl - phenylene-2,4-diisocyanate, naphthylene - 1,4 - diisocyanate, diphenyl-4,4'-diisothiocyanate and diisocyanate, benzene-1, 2,4-triisothiocyanate, 5-nitro-1,3-phenylene diisocyanate, xylylene-1,4-diisocyanate, xylylene-1,3-diisocyanate, 4,4'-diphenylenemethane diisocyanate, 4,4' - diphenylenepropane diisocyanate and xylylene-1,4-diisothiocyanate and the like; alicyclic diisocyanates, such as dicyclohexamethane-4,4'-diisocyanate and the like; alkylene diisocyanates such as tetramethylene diisocyanate, hexamethylene diisocyanate and the like, as well as mixtures thereof and including the equivalent isothiocyanates. Of these compounds, the aryl diisocyanates are preferred because of their solubility and availability.

Additional isocyanates include polymethylene diisocyanate and diisothiocyanates, such as ethylene diisocyanate, dimethylene diisocyanate, dodecamethylene diisocyanate, hexamethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, and the corresponding diisothiocyanates; alkylene diisocyanates and diisothiocyanates such as propylene-1,2-diisocyanate, 2,3-dimethyltetramethylene diisocyanate and diisothiocyanate, butylene-1,2-diisocyanate, butylene-1,3-diisothiocyanate, and butylene-1,3-diisocyanate; alkylidene diisocyanates and diisothiocyanates such as ethylidene diisocyanate

$$(CH_3CH(NCO)_2)$$

and heptylidene diisothiocyanate

$$(CH_3(CH_2)_5CH(CNS)_2)$$

cycloalkylene diisocyanates and diisothiocyanates such as 1,4-diisocyanatocyclohexane, cyclopentylene-1,3-diisocyanate, and cyclohexylene-1,2-diisothiocyanate; aromatic polyisocyanates and polyisothiocyanates such as aliphatic-aromatic diisocyanates and diisothiocyanates such as phenylethylene diisocyanate ($C_5H_6CH(NCO)CH_2NCO$); diisocyanates and diisothiocyanates containing heteroatoms such as $SCNCH_2OCH_2NSCSCNCH_2CH_2OCH_2CH_2NSC$, and $SCN(CH_2)_3$—S—$(CH_2)_3NSC$; 1,2,3,4-tetraisocyanatobutane, butane-1,2,2-triisocyanate, tolylene-2,4,6-triisocyanate, tolylene-2,3,4-triisocyanate, benzene-1,3,5-triisocyanate, benzene-1,2,3-triisocyanate, 1-isocyanato-4-isothiocyanatohexane, and 2-chloro-1,3-diisocyanatopropane.

The preferred diisocyanates, diisothiocyanates and mixed isocyanate-isothiocyanates have the general formula ZCN—R—NCZ in which R is a divalent hydrocarbon radical, preferably aryl, and Z is a chalcogen of atomic weight less than 33. For availability, tolylene-2,4-diisocyanate is preferred.

By "polymeric polyhydroxy compound" is meant a linear long-chain polymer having terminal hydroxyl groups including branched, polyfunctional polymeric hydroxy compounds as set forth below. Among the suitable polymeric polyhydroxy compounds, there are included polyether polyols such as polyalkyleneether glycols, and polyalkylenearyleneether-thioether glycols and polyalkyleneether triols. Polyalkyleneether glycols and triols are preferred. Mixtures of these polyols may be used when desired.

The polyalkyleneether glycols may be represented by the formula $HO(RO)_nH$, wherein R is an alkylene radical which need not necessarily be the same in each instance and *n* is an integer. Representative glycols include polyethyleneether glycol, polypropyleneether glycol, polytrimethyleneether glycol, polytetramethyleneether glycol, polypentamethyleneether glycol, polydecamethyleneether glycol, polytetramethyleneformal glycol and poly-1,2-dimethylethyleneether glycol. Mixtures of two or more polyalkyleneether glycols may be employed if desired.

Representative polyalkyleneether triols are made by reacting one or more alkylene oxides with one or more low molecular weight aliphatic triols. The alkylene oxides most commonly used have molecular weights between about 44 and 250. Examples include: ethylene oxide; propylene oxide; butylene oxide; 1,2-epoxybutane; 1,2-epoxyhexane; 1,2-epoxyoctane; 1,2-epoxyhexadecane; 2,3-epoxybutane; 3,4-epoxyhexane; 1,2-epoxy-5-hexene; and 1,2-epoxy-3-butane, and the like. Ethylene, propylene, and butylene oxides are preferred. In addition to mixtures of these oxides, minor proportions of alkylene oxides having cyclic substituents may be present, such as styrene oxide, cyclohexene oxide, 1,2-epoxy-2-cyclohexylpropane, and a-methyl styrene oxide. The aliphatic triols most commonly used have molecular weights between about 92 and 250. Examples include glycerol, 1,2,6-hexanetriol;1,1,1-trimethylolpropane; 1,1,1-trimethylolethane; 2,4-dimethylol-2-methylol-pentanediol-1,5 and the trimethylether of sorbitol.

Representative examples of the polyalkyleneether triols include: polypropyleneether triol (M.W. 700) made by reacting 608 parts of 1,2-propyleneoxide with 92 parts of glycerine; polypropyleneether triol (M.W. 1535) made by reacting 1401 parts of 1,2-propyleneoxide with 134 parts of trimethylolpropane; polypropyleneether triol (M.W. 2500) made by reacting 2366 parts of 1,2-propyleneoxide with 134 parts of 1,2,6-hexanetriol; and polypropyleneether triol (M.W. 6000) made by reacting 5866 parts of 1,2-propyleneoxide with 134 parts of 1,2,6-hexanetriol.

