STABILIZATION OF WOOL THROUGH TREATMENT WITH A REDUCING AGENT AND A POLYMER OR POLYMER FORMING MATERIALS

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ABSTRACT OF THE DISCLOSURE

A two step durable setting in the desired configuration of textile materials containing keratinous fibers comprising (1) an external stabilization and (2) an internal stabilization. The external stabilization involves polymer formation through treatment with a polysaccharide and an active hydrogen containing polymer. The internal stabilization involves treatment with a reducing agent.

This invention relates to a textile fabric which contains keratinous fibers and which has a propensity to conform durably to a preselected configuration, and more specifically, to wool fabrics having creases which are durable to laundering and dry cleaning operations.

Garments prepared from cellulose fabrics having creases set therein which are durable to laundering have recently found wide acceptance in the textile industry. Cellulose 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.

Garments made from wool fabrics have been sprayed with reducing agent solutions and pressed on a steam press in an attempt to produce durable creases in the garments. The creases as produced are quite durable to mere wetting but will not withstand a combination of wetting and agitation, such as occurs in a washing machine.

It has now been discovered that configurations which will withstand washing can be produced in wool garments by subjecting the fabric to an external stabilizing operation, treating the externally stabilized fabric with a reducing agent, maintaining the reducing agent treated fabric in a desired configuration while reforming the split linkages of the keratinous fibers.

The preferred process for splitting internal linkages of keratinous fibers is treatment with a reducing agent. Preferred among the linkage reforming processes are steam and heat processes. The preselected configurations which are contemplated include any shape desired in the fabrics or garments made from such fabrics, e.g., pleats, creases, texturing effects, such as pupille textures, and the like.

The external setting of the keratinous fiber is accomplished by means of a polymeric chemical reagent. Typical examples of such setting processes are additive type shrinking processes wherein polymeric reagents are added to keratinous fabrics. These reagents preferably react with the keratinous component for improved washability characteristics. 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 non-reactive polymeric coating composition so as to secure the fibers in the desired configuration by means of the mechanical forces exerted by the coating, e.g., according to the Wurlan process developed at the Western Regional Laboratories of the United States Department of Agriculture. While the preferred external setting medium is a medium of the type which produces new chemical bonds by reacting with a keratinous fiber, a non-reactive medium is acceptable for a reactive reagent.

The use of polymeric external stabilizing agents provides many advantages over techniques involving the use of monomeric oxidizing agents such as sodium chlorite and various permanganate salts. Polymeric compounds not only provide a higher level of stability to washing in fabrics so treated, but also provide a higher level of finish stability as well as dry cleaning property than is possible with monomeric type treating agents. In other words, when a wool fabric is first treated with a monomeric shrinking agent and then durably set with reducing agent solutions, the results, if anything, are less than additive.

The fabric, during washing, tends to shrink slightly more than if no reducing agent had been employed and the flat drying properties and finish are not satisfactory. On the other hand, when a polymeric shrinking agent is utilized in combination with the reducing agent treatment, a synergistic effect on crease retention, flat drying properties and finish stability is attained in that these properties are far superior to the same properties measured on the fabric after either treatment separately.

The most preferred external stabilizing agents for purposes of the invention are isocyanate reaction products. These reaction products, in combination with the internal stabilizing treatment, provide greatly improved washability characteristics. For example, garments made from fabrics treated with these products accept creases quite readily and retain these creases after washing and tumble drying to a much greater extent when compared with other externally stabilized fabrics, although these latter products are entirely satisfactory.

Among the isocyanate reaction products which may be employed are isocyanate reaction products selected from two general categories, the first of which is a urethane prepared from a polyfunctional isocyanate and a polymeric polyol 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, poly-epoxides and reaction products of phenol and alkyl oxides, formaldehyde resins, hydrogenation products of olefinic compounds and polyolefin polyhydrins. 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 one-shot applications forming the isocyanate reaction product on the fabric in situ.

