March 3, 1970 J. CAIN 3,498,740

IMPARTING PERMANENT DIMENSIONAL STABILITY AND FINISH STABILITY TO FABRICS CONTAINING KERATINOUS FIBERS

Filed March 14, 1966 2 Sheets-Sheet 1

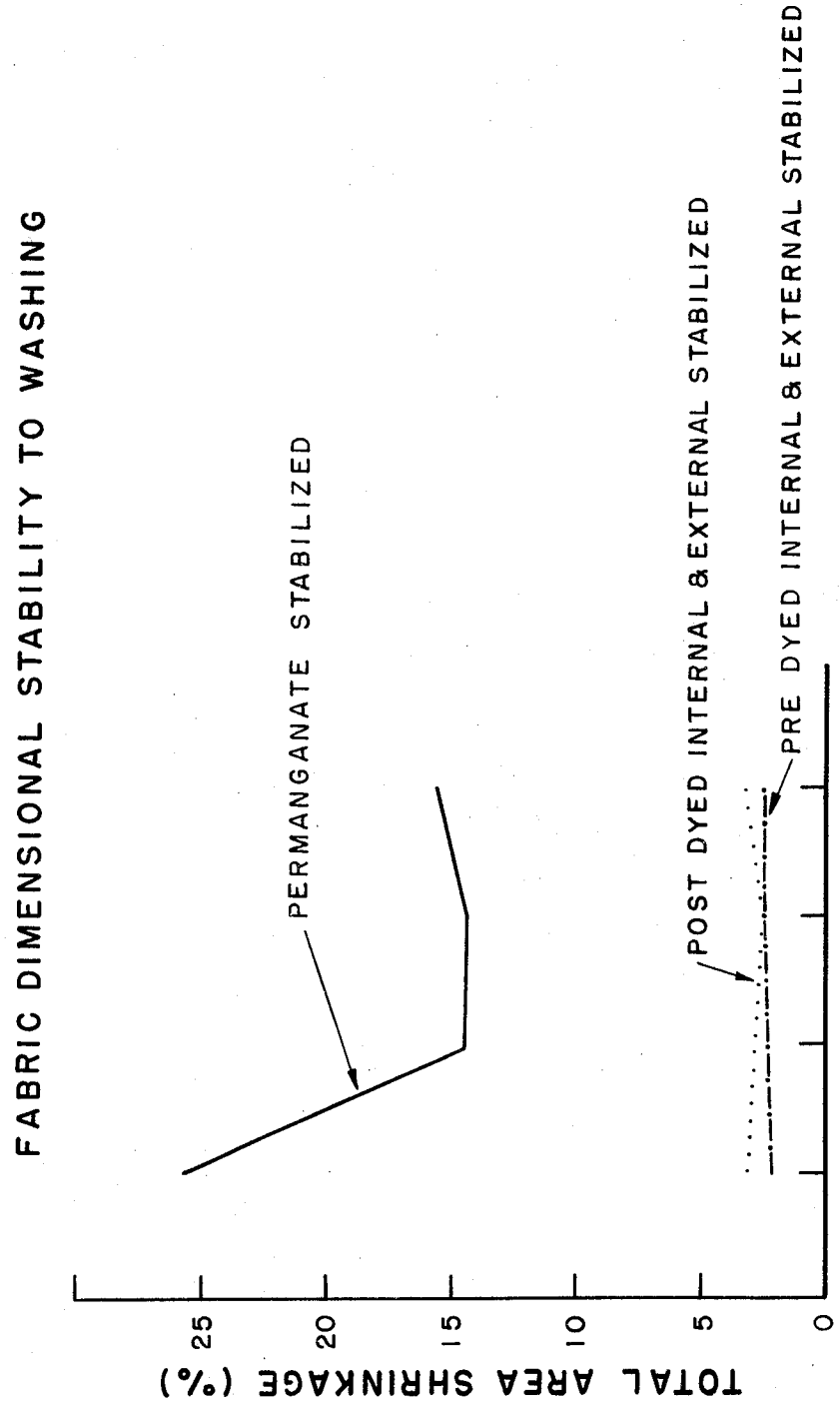



FIG. I

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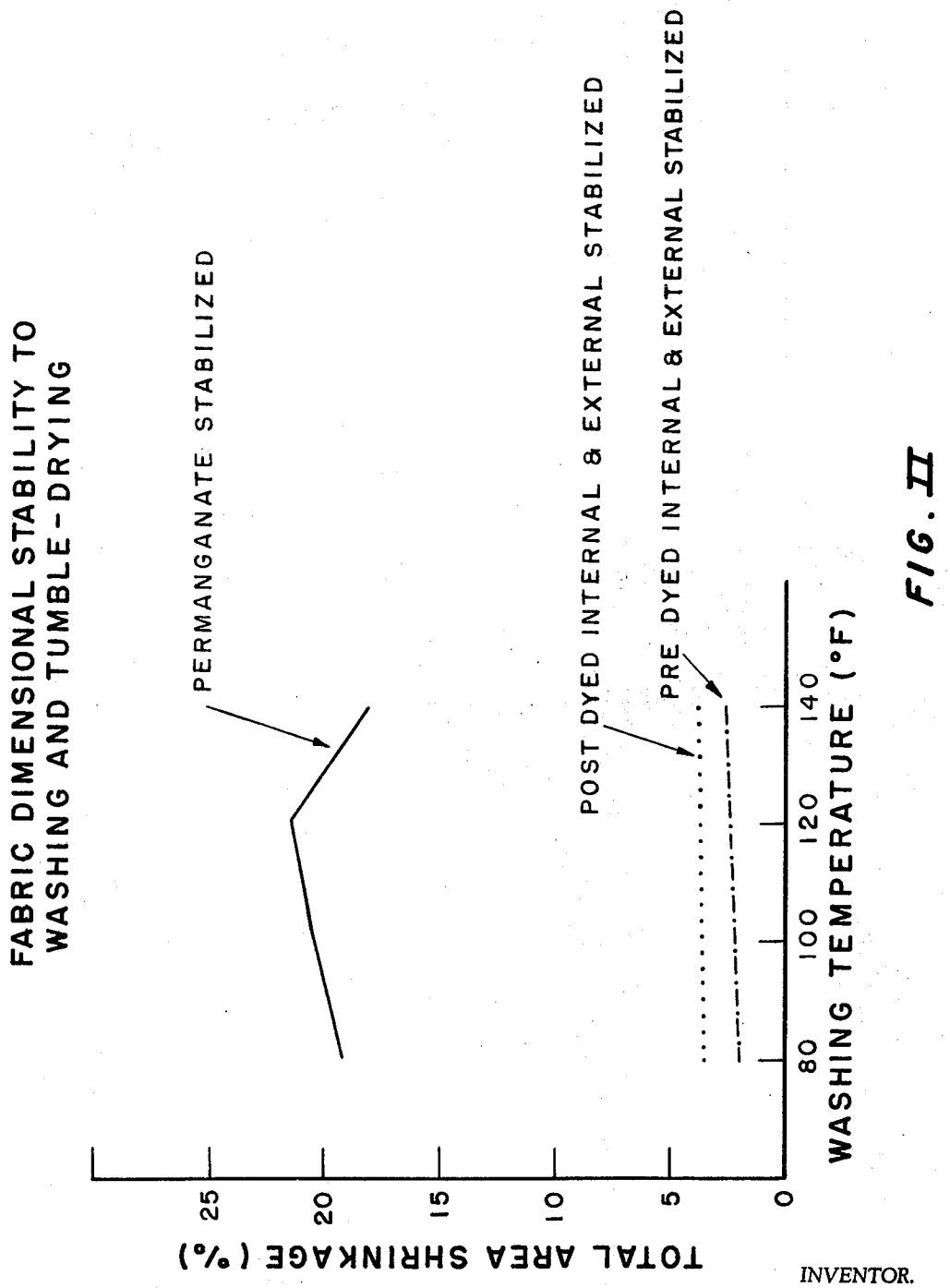



FIG. II

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United States Patent Office

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3,498,740

# IMPARTING PERMANENT DIMENSIONAL STABILITY AND FINISH STABILITY TO FABRICS CONTAINING KERATINOUS FIBERS

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U.S. Cl. 8—127.6 10 Claims

## ABSTRACT OF THE DISCLOSURE

Textile fabrics containing keratinous fibers having laundry durable dimensional and finish stability are prepared by the process comprising treating the fabric with a polymer to externally stabilize the fabric, and treating the fabric with a reducing agent followed by leveling and decating.

This invention relates to a textile fabric containing keratinous fibers and which has substantially permanent dimensional stability and finish stability and, more specifically, to woolen fabrics having wash-and-wear characteristics and to the methods for producing such fabrics.

Many processes are known for the preparation of woolen or worsted fabrics having dimensional stability to machine laundering operations. None of the processes known to the prior art, however, will impart both dimensional stability and finish stability to a machine washable woolen fabric. For purposes of this invention, the phrase "dimensional stability" is definitive of shrink resistance, that is to say substantially undiminished length in both warp and fill directions, subsequent to machine laundering. For purposes of this invention, the phrase "finish stability" is meant to define permanent surface characteristics such as, for instance, substantially permanent luster.

One of the few processes which have heretofore been available for imparting dimensional and finish stability incorporates an oxidative shrink-proofing (permanganate salt) process with a reducing agent flat setting process. This process is described in an article entitled, "Washable Non-Iron Fabrics from Wool" by A. J. Farnsworth, M. Lipson and J. R. McPhee in the Textile Research Journal, volume 51, No. 12, Part II, December 1960, pages T1504–1516. Particular attention is also drawn to the first Reference cited after these articles, in the names of the same authors. These two processes when used in sequence on a wool fabric produce substantial strength reductions and severely limit the application of the process; that is to say, the process is only applicable to heavy construction fabric. If fabrics of lighter apparel weight are employed, such as fabrics now commonly used in the United States of America, strength losses are so great as to render the fabric unsuitable for garments.

Furthermore, even on the heavier fabrics, this process fails to provide the high level of finish retention which is possible by the process of the present invention, particularly at the low levels of shrinkage and high level of flat dry ratings which are produced by the present invention.

It is therefore an object of this invention to provide a process for the preparation of a fabric containing keratinous fibers and having dimensional and finish stability.

It is another object of this invention to provide a process for the preparation of a fabric having dimensional and finish stability without substantial loss in strength.

It is a further object of this invention to provide a keratinous fiber