Additional suitable polytriols include polyoxypropylene triols, polyoxybutylene triols, Union Carbide's Niax triols LG56, LG42, LG112 and the like; Jefferson Chemical's Triol G–4000 and the like; Actol 32–160 from National Aniline and the like.

The polyalkylene-aryleneether glycols are similar to the polyalkyleneether glycols except that some arylene radicals are present. Representative arylene radicals include phenylene, naphthalene and anthracene radicals which may be substituted with various substituents, such as alkyl groups. In general, in these glycols there should be at least one alkyleneether radicals having a molecular weight of about 500 for each arylene radicals which is present.

The polyalkyleneether-thioether glycols and the polyalkylenearyleneether glycols are similar to the above-described polyether glycols, except that some of the ether-oxygen atoms are replaced by sulfur atoms. These glycols may be conveniently prepared by condensing together various glycols, such as thiodiglycol, in the presence of a catalyst, such as p-toluene-sulfonic acid.

By "polymeric polyfunctional compound" is meant a long-chain polymer of the types described containing at least two groups having at least one active hydrogen atom as determined by the Zerewitinoff method. In the process of this invention, there may be utilized such compounds as polyesters, polyamides, polyepoxides, reaction products of phenols and alkylene oxides, formaldehyde resins, hydrogenation products of olefin-carbon monoxide copolymers, and polyepihalohydrins.

The polyesters suitable for use in accordance with this invention are well known and are generally prepared by conducting a condensation reaction between an excess of a monomeric or polymeric polyhydroxy compound and a polyacid or by esterifying a hydroxy substituted acid and a polyhydroxyl alcohol.

Among the suitable acids there are included the alkane dibasic acids, alkene dibasic acids, cycloalkene dibasic acids, cycloalkane dibasic acids, aryl dibasic acids, or any of the foregoing types wherein the hydrocarbon radical is substituted with an alkyl, alkenyl, cycloalkyl, cycloalkenyl or aryl radical.

Representative dibasic carboxylic acids which can be employed for reaction with polyols in preparation of polyesters for use in accordance with this invention include the following: succinic; monomethyl succinic; glutaric; adipic; pimelic; suberic; azelaic; sebacic; brassylic; thapsic; 6-oxoundecanedioic; octadecanedoic; 8-octadecenedioic; eicosanedioic; 6,8-octadecadienedioc; malic; and the like. Other acids include: unsaturated acids such as maleic, fumaric, glutaconic, and itaconic; the cycloalkane dicarboxylic acids as cyclopentane-1,2-dicarboxylic and cyclopentane-1,3-dicarboxylic; aromatic dicarboxylic acids such as phthalic, isophthalic, terephthalic, naphthalene-1,2 - dicarboxylic, naphthalene - 1,3 - dicarboxylic, naphthalene-1,4-dicarboxylic, naphthalene-1,5-dicarboxylic, naphthalene-1,8-dicarboxylic, diphenyl-2,2′-dicarboxylic, diphenyl-4,4′-dicarboxylic and diphenyl-2,4′-dicarboxylic; and aliphatic-aromatic dicarboxylic acids such as 2,6-dimethylbenzene-1,4-dicarboxylic acid, and 4,5-dimethylbenzene - 1,2 - dicarboxylic acid; and the like. Natural products which are particularly useful include castor oil, which comprises a glyceride of recinoleic acid, and recinoleyl alcohol, and mixtures thereof.

Representative monomeric polyols for reaction with the above acids for the production of polyesters for use in accordance with this invention include the polyalkyleneether glycols represented by the formula $HO(RO)_nH$, wherein R is an alkylene radical which need not necessarily be the same in each instance and n is an integer. Representative glycols include polyethyleneether glycol, polypropyleneether glycol, polytrimethyleneether glycol, polytetramethyleneether glycol, polymethyleneether glycol, polydecamethyleneether glycol, polytetramethyleneformal glycol and poly-1,2-dimethyleneether glycol. Mixtures of two or more polyalkyleneether glycols may be employed if desired.

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Additional polyesters include those obtained by reacting one or more of the above acids with a mixture of polyhydric alcohols comprising (1) polyhydric alcohols of the general formula:

$$\left(\text{H}\!-\!(\text{O}\!-\!\text{alkylene})_z\right)(\text{R})\text{N}\!-\!\text{alkylene}\!-\!\text{N}\left(\text{alkylene}\!-\!\text{O})_{+}\!-\!\text{H}\right)\left((\text{alkylene}\!-\!\text{O})_y\!-\!\text{H}\right)$$

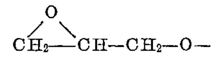
wherein alkylene means a divalent saturated aliphatic radical having at least 2 carbon atoms, preferably not more than 5 carbon atoms, x, y and z are whole numbers and the sum of x, y and z is from 3 to 10, preferably from 3 to 6, at least two of the—$(\text{alkylene-O})_{x,y,z}$H groups contain primary alcoholic hydroxyl groups and R is a large alkyl group containing from 10 to 25 carbon atoms, and (2) polyhydric alcohols containing only carbon, hydrogen and oxygen, and the polyhydric alcohols from (1) and (2) are employed in such proportions that from 1 to 15 alcoholic OH groups are contributed by (1) for every 10 alcoholic OH groups contributed by (2).