Regardless of the system utilized, it is preferred that the ratio of isocyanate to active hydrogen compound be at least about 0.4, but most preferably, greater than 1.0, e.g., from 1.01 to about 2.0, preferably 1.05 to 1.6. Systems containing an excess of isocyanate are much more highly reactive with keratin fibers, so that stabilization is provided to the desired level, permitting washing with
little or no degradation of the hand, or feel, of the fabric. Surprisingly, configurations imparted to such fabrics by subsequent reducing agent treatments are durable to washing even at low levels of polymer, e.g., as little as 1%, but preferably between 3 and 10%, although amounts on the order of 15–25% produce excellent results, even though producing stiffening effect on fabrics so treated.

By "pre-polymer" herein is meant the reaction product of the polyfunctional isocyanate and the preselected second polymeric compound carried to an extent below which a gel is produced, which is insoluble in any of the organic solvents for each of the two reaction components and particularly the chlorinated hydrocarbons. When the pre-polymer is prepared from an excess of isocyanate as preferred, the resulting product is believed to be an isocyanate-terminated polyurethane, which is highly reactive with keratin fibers.

The term "one-shot" as employed herein is meant to define a process wherein the isocyanate and active hydro- gen compound are applied to the substrate material directly from solution. The desired polymer is then formed in situ on the fabric. In general, the degree of polymerization of the resulting polymer exceeds that of the pre-polymer.

Among the suitable isocyanates that may be used in accordance with this invention are aryl disocyanates such as 2,4-tolylenedisocyanate, 2,6-tolylenedisocyanate, 4,4' -diphenylmethane disocyanate, m-phenylene disocyanate, 1,5-naphthylene disocyanate, m-phenylene diisocyanate, diphenyl-1,4'-diisocyanate, azobenzene-4,4'- diisocyanate, diphenylsulfone-4,4'-disocyanate, 1-isopropylbenzene-3, 5-disocyanate, 1-methyl-phenylene-2,4-di- isocyanate, naphthenylene-1,4-disocyanate, diphenyl-4,4'- diisocyanate, diphenylmethane and isocyanate, benzene-1, 2,4-triisocyanatocyanate, 5-nitro-1,3-phenylene disocyanate, xylene-1,4-diisocyanate, xylene-1,3,4-disocyanate, 4,4'-diphenyle- methane diisocyanate, 4,4'-diphenylpropane diisocya- nate and xylene-1,4-diisocyanate and the like; cyclic disocyanates, such as dicyclohexamethane-4,4'-diisocyanate; and the like; alkylenediisocyanates such as tetramethylene disocyanate, hexamethylenediocyanate and the like, as well as mixtures thereof and including the equivalent isothiocyanates. Of these compounds, the aryl disocyanates are preferred because of their solubility and availability.

Additional isocyanates include polymethylene disocyanates and disodiisocyanates, such as ethylene diisocyanate, dimethylene diisocyanate, dodecamethylene diisocyanate, hexamethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, and the corresponding diisocyanates; alkylenediisocyanates and disodiisocyanates such as propylene-1,2-diisocyanate, 2,3-dimethyltetra- methylene diisocyanate and diisocyanate, butylene-1,2- diisocyanate, butylene-1,3-diisocyanate, and butylene-1, 3-diisocyanate; alkylienediisocyanates and diisodiisocyanates such as ethylene diisocyanate

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\text{(CH}_2\text{CH(NCO)}_2)\]

and heptylienediisocyanate

\[
\text{(CH}_3\text{CH}_2\text{CH(NCO)}_2)\]

cycloalkylene diisocyanates and disodiisocyanates such as 1,4-disocyanatocyclohexane, cyclopentylene-1,3-disocyanate, and cyclohexylene-1,2-disodiisocyanate; aromatic polyisocyanates and polysiisodiisocyanates such as aliphatic-aromatic diisocyanates and disodiisocyanates such as phenylmethane diisocyanate \((\text{CH}_3\text{CH(NCO)}_2)\); diisocyanates and disodiisocyanates containing heteroatoms such as SCNCH\text{OCH}_2\text{NSC},

\[
\text{SCNCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{NSC}
\]

and SCN(CH\text{H}_2)_2S—(CH\text{H}_3)_2NSC; 1,2,3,4-tetramethylenediamine, butyan-1,2,3,4-tetraisocyanate, tolylene-2,4,6-triisocyanate, tolylene-2,3,4-triisocyanate, benzene-1,3,5-triisocyanate, benzene-1,2,3,4-tetraisocyanate, 1-isocyanato-4-isothiocyanatohexane, and 2-chloro-1,3-diisocyanatopropane.