The polyepoxides used in accordance with the invention are organic compounds having at least two epoxy groups per molecule and may be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic and may be substituted with non-interfering substituents such as hydroxyl groups, ether radicals, and the like. Polyepoxides containing ether groups, generally designated as polyepoxide polyethers, may be prepared as well known in the art by reacting a polyol with a halogen-containing epoxide employing at least 2 moles of the halogen-containing epoxide per mole of polyol. Thus, for example, epichlorohydrin may be reacted with a polyhydric phenol in an alkaline medium. In another technique the halogen-containing epoxide is reacted with a polyhydric alcohol in the presence of an acid-acting catalyst such as hydrofluoric acid or boron trifluoride and the product is then reacted with an alkaline compound to effect a dehydrohalogenation. A preferred example of the halogen-containing epoxide is epichlorohydrin; others are epibromohydrin, epiodohydrin, 3-chloro-1,2-epoxybutane, 3-bromo-1,2-epoxyhexane, and 3-chloro-1,2-epoxy-octane. Illustrative examples of polyepoxide polyethers are as follows:

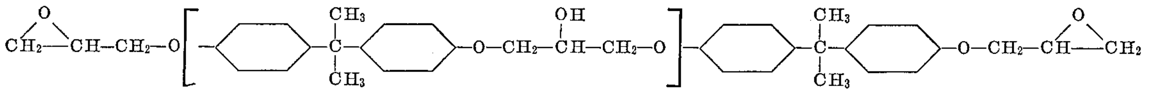
1,4 - bis(2,3-epoxypropoxy)benzene; 1,3-bis(2,3-epoxypropoxy)benzene; 4,4′ - bis(2,3 - epoxypropoxy)diphenyl ether; 1,8 - bis(2,3 - epoxypropoxy)octane; 1,4 - bis(2,3-epoxypropoxy)cyclohexane; 4,4′ - bis(2 - hydroxy - 2,4-epoxybutoxy)diphenyl dimethylmethane; 1,3 - bis(4,5-epoxypentoxy) - 5 - chlorobenzene; 1,4 - bis(3,4 - epoxybutoxy) - 2 - chlorohexane; diglycidyl thioether; diglycidyl ether; ethylene glycol diglycidyl ether; propylene glycol diglycidyl ether; diethylene glycol diglycidyl ether; resorcinol diglycidyl ether; 1,2,3,4-tetrais (2-hydroxy-3,4-epoxybutoxy)butane; 2,2 - bis(2,3-epoxypropoxyphenyl) propane; glycerol triglycidyl ether; mannitol tetraglycidyl ether; pentaerythritol tetraglycidyl ether; sorbitol tetraglycidyl ether; glycerol di-glycidyl ether; etc. It is evident that the polyepoxide polyethers may or may not contain hydroxy groups, depending primarily on the proportions of halogen-containing epoxide and polyol employed. Polyepoxide polyethers containing polyhydroxyl groups may also be prepared by reacting, in known manner, a polyhydric alcohol or polyhydric phenol with a polyepoxide in an alkaline medium. Illustrative examples are the reaction product of glycerol and di-glycidyl ether, the reaction product of sorbitol and bis(2,3-epoxy-2-methylpropyl)ether, the reaction product of pentaerythritol and 1,2,3,5-diepoxy pentane, the reaction product of 2,2,-bis (parahydroxyphenyl)propane and bis(2,3 - epoxy - 2-methylpropyl)ether, the reaction product of resorcinol and diglycidyl ether, the reaction product of catechol and diglycidyl ether, and the reaction product of 1,4-dihydroxy-cyclohexane and diglycidyl ether.

Polyepoxides which do not contain ether groups may be employed as for example 1,2,5,6-diepoxyhexane; butadiene dioxide (that is, 1,2,3,4-diepoxybutane); isoprene dioxide; limonene dioxide.

For use in accordance with the invention, we prefer the polyepoxides which contain ether groups, that is, polyepoxide polyethers. More particularly we prefer to use the polyepoxide polyethers of the class of glycidyl polyethers of polyhydric alcohols or glycidyl polyethers of polyhydric phenols. These compounds may be considered as being derived from a polyhydric alcohol or polyhydric phenol by etherification with at least two glycidyl groups—



The alcohol or phenol moiety may be completely etherified or may contain residual hydroxy groups. Typical examples of compounds in this category are the glycidyl polyethers of glycerol, glycol, diethylene glycol, 2,2-bis (parahydroxyphenyl) propane, or any of the other polyols listed hereinabove as useful for reaction with halogen-containing epoxides. Many of the specific glycidyl polyethers derived from such polyols are set forth hereinabove. Particularly preferred among the glycidyl polyethers are those derived from 2,2-bis(parahydroxyphenyl) propane and those derived from glycerol. The compounds derived from the first-named of these polyols have the structure—



wherein n varies between zero and about 10, corresponding to a molecular weight about from 350 to 8,000. Of this class of polyepoxides it is preferred to employ those compounds wherein n has a low value, i.e., less than 5, most preferably where n is zero.

In commerce, the polyepoxide polyethers are conventionally termed as epoxy resins even though the compounds are not technically resins in the state in which they are sold and employed because they are of relatively low molecular weight and thus do not have resinous properties as such. It is only when the compounds are cured that true resins are formed. Thus it will be found that manufacturer's catalogs conventionally list as epoxy resins such relatively low-molecular weight products as the diglycidyl ether of 2,2-bis(parahydroxyphenyl)propane, the diglycidyl ether of glycerol, and similar polyepoxide polyethers having molecular weights substantially less than 1,000.

It is within the purview of the invention to employ mixtures of different polyepoxides. Indeed, it has been found that especially desirable results are attained by employing mixtures of two commercially-available polyepoxides, one being essentially a diglycidyl ether of glycerol, the other being essentially a diglycidyl ether of 2,2-bis (parahydroxyphenyl) propane. Particularly preferred to attain such result are mixtures containing more than 1 and less than 10 parts by weight of the glycerol diglycidyl ether per part by weight of the diglycidyl ether of 2,2-bis(parahydroxyphenyl) propane.

The polyamides used in accordance with the invention are those derived from polyamines and polybasic acids. Methods of preparing these polyamides by condensation of polyamines and polycarboxylic acids are well known in the art. One may prepare polyamides containing free amino groups or free carboxylic acid groups or both free amino and free carboxylic acid groups. The polyamides may be derived from such polyamines as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, 1,4-diaminobutane, 1,3-diaminobutane, hexamethylene diamine, 3-(N-isopropylamino)propylamine, 3,3'-imino-bispropylamine, and the like. Typical polycarboxylic acids which may be condensed with the polyamines to form polyamides are glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, isophthalic acid, terephthalic acid, beta-methyl adipic acid, 1,2-cyclohexane dicarboxylic acid, malonic acid, polymerized fatty acids, and the like. Depending on the amine and acid constituents and the conditions of condensation, the polyamides may have molecular weights varying about from 1,000 to 10,000 and melting points about from 20–200° C. Particularly preferred for the purpose of the invention are the polyamides derived from aliphatic polyamines and polymeric fatty acids. Such products are disclosed for example by Cowan et al., U.S. Patent No. 2,450,940. Typical of these polyamides are those made by condensing ethylene diamine or diethylene triamine with polymeric fatty acids produced from the polymerization of drying or semi-drying oils, or the free acids, or simple aliphatic alcohol esters of such acids. The polymeric fatty acids may typically be derived from such oils as soybean, linseed, tung, perilla, oiticica, cottonseed, corn, tall, sunflower, safflower, and the like. As well known in the art, in the polymerization the unsaturated fatty acids combine to produce a mixture of dibasic and higher polymeric acids. Usually the mixture contains a preponderant proportion of dimeric acids with lesser amounts of trimeric and higher polymeric acids, and some residual monomeric acid. Particularly preferred are the polyamides of low melting point (about 20–90° C.) which may be produced by heating together an aliphatic polyamine, such as diethylenetriamine, triethylene tetramine, 1,4-diaminobutane, 1,3-diaminobutane, and the like with the polymerized fatty acids. Typical among these is a polyamide derived from diethylene triamine and dimerized soybean fatty acids. The polyamides derived from aliphatic polyamides and polymerized fatty acids, like the polyepoxides, are often referred to in the trade as resins even though not actually resins in the state in which they are sold and applied. Particularly good results are obtained in the use of low molecular weight, non-fiber forming polyamides sold under the trade name of Versamids.

Any suitable condensation product of a phenol and an alkylene oxide may be used such as, for example, the condensation product of cresol or 4,4'-isopropylidene-diphenol with one of the aforementioned alkylene oxides.

Any suitable formaldehyde resin may be used such as, for example, the condensation product of formaldehyde per se or a compound capable of yielding formaldehyde such as, for example, paraformaldehyde or reaction products thereof with the condensation products of alkylene oxides to prepare polyoxymethylene compounds having terminal hydroxyl groups.

Any suitable hydrogenation product of olefin-carbon monoxide copolymers may be used such as, for example, the hydrogenation product of an ethylene-propylene-carbon monoxide copolymer and others disclosed in U.S. Patent 2,839,478, issued to Wilms et al. June 17, 1958, and U.S. Patent 2,495,292, issued to Scott, Jan. 24, 1950.

In the process of this invention, it is preferred to react the polyfunctional isocyanates and polymeric polyfunctional compound or polyfunctional isocyanate and polymeric polyhydroxy compound as the case may be with or without a coreactant and unblocked or blocked with the keratinous fibers in the presence of a catalyst. Any of the well-known catalysts for the reaction of active hydrogen atoms with isocyanates may be used. Of these catalysts which are used in the production of polyurethanes the organo-tin compounds are preferred. Particularly stannous octoate.

The various isocyanate reaction product systems described above should be applied to the keratinous fiber containing fabric in the form of a solution, the solution employing a non-reactive solvent. By "non-reactive" as used herein is meant a solvent in which reactivity between the isocyanate and active-hydrogen containing components even in the presence of catalyst is substantially inhibited. Small amounts of reactive solvents may be present provided the amount present is sufficiently low as not to precipitate a substantial amount of the components with which it is reacted. In other words, sufficient components remain reactive with the keratin fibers to provide adequate inhibition of shrinkage and/or settability in the fabric or other structure being treated.