The preferred disocyanates, disodiisocyanates and mixed isocyanate-isothiocyanates have the general formula R—N=C=O or R—N—N=C=O 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. Groups may be present by dehydrocondensation of polyhydroxy compounds as set forth below. Among the suitable polymeric polyhydroxy compounds, there are included polyether polyols such as polyalkyleneether glycols, and polyalkylene-aryleneether-thioether glycols and polyalkyleneether triols. Polyaldehydicether and 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)xH, wherein R is an aryl radical which need not necessarily be the same in each instance and x is an integer. Representative glycols include polyethyleneglycol, polypropylene glycol, polytrimethylene glycol, polytetramethylene ether glycol, polytetramethyleneglycol, polytetramethylenether glycol, polytetramethylene formal glycol and poly-1,2-dimethyleneglycol. Mixtures of two or more polyalkyleneether glycols may be used.

Representative polyalkyleneether triols are made by reacting one or more alkyleneglycol with one or more more molecular weight aliphatic triols. The alkyleneglycols most commonly used have molecular weights between about 44 and 250. Examples include: ethylene oxide; propylene oxide; butylene oxides, 1,2-epoxypropane; benzyl alcohol; 2-chloro-1,2- epoxycyclohexane; 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 alkyleneglycols having cyclic substitutents may be present, such as styrene oxide, cyclohexene oxide, 1,2-epoxy-2-cyclohexyloxy propane, 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-trimethylylpropane; 2,4-dimethyl-2-methylpentanol-1,5 and the trimethylol of sorbitol.

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

Additional suitable polyols include polyoxypropylene triol, poloxybutylene triol, 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, naphthenylene and anthracene radicals which may be substituted with various substitutents, such as alkyl groups. In general, these glycols there should be at least one arylene radical having a molecular weight of about 500 for each arylene radical which is present.

The polyalkyleneether-thioether glycols and the polyalkylene-aryleneether glycols are similar to the above-described polyether glycols, except that some of the ether-oxygen atoms are replaced by sulfur atoms. These glycols
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 polyglycols, polyglylons, reaction products of phenols and alkylene oxides, formaldehyde resins, hydrogenation products of olefine-carbon monoxide copolymers, and polyephalhydrins.

The polysters 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 polyhydroxy alcohol.

Among the suitable acids there are included the alkane dibasic acids, alkene dibasic acids, cycloalkane dibasic acids, cycloalkene dibasic acids, alkyl 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 include polyhydric alcohols with polyols and polyesters for use in accordance with this invention include the following: succinic; monomethyl succinic; glutaric; adipic; pimelic; suberic; azelaic; sebacic; brassilic; thirpic; 6-o xo undecanedioic; octadecanedioic acid; 8-octadecenedioic acid; ricinoleic acid; 6,9-octadecadienoic acid; maleic; and the like. Other acids include: unsaturated acids such as maleic, fumaric, glutaconic, and itaconic; the cycloalkane dicarboxylic acids such as cyclopentane-1,2-dicarboxylic acid; and cyclopentane-1,3-dicarboxylic acid; aromatic dicarboxylic acids such as phthalic, isophthalic, terephthalic, naphthalene-1,2-dicarboxylic acid; and naphthalene-1,3-dicarboxylic acid; naphthalene-1,4-dicarboxylic acid; naphthalene-1,5-dicarboxylic acid; naphthalene-1,8-dicarboxylic acid; diphenyl-2,2'-dicarboxylic acid; diphenyl-4,4'-dicarboxylic acid; and diphenyl-2,4'-dicarboxylic acid; and aliphatic and aromatic dicarboxylic acids such as 2,6-dimethylenzen-1,4-dicarboxylic acid, and 4,5-dimethylenbenzen-1,2-dicarboxylic acid; and the like.