Suitable organic solvents include halogenated hydrocarbons such as trichloroethylene, methylene chloride, perchloroethylene, ethylene dichloride, chloroform and the like; aromatic solvents such as toluene, xylene, benzene, mixed aromatics, such as the Solvesso types and the like, n-butyl acetate, n-butyl ether, n-butyl phosphate, p-dioxane, ethyl oxalate, methyl isobutyl ketone, pyridine, quinoline, N,N-dimethylformamide, N,N-dimethylacetamide, 2,2,4-trimethylpentane and the like. Mixtures of solvents may be used.

The internal reformation of the keratinous fibers is preferably accomplished by means of a chemical reagent which has the ability to temporarily rupture polymeric linkages within the structure of keratin and then allow these linkages to reform when the keratinous fiber is in the desired configuration. The preferred chemical reagent for accomplishing the aforementioned splitting and reformation of polymeric linkages is a reducing agent. The reaction which appears to take place in setting the keratinous fibers in the new shape is reformation of the cystine linkages and reformation of hydrogen bonds of the keratinous fibers, the bonds and linkages having previously been split by contact with the reducing agent. The cystine linkages are split and reunited to form at least some of the disulfide bonds. While the keratinous fibers remain substantially unchanged chemically by the reduction and oxidation operations, some relocation of the cystine linkages apparently takes place along with some changes in hydrogen bonding. These changes in location of cystine linkages and changes in hydrogen bonding produce a reformed fiber. The reformation of the fiber gives the individual keratinous fibers of this invention their internal setting which results in a fabric which has stabilization to dimensional finish changes.

It should be understood that the objective of rupturing the characteristic linkages of keratin followed by a reformation of the linkages when the fiber is in the desired geometric configuration may be accomplished by the use of steam. Where, however, maximum setting of the keratinous fibers is desired a reducing agent should be employed. Among the suitable reducing agents, there are included lower alkanol amine sulfites such as monoethanolamine sulfite and isopropanolamine sulfites, and others containing up to about 8 carbon atoms in the alkyl chain, such as n-propanolamine sulfite, n-butanolamine sulfite, dimethylbutanolamine sulfite, dimethylhexanolamine sulfite and the like; metallic formaldehyde sulfoxylates, such as zinc formaldehyde sulfoxylate; the alkali metal sulfoxylates, such as sodium formaldehyde sulfoxylate and potassium formaldehyde sulfoxylate; the alkali metal borohydrides, such as sodium borohydride, potassium borohydride and sodium potassium borohydride; alkali metal sulfites, such as sodium or potassium bisulfite; sulfite, metabisulfite; ammonium bisulfite; sodium sulfide, sodium hydrosulfide; sodium hypophosphite, sodium thiosulfate, sodium dithionate, titanious chloride; sulfurous acid; mercaptan acids, such as thioglycollic acid and its water soluble salts, such as sodium, potassium or ammonium thioglycolate; mercaptans, such as hydrogen sulfide, alkyl mercaptans such as butyl or ethyl mercaptans and mercaptan glycols, such as β-mercapto ethanol; and mixtures of these reducing agents.

Beneficial results are often obtained if the reducing agent is employed in conjunction with a "low molecular weight polyhydroxy compound" or other auxiliary agent. Urea constitutes the most readily available and desirable auxiliary agent, although any other material which will swell keratinous fibers in an aqueous medium is suitable. For example, guanidine compounds such as the hydrochloride; formamide, N,N-dimethylformamide, acetamide, N,N-dimethylacetamide, thiourea, phenol, lithium salts, such as the chloride, bromide, and iodide and the like are similarly useful.

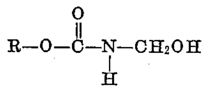
By the term "low molecular weight polyhydroxy compound" is meant a compound containing more than one hydroxy group and having a molecular weight preferably no greater than about 4000. Of these compounds, the most readily available and desirable compound, from the standpoint of ease of application, comprises ethylene glycol. A particularly preferred group of glycols includes the polyfunctional glycols having terminal hydroxyl groups separated by 2 to 10 methylene groups, including, of course, the preferred ethylene glycol as well as trimethylene glycol, tetramethylene glycol, pentamethylene glycol, hexamethylene glycol and decamethylene glycol, or such glycols as 1,2-propylene glycol, dipropylene glycol, 1,3-butylene glycol, diethylene glycol, polyethylene glycol or the like.

Polyfunctional compounds containing more than 2 hydroxyl groups include the polyfunctional alcohol glycerols such as glycerine and diethylglycerol as well as trimethylol ethane, trimethylol butane, tris-hydroxymethyl-amino methane and others. Glycol ethers, such as the water-soluble or dispersible polyethylene glycols or polypropylene glycols having molecular weights preferably no greater than about 4000 also provide satisfactory results when utilized in acordance with this invention.

The reducing agent with or without the auxiliary agent agent or polyhydroxy compound may be applied to the fabric in any desired amount, depending upon the degree of reducing desired. In general, optimum results are obtained when aqueous solutions containing from about 0.01 to about 20% by weight and most preferably from 1 to about 10% by weight of the reducing agent is applied to the fabric. The swelling agent or polyhydroxy compound if employed may be applied to the fabric by addition to the aqueous solution of reducing agent of amounts of from about 3 to about 30% and most preferably from about 5 to about 20% by weight. Higher concentrations may be utilized where the fabric is to be exposed to the treating medium for only a short time.

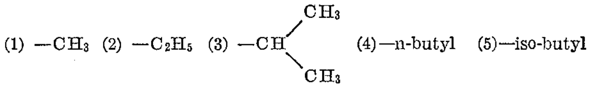
Subsequent to the external stabilization operation the fabric may be converted to a garment and the garment subjected to the reducing agent treatment. The conversion to a garment is preferable where the object of the process is to produce home laundering durable permanent creases. Where, however, a fabric having a durable texture effect such as a pebble effect is to be produced, the fabric need not of course be converted to a garment prior to application of the reducing agent. The mechanical steps of producing the texture effect, the crease and the pleats and the like may be carried out with any of the well-known existing pieces of textile finishing equipment. For the preparation of creases, however, a Hoffman press is preferred.

The final operation in the process of this invention is the aldehyde treatment of the externally stabilized internally reformed keratinous fiber. It should be understood that the aldehyde may be present in the reducing agent in the form of an organic compound which releases aldehyde on thermal decomposition or may be applied as a separate operation subsequent to the reducing agent treatment. The fabric must, however, be in its preferred configuration (creased or textured) prior to being subjected to the action of an aldehyde. Compounds which will release an aldehyde on thermal degradation are also suitable for separate application after the reducing agent treatment provided that the thus treated fabric must go through a final heating operation such as in a curing oven. Suitable compounds which release aldehydes on thermal degradation and which may be incorporated in the reducing agent solution for simultaneous application are compounds having the general formula:



$$R-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-CH_2OH$$

wherein R is a member selected from the group consisting of



$$(1)\ -CH_3\quad(2)\ -C_2H_5\quad(3)\ -CH(CH_3)_2\quad(4)\text{—n-butyl}\quad(5)\text{—iso-butyl}$$

when compounds of this type are incorporated in the reducing agent bath, the reducing must be of the type which will not undergo an organic reaction with the thermally degradated compound. For this reason it is preferred that an inorganic reducing agent be employed in conjunction with the thermally degradable compopnd.

Typical aldehydes which may be applied subsequent to application of a reducing agent include formaldehyde, saturated aliphatic aldehydes, such as acetaldehyde, propionaldehyde, butylaldehyde, isobutylaldehyde, valeraldehyde, isovaleraldehyde, caproaldehyde, enanthaldehyde, caprylaldehyde, pelargonaldehyde, capraldehyde, lauraldehyde, palmitic aldehyde, stearaldehyde and the like; unsaturated aliphatic aldehydes, such as acrolein, crotonaldehyde, tiglic aldehyde, citronellal, citral, propionaldehyde and the like; alicyclic monofunctional aldehydes, such as formylcyclohexane and the like; aliphatic dialdehydes, such as glyoxal, pyruvaldehyde, malonaldehyde, succinaldehyde, glutaraldehyde, adipaldehyde, maldealdehyde and the like; substituted aldehydes, such as chloral, aldol and the like; aromatic aldehydes wherein the aldehyde group is attached to a ring, such as benzaldehyde, phenylacetaldehyde, p-tolualdehyde, p-isopropylbenzaldehyde, o-chlorobenaaldehyde, o-nitrobenzaldehyde, m-nitrobenzaldehyde, p-nitrobenaaldehyde, salicylaldehyde, anisaldehyde, vanillin, veratraldehyde, piperolnal, α-naphthaldehyde, anthraldehyde and the like; and aromatic aldehydes wherein the aldehyde group is not attached to a ring, such as phenylacetaldehyde, cinnamaldehyde and the like; and heterocyclic aldehydes, such as α-formylthiophene, α-formylfurfural, furfural, tetrahydrofurfural and the like.

Typical aldehyde generating compounds suitable for application subsequent to but not simultaneously with application of the reducing agent include linear polymers, particularly those of the general formula $HO(CH_2O)_n \cdot H$ which depolymerize to monomeric formaldehyde gas upon vaporization. In this class of compounds, there are included lower polyoxymethylene glycols, wherein *n* is from about 2 to about 8; paraformaldehyde, wherein *n* ranges from about 6 to about 100; alphapolyoxymethylenes, wherein *n* is greater than about 100; beta-polyoxymethylene wherein *n* is greater than about 100 and a trace of H_2SO_4 is present, and the like.

Polyoxymethylene glycol derivatives may also be utilized, e.g., such as the polyoxymethylene diacetates, the lower polyoxymethylene dimethyl esters, gamma-polyoxymethylenes (higher polyoxymethylene dimethyl ethers), delta-polyoxymethylenes, epsilon-polyoxymethylenes and the like. In general, higher temperatures, e.g., up to about 200° C. are utilized to effect depolymerization of these derivatives. In many instances, depolymerization, with formaldehyde generation, is most readily effected by treatment with dilute alkali or acid to produce the corresponding glycol which can then be hydrolyzed to formaldehyde solution.

Formaldehyde acetate (formals) may also be utilized. Preferred formals are produced by reaction of formaldehyde with alcohols of the formula $CH_2(OR)_2$ in the presence of an acid catalyst, wherein R is alkyl or aralkyl. These compounds hydrolyze to formaldehyde and the parent alcohol. Preferred formals include methylal and 1,3-dioxolane. The latter compound hydrolyzes to formaldehyde and ethylene glycol and is particularly preferred among this class of compounds when used in presensitizing processes.

Additional suitable generating compounds include the various methylol compounds, for example, methylolalkanolamine sulfites, such as N-methylolethanolamine sulfite, N,N-dimethylolethanolamine sulfite, N,N-dimethylolisopropanolamine sulfite and the like; methylol amides, such as N-methylolformamide, N-methylolacetamide, N-methlolacrylamide and the like; amines, such as hexamethylene tetramine, trimethylolmelamine and the like; and compounds such as the alkali-metal formaldehyde bisulfites including sodium and potassium formaldehyde bisulfites.