Natural products which are particularly useful include castor oil, which comprises a glyceride of ricinoleic acid, and rincinoleal alcohol, and mixtures thereof.

Representative monomeric polysters for reaction with the above mentioned of polyester for use in accordance with this invention include the polyalkylene ether glycols represented by the formula HO(RO)NH, wherein RO is an alkylene radical which need not necessarily be the same in each instance and n is an integer. Representative glycols include polyethylene glycol, polypropylene glycol, polytetramethylene glycol, polypropylene glycol, polypentamethylene glycol, polydecamethylene glycol, polytetramethylene glycol, and poly-1,2-dimethylethylene glycol. Mixtures of two or more polyalkylene 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-epoxydecane; 2,3-epoxybutane; 3,4-epoxyhexane; 1,2-epoxy-5-hexene; and 1,2-epoxy-3-butane, and the like. Ethylene, propylene, 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-tri-methylolpropan; 1,1,1-trimethylolethane; 2,4-dimethylol-2-methylpentanediol-1,5 and the trimethylether of sorbitol.

Representative examples of the polyalkyleneether triols include: propyleneether triol (M.W. 700) made by reacting 60 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 dimethylolpropylene; polypropyleneether triol (M.W. 250) 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 polyesters 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-aryl ether 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, these glycols should be at least one arylene radical having a molecular weight of about 500 for each arylene radical which is present.

The polyalkyleneether-thioether glycols and the polyalkylene-aryl ether glycols are similar to the above described polyster glycols, except that some of the ether-oxygen atoms are replaced by sulfur atoms. This 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.

Additional polysters 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:

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 —(alkylene-O)Rg—H groups contain primary alcoholic hydroxy 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 polyether polyoxides, may be prepared as well known in the art by reacting a polyl 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-catalyzed catalyst such as hydrofluoric acid or boron trifluoride and the product is then reacted with an alkyl carbonate by way of halogenation. A preferred example of the halogen-containing epoxide is epichlorohydrin; others are epibromo-
hydrin, epiodhydrin, 3-chloro-1,2-epoxybutane, 3-bromo-1,2-epoxyhexane, and 3-chloro-1,2-epoxy-octane. Illustrative examples of polyoxide polymers are as follows:

1. 3,687,605 7 hydrin, epiodhydrin, 3-chloro-1,2-epoxybutane, 3-bromo-1,2-epoxyhexane, and 3-chloro-1,2-epoxy-octane. In commerce, the polyoxide polymers containing polyhydroxyl groups may also be prepared by reacting, in known manner, a polyhydric alcohol or polyhydric phenol with a polyoxypolyether in an alkaline medium. Illustrative examples are the reaction product of glycerol and diglycidyl ether, the reaction product of sorbitol and bis(2,3-epoxy-2-methylpropyl)ether, the reaction product of pentaerythritol and 2,3,5-diyoxy pentane, the reaction product of 2,2-bis(parahydroxyphenyl)propene 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-diphenoxy-cyclohexene and diglycidyl ether.

The polyoxide polymers which do not contain ether groups may be employed as for example 1,2,5,6-diphenoxiethane; butadiene dioxoide, is 1,2,5,6-diphenoxiethane; isopropene dioxide; limonene dioxide.

For use in accordance with the invention, I prefer the polyoxide polymers which contain ether groups, that is, polyoxide polymers. More particularly I prefer to use the polyoxide polymers of the class of glycidyl polymers of polyhydric alcohols of polyhydric phenol etherification with at least two glycidyl groups

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\begin{align*}
&\text{O} \\
&\text{CH}_2\text{CH}_2\text{CH}_2\text{O} \\
&\text{wherein } n \text{ varies between zero and about } 10, \text{ corresponding to a molecular weight about from } 350 \text{ to } 8,000.\end{align*}
\]

Of this class of polyoxide polymers is employed to those compounds wherein \( n \) has a low value, i.e., less than 5, most preferably where \( n \) is zero.

In commerce, the polyoxide polymers 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 polyoxide polymers having molecular weights substantially less than 1,000.