The following specific examples of the process of this invention are given for purposes of illustration and should not be considered as limiting the spirit or scope of this invention.

EXAMPLE I

Into a jacketed stainless steel reactor is poured 225 lbs. of polypropylene glycol adduct of glycerine having a molecular weight of about 5,000. The reactor is then closed and the pressure therein reduced to about 10 mm. mercury after which the reactor is flushed with dry nitrogen. The pressure regulation and flushing operation is repeated for 3 cycles, after which 23 lbs. of dry toluene is poured into the reactor. A blanket of nitrogen gas is maintained in the vessel throughout the reaction. The pressure is again reduced to 10 mm. mercury and the reactor is heated to 140° C. to distill off the toluene, after which it is cooled to room temperature using cold water in the jacket around the reactor. The pressure is returned to room conditions. After stirring for 15 minutes to thoroughly mix the components about twice the stoichiometric quantities for reaction with the glycol of tolylene-2,4-diisocyanate is added rapidly and stirred until the heat of reaction ceases and the temperature has risen slowly up to 40–45° C. from room temperature of about 28° C. The reaction mix is then heated at a rate of about 2° C. per minute to a temperature of 146° C. where it is held for 18 minutes and then cooled at a rate of about 2° C. per minute to a maximum temperature of 100° F. Sufficient trichloroethylene is then added to provide a solution containing 70% of the resulting pre-polymer. The pre-polymer solution is then transferred from the reactor to a pre-dried drum under a dry nitrogen atmosphere to avoid water contamination. At the time of the transfer, the prepolymer solution has a color of from colorless to a very pale straw color.

A solution is then prepared from the 70% solution of prepolymer by dilution with additional trichloroethylene, the dilution being conducted to the point so that a pickup of 3.5% based on the dry weight of the fabric of prepolymer is picked up on the fabric. N,N,N',N'-tetrakis 2-hydroxy propyl ethylene diamine in the amount of about 3% of the weight of pure prepolymer is added to the bath. The solution is padded onto the wool fabric and the padded fabric is then placed in an oven at 160° F. for 5 minutes for drying and then placed in a second oven at 250° F. for 5 minutes for curing. The treated fabric is then scoured, dried and pressed. Trousers are then prepared from the urethane treated fabric. The trousers are sprayed with a 6.4% solution of monoisopropynolamine sulfite to a wet pickup of 40%, allowed to stand in the damp state for one hour and then creases are pressed in the trousers by means of a Hoffman press employing a 30 second top steam, a 30 second bake and a ten second vacuum. The trousers are then sprayed with a solution of 10% formaldehyde to a wet pickup of 40% and allowed to stand in the damp state for one hour before being dried. The creases and dimensional stability of the trousers are found to be durable to 10 washing cycles employing commercially available detergents and employing tumble drying cycles after each wash cycle.

EXAMPLE II

The procedure of Example I was again repeated with the exception that in place of the 70% solution of the prepolymer employed in Example I to effect the external stabilization, a "one shot" polyurethane external stabilization technique is employed. The "one shot" polyurethane solution is prepared as follows: Sufficient amount of the polypropylene glycol adduct of glycerine employed in Example I to prepare the prepolymer is added to the trichloroethylene pad bath so that pickup of 2.5% based on the dry weight of the fabric of polypropylene glycol adduct is effected. Sufficient methylene-p-phenyl diisocyanate is added so that a pickup of 0.5% based on the dry weight of the fabric of the diisocyanate is effected. A quantity of 8% zinc naphthenate solution is added amounting to 3% of the weight of polypropylene glycol adduct and employed diisocyanate. The solution is padded onto the fabric and process thereafter carried out substantially as set forth in Example I. The finished product is found to have a crease and dimensional stability which is durable to 10 washing cycles employing commercially available detergents and employing tumble drying cycles after each wash cycle.

EXAMPLE III

An all wool worsted flannel fabric is given the external stabilization treatment as set forth in Example I. The open width externally stabilized fabric is then padded with a solution containing 3% by weight sodium bisulfite and 17.5% by weight methylol methyl urethane and 0.2% by weight Deceresol OT. The treated fabric is dried at 175° F. and given a light press. The fabric is then fashioned into a pair of trousers, the trousers sprayed with water containing 0.2% Deceresol OT to a pickup of about 40% by weight based on the dry weight of the fabric. The treated fabric is then allowed to stand in the damp state for 30 to 60 minutes and then creases are pressed into the trousers by means of a Hoffman press. The creased garment is then placed in a drier oven at a temperature of 275° F. for 15 minutes. The crease and dimensional stability of the fabric is found to be durable to 10 home laundering operations the laundering operation employing commercially available detergents and tumble drying operations.

EXAMPLE IV

The polyurethane external stabilization process set forth in Example I was again repeated and the externally stabilized fabric again subjected to a scouring, drying and finally a pressing operation. The stabilized fabric is then converted into trousers and the trousers sprayed with an aqueous solution containing 2% by weight sodium bisulfite 17.5% by weight methylol-methyl urethane and 0.2% by weight Deceresol OT (synthetic surfactant agent marketed by American Cyanamid Company). The spraying is conducted in a fashion so as to produce a pickup of about 40% by weight based on the dry weight of the fabric. The sprayed trouser is then pressed in a Hoffman press and then passed through a garment drying oven at a temperature of 275° F. for a period of about 15 minutes. The crease and dimensional stability of the final product is found to be durable to 10 home laundering operations, the home laundering operations being carried out with commercially available detergents and with tumble drying operations.