It is within the purview of the invention to employ mixtures of different polyoxide polymers. Indeed, it has been found that especially desirable results are attained by employing mixtures of two commercially available polyoxide polymers, 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 polyanimes and polybasic acids. Methods of preparing these polyamides by condensation of polyanimes and polybasic 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 polyanimes as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, 1,4-diaminobutane, 1,3-diaminobutane, hexamethylenediamine, 3-(N-isopropylaminomethyl)propyamine, 3,3'-iminobispropylamine, and the like. Typical polycarboxylic acids which may be condensed with the polyanimes to form polyamides are glutaric acid, adipic acid, pimelic acid, suberic acid, sebacic acid, isophthalic acid, terephthalic acid, betamethyl adipic acid, 1,2-cyclohexanedicarboxylic 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 10,000 to 10,000 and melting points about from 20-200 °C. Particularly preferred for the purpose of this invention are the polyamides derived from aliphatic polyanimes and polymeric fatty acids. Such products are disclosed for example by Cowan et al., Pat. 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 form dibasic and higher polyacids. Usually the mixture contains a preponderant proportion of dimeric acids with lesser amounts of trimeric and higher polyacids, 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 polyanime, such as diethylenetriamine, triethylene tetramine, 1,4-diaminobutane, 1,3-diaminobutane, and the like with the polymerized fatty acids. Typically among these is a polyanime derived from diethylene triamine and dimerized soybean fatty acids. The polyamides derived from aliphatic polyanimes and poly-
ized fatty acids, like the polyepoxides, are often referred to in the trade as resins even though not actually resins in the mixed aromatics, such as the Solvay types and 8
larly good results are obtained in the use of low molecular weight, non-fiber forming polymides 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 conventional cresol-n-propanolamine resin, cresol-n-butanolamine resin, di-

Any suitable hydrogenation product of olefin-carbon monoxide copolymers may be used such as, for example, the hydrogenation product of an ethylenepropylene-car-


In the process of this invention, it is preferred to re-

act the polyfunctional isocyanate and polymeric polyfunc-
tional compound or polyfunctional isocyanate and poly-

mERIC hyDROXY compound as the case may be with or without a curant or unblocked or blocked in a "one-shot" procedure with the keratinous fibers in the presence of a catalyst. Any of the well-known catalysts for the reaction of active hydrogen atoms with isocy-

anates may be used. Of these catalysts which are used in the polyurethanes, organo-tin or organo-

zinc compounds are preferred. Particularly preferred are either stannous octoate or zinc naphthenate.

The various isocyanate reaction product systems de-
scribed above preferably are applied to the keratin fiber containing fabric in the form of a solution, the so-
lution containing a non-reactive solvent although aque-

ous emulsions may be utilized if desired. By "non-reactive" as used herein is meant a solvent in which reac-
tivity between the isocyanate and active-hydrogen con-
taining components of the solvent mixture even in the presence of catalyst is substantially inhibited. Small amounts of water, if present, is preferred to be present in the amount present is sufficiently low so as not to precipitate a substantial amount of the components with which it is rea-
ted. In other words, sufficient components remain reactive with the keratin fibers to provide adequate inhi-
bition of shrinkage and/or setiability in the fabric or other structure being treated.

Suitable organic solvents include halogenated hydro-
carbons such as trichloroethylene, methylene chloride, perchloroethylene, ethylene dichloride, chloroform and the like, aromatic solvents such as toluene, xylene, benz-

zenes, dimethyl ethylene glycol, trimethylolpropane, the like, n-butyl acetate, n-butyl ether, n-butyl phosphate,
p-dioxane, ethyl oxalate, methyl isobutyl ketone, pyridine, quinoline, N,N,N-dimethylformamide, N,N,N-dimethylacet-

amide, dimethylsulfoxide, 2,2,4-trimethyl-pentane and the like. Mixtures of solvents may be used.

The internal setting of the keratinous fibers is prefer-

ably accomplished by means of a reducing agent. Such compounds are well-known in the art and have the abil-

ity to rupture polymeric linkages, within the structure of keratin. These ruptured linkages, specifically the disulfide linkages, may be at least partially reformed while hold-
ing the fiber in a desired configuration, thereby setting this configuration durably in the fiber. The reaction which appears to take place in setting the keratinous fibers in the new shape is reformulation of the cystine linkage and reformation of hydrogen bonds and/or hydrophobic bonds of the keratinous fibers, the bonds and linkages having been set 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 and/or hydrophobic bonding. These changes in location of cystine linkages and changes in hydrogen and hydrophobic bonding produce a re-

formed fiber. The reformation of the fiber gives the in-
dividual keratinous fibers of this invention their internal setting which results in a fabric which has stabilization to dimensional and finish changes.

Among the suitable reducing agents, there are included lower alkanolamine sulfites, such as monoethanolamine sulfite and isopropanolamine sulfites, and others containing up to about 8 carbon atoms in the alkyl chain, such as mono-n-butanolamine sulfite, di-
methylbutanamine sulfite, dimethyloctanamine sulfite and the like; metallic formaldehyde sulfonates, such as zinc formaldehyde sulfonate, the alkali metal sulfox-

ytes, such as sodium formaldehyde sulfonate and pot-
tassium formaldehyde sulfonate; alkali metal borohy-

rides, such as sodium borohydride, potassium borohy-

dride and sodium potassium borohydride; alkali metal sulfites, such as sodium or potassium bisulfite, sulfite, and metabisulfite; and ammonium bisulfite, sodium sulfide, sodium hydroxide; sodium hydrosulfite, sodium thio-
sulfate, sodium dithionate, titanous chloride, sulfuric acid, mercaptan acids, such as thioglycollic acid and its water soluble salts, such as sodium, potassium or am-
onium thioglycolate; mercaptans, such as hydrogen sul-

 tide, alkyl mercaptans such as butyl or ethyl mercaptans and mercaptan glycols, such as β-mercapto ethanol; and mixtures of these reducing agents.

Particularly beneficial results are obtained if the redu-
cing agent is employed in conjunction with a "low molecular weight polyhydroxy compound" or other aux-

iliary agent. Urea constitutes the most readily available and desirable auxiliary agent, although any other mate-

rial which will swell keratinous fibers in an aqueous me-
dium is suitable. For example, guanidine compounds such as hydrochloride; formamide, N,N-dimethylform-
amide, acetamide, N,N,N-dimethylacetamide, thiourea, di-
methylsulfoxide, phenol, lithium salts, such as the chlor-

e, bromide, and iodide and the like are similarly useful.

By the term "low molecular weight polyhydroxy com-
pound" is meant a compound containing more than one hydroxy group and having a molecular weight prefer-

ably no greater than about 4000. Of these compounds, the most readily available and desirable compound, from the standpoint of ease of application, comprises ethyl-

e glycol. A particularly preferred group of glycols in-
cludes the polyfunctional glycols having terminal hy-
droxy groups separated by 2 to 10 methylene groups, including, of course the preferred ethylene glycol as well as trimethylene glycol, tetramethylene glycol, penta-

e, hexamethylene glycol, and decamethylene glycol, or such glycols as 1,2-propylene glycol, di-

crylene glycol, 1,3-butyleneglycol, diethylene glycol, propylene glycol or the like.

Polyfunctional compounds containing more than 2 hydroxy groups include the polyfunctional alcohol gly-

cols such as glycercin and diethylylglycerol as well as trimethyl oxethane, trimethyl butane, trihydroxyethyl-
yl-amino methane and others. Glycol ethers, such as the water-soluble or dispersible polyethylene glycols or poly-

propylene glycols having molecular weights preferably no greater than about 4000 also provide satisfactory results when utilized in accordance with this invention.