EXAMPLE V

An all wool worsted flannel is solvent dry cleaned and is dried free of solvent. The cleaned fabric is then dipped into an emulsion prepared as follows: (a) 4 grams of the polyester reaction product of adipic acid and glycerol is dissolved in 4 milliliters of methylethyl ketone (b) 4 grams of 2,2 bis(2-3-epoxy-propoxy phenyl) propane is dissolved in 4 milliliters of methylethyl ketone (c) 4 grams of polyamide condensation product of diethylene triamine and dimerized unsaturated fatty acid was dissolved in 4 milliliters of methylethyl ketone. The 3 solutions of (a), (b), and (c) are then mixed together and the composite solution poured into 375 milliliters of water with stirring so as to form an emulsion. The dry cleaned cloth is then dipped into the emulsion and passed through squeeze rolls so as to give a weight increase of 65%. The impregnated fabric is air dried to about 30% moisture and then heated in an oven for 30 minutes at 250 F. A pair of trousers is then prepared from the externally dimensionally stabilized fabric. The trousers are then sprayed with a 6.4% solution of N-propanolamine sulfite to a wet pickup of about 50%. The trousers are then allowed to stand for one hour in the damp state and then creases are pressed in the trousers by means of a Hoffman press employing a 30 second top steam, a 30 second bake and a 10 second vacuum. The trousers are then sprayed with a solution of 10% formaldehyde to a wet pickup of 40%, and allowed to stand in the damp state for one hour before being dried. The trousers are found to have dimensional stability and crease stability after 10 washing cycles employing commercially available detergents and employing tumble drying cycles after each wash cycle.

EXAMPLE VI

The external stabilization process set forth in Example III was again repeated and the externally stabilized fabric formed into a pair of trousers. The trousers are then sprayed with an aqueous solution containing 2% by weight sodium bisulfite, 17.5% by weight methylolmethyl urethane and 0.2% by weight Deceresol OT. The remainder of the processing operations were conducted substantially in accordance with the process set forth in Example II. The final product was found to have dimensional stability and crease stability after 10 home laundering operations employing commercially available detergents and employing tumble dry operations after each laundering cycle.

EXAMPLE VII

A 50% polyester, 50% wool worsted flannel fabric is immersed in a 3.3% aqueous solution of polyaminocaproic acid, diethyl amino ethanol derivative, the specific means of preparation of which is set forth in U.S. Patent No. 2,696,448. Excess pad liquor is removed by passing the fabric through squeeze rollers. The fabric is dried at about 80° C. and then cured at 130° C. for 15 minutes. The externally stabilized fabric is then treated with the reducing agent solution followed by treatment with formaldehyde substantially as set forth in Example I. The finished produce is found to have dimensional stability and crease stability even after being subjected to 10 home laundering operations which include the use of commercial detergents and tumble drying operations.

EXAMPLE VIII

The procedure of Example V is repeated with the exception that subsequent to the external stabilization operation, the fabric upon being formulated into a pair of trousers is sprayed with an aqueous solution containing 2% by weight sodium bisulfite, 17.5% by weight methylolmethyl urethane and 0.2% by weight Deceresol OT, the treatment being conducted substantially as set forth in Example II. The finished product is found to have dimensional and crease stability after having been subjected to 10 home laundering operations which include the use of commercially available detergents and tumble drying operations.

While certain of the commercially available external stabilizing agents for wool fabrics have not been mentioned by their trade names such as, for instance Zeset TP (terpolymer setting agent marketed by E. I. du Pont de Nemours & Co.) and Wurlan (Interfacial polymerization treatment device by the Western Regional Laboratory of the United States Department of Agriculture). It should be understood that these and other well recognized wool stabilization media and processes are also satisfactory for use in conjunction with this invention and may be substituted in place of the aforementioned external wool stabilizing agents specifically set forth in the foregoing examples.

Having thus disclosed the invention, what is claimed is:

1. A process for durably securing a fabric containing

at least some keratinous fibers in a desired configuration, said process comprising

(a) treating the fabric with a polymer and curing the polymer on the fabric to externally stabilize the fabric,

(b) treating the stabilized fabric with a reducing agent capable of rupturing the cystine linkages of the keratin fiber,

(c) securing and heating the reducing agent treated fabric in the desired configuration to set the fabric in the desired configuration and

(d) subjecting the fabric to the action of an aldehyde or reactive ketone while in said configuration.

2. The process of claim **1** wherein said keratinous fiber containing fabric is an all wool fabric.

3. The process of claim **1** wherein said aldehyde is formaldehyde.

4. The process of claim **1** wherein said aldehyde is generated from a thermally decomposable organic compound.

5. The process of claim **1** wherein said desired configuration is a crease.

6. The process of claim **1** wherein said aldehyde is generated from a thermally decomposable organic compound said thermally decomposable organic compound being applied to said fabric simultaneously with said reducing agent.

7. The process of claim **1** wherein the stabilized fabric is converted to a garment prior to treatment with said reducing agent.

8. The product produced by the process of claim **1.**

9. The process of claim **1** wherein the polymer is a urethane polymer.

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RICHARD D. LOVERING, Primary Examiner

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