The reducing agent with or without the auxilarly agent or polyhydroxy compound may be applied to the fabric in any desired amount, depending upon the degree of re-
nouncing desired. In general, optimum results are obtained when aqueous solutions containing from about 0.01 to about 20% by weight of the reducing agent are applied to the fabric. The swelling agent or polyhydroy compound 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. The latter concentrations may be utilized where the fabric is to be exposed to the treating medium for only a short time.
3,687,605

11. Subsequent to the external stabilization operation, the fabric may be converted to a garment and the garment subjected to the reducing agent treatment for setting durable configurations in the garment. The conversion to a garment is preferable where the object of the process is to produce creases in the garment which are durable to home laundering. Alternatively, however, the externally stabilized fabric may be impregnated with the desired reducing agent solution, preferably containing a swelling agent or low molecular weight polyhydroxy compound, and then dried under conditions which are not capable of reforming any split linkage in the keratinous fibers. The resulting fabric is thereby pressurized for subsequent durable setting in garment or fabric form on any of the well-known equipment used for setting operations. A particular advantage of such a fabric, with or without a swelling agent and/or low molecular weight polyhydroxy compound, can be made into garments and the garments durably set by standard pressing and curing, for example, using a Hoffman press to impart creases to the garments and then reforming any split linkages in a curing oven. The configurations set in garments in this manner are durable, at the very least, to the wetting, tumbling action of a coin-operated dry cleaning machine. Furthermore, excellent appearance of such fabrics is substantially retained after wetting. It is preferred, however, for washability characteristics that water in an amount of at least about 5%, preferably 10 to 40%, or even more, be applied to the presensitized fabrics before pressing and curing.

The mechanical steps of producing a texture effect, crease, 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 process of this invention is applicable to any keratinous substrate, including, of course, fabrics made from blends of keratinous fibers with other natural fibers, including silk, cellulose fiber and the like, or with synthetic fibers, such as synthetic cellulose fibers including acetylated cellulose, for example, the cellulose acetate, acetylated rayon, rayon per se and the like; polyamides, particularly nylon, both 6 and 66 types; polyesters, such as polyethylene terephthalate and the like; polyelefins, such as polyethylene, polypropylene and the like; acrylic fibers such as those produced from acrylonitrile and copolymers thereof, and the like.

It is preferred, however, that a substantial amount of keratinous substrate, for example, at least about 20%, preferably at least about 40%, by weight be present in the substrates being treated.

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 glycercin 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 toluylene - 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 prepolymer. The prepolymer 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 prepared from the 70% solution of the 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'-tetraakis 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 the second oven at 250°F. for 5 minutes for curing. The treated fabric is then scoured, dried and pressed.

Trouser are then formed from the urethane treated fabric. The trousers are sprayed with a 6.4% solution of monoisopropanolamine sulfate 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 stream, a 30 second bake and a ten second vacuum. The creases and dimensional stability of the trousers are found to be durable to several washing cycles in a Kenmore washer, employing commercially available detergents, e.g., Tide brand detergent, in recommended quantities, and employing tumble drying cycles after each wash cycle. The creases and dimensional stability of the trousers are also durable to multiple dry cleaning operations.

EXAMPLE II

The procedure of Example I is 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 glycercin 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-di-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 several washing cycles employing commercially available detergents, e.g., Tide brand detergent, in recommended quantities, and employing tumble drying cycles after each wash cycle.

EXAMPLE III

The procedure of Example II is repeated with the exception that the fabric upon being formulated into a pair of trousers is sprayed instead with an aqueous solution containing 2% by weight sodium bisulfite, 5% urea and 0.2% Decresol OT.

EXAMPLE IV

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 0.2% by weight Dercosol OT. Alternatively, a solution containing 3% by weight sodium bisulfite, 5% by weight urea, and 0.2% by weight Dercosol OT may be employed. The treated fabric is dried at 175° F. and given a light press. The fabric is then fashioned into two pairs of trousers. One pair of trousers is sprayed with water containing 0.2% Dercosol OT so that about 40% by weight based on the dry weight of the fabric. After standing in the damp state for 30 to 60 minutes creases are pressed into the trousers by means of a Hoffman press, using a cycle of 30 seconds top steam, 30 seconds bake, 10 seconds vacuum, at a steam pressure of 80 p.s.i. The trousers are then dried for 15 minutes in an oven at a temperature of 325° F. The crease and dimensional stability of the fabric is found to be durable to several washing cycles in a Kenmore washer, employing commercially available detergents, e.g., Tide brand detergent, in recommended quantities, and employing tumble drying cycles after each wash cycle.

The other pair of trousers is similarly pressed and heated in the oven but without prior wetting with water. The creases so imparted are durable to the effects of a coin-operated dry cleaning unit, but do not withstand the washing operations as well as the other pair of trousers which were wetted before pressing. Similar, though slightly improved, results are obtained when ethylene glycol is substituted for urea and the above procedures are repeated.

EXAMPLE V

The procedure as set forth in Example IV is repeated with the exception that the fabric is stabilized externally according to the procedure set forth in Example II.

EXAMPLE VI

The procedure as set forth in Example IV is repeated with the exception that the externally stabilized fabric is padded with a solution containing 3% by weight sodium bisulfite, 5% urea and 0.2% Dercosol OT.

EXAMPLE VII

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 conveyed to the trousers sprayed with an aqueous solution containing 2% by weight sodium bisulfite and 0.2% by weight Dercosol OT (synthetic surfactant agent marketed by American Cyanamid Company) and 5% by weight urea. 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. The crease and dimensional stability of the final product is found to be durable to several washing cycles in a Kenmore washer, employing commercially available detergents, e.g., Tide brand detergent, in recommended quantities, and employing tumble drying cycles after each wash cycle.

EXAMPLE VIII

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 methyl ketone (b) 4 grams of 2, 2-bis(3, 4-epoxy-propoxy phenyl) propane was dissolved in 2 milliliters of methyl ketone (c) 4 grams of dodecylamine and dimerized unsaturated fatty acid was dissolved in 4 milliliters of methylketone. 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 sulfate to a wet pickup of about 50%. The trousers are then allowed to stand for about 40 minutes. 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 found to have dimensional stability and crease stability after several washing cycles in a Kenmore washer, employing commercially available detergents such as, e.g., Tide brand detergent, in recommended quantities, and employing tumble drying cycles after each wash cycle.

EXAMPLE IX

The external stabilization process set forth in Example II 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 and 0.2% by weight Dercosol 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 several home laundering cycles in a Kenmore washer, employing commercially available detergents, e.g., Tide brand detergent, in recommended quantities, and employing tumble drying cycles after each wash cycle.

EXAMPLE X

A 50% polyester, 50% wool worsted flannel fabric is immersed in a 3.5% aqueous solution of polyamino-caproic 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 substantially as set forth in Example I. The finished product is found to have dimensional stability and crease stability even after being subjected to several washing cycles in a Kenmore washer, employing commercially available detergents, e.g., Tide brand detergent, in recommended quantities, and employing tumble drying cycles after each wash cycle. The finished product is also found to have dimensional stability and crease stability to multiple dry cleaning operations.

EXAMPLE XI

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 and 0.2% by weight Dercosol OT, the remaining treatment being conducted substantially as set forth in Example V. The finished product is found to have dimensional and crease stability after having been subjected to several home laundering operations which include the use of commercially available detergents and tumble drying operations.

Having thus disclosed the invention, what is claimed is:

1. A process for durably setting a fabric containing keratinous fibers in a desired configuration comprising (a) treating said fabric with a monomeric polysiocyanate and a polymeric polyfunctional compound selected from the class consisting of polycyclic polyhydroxy compounds, polymers, polyamines, polyepoxides and reaction products of phenol and alkanol oxides, formaldehyde resins, hydrogenation products.
of olefin-carbon monoxide copolymers and polyepihalohydrins,
(b) curing said treated fabric to externally stabilize the
fabric,
(c) treating the stabilized fabric with a reducing agent,
(d) maintaining the reducing agent treated fabric in
a desired configuration, and
(e) heating the fabric to a temperature sufficient to
set the fabric in the desired configuration.
2. The process of claim 1 wherein the fabric is an all
wool fabric.
3. The process of claim 1 wherein the polymeric poly-
functional compound is a polyether polyl.
4. The process of claim 1 wherein the isocyanate is an
aryl disocyanate.
5. The process of claim 1 wherein the isocyanate is a
blocked isocyanate which is activated by heating at an
elevated temperature.
6. The product of the process of claim 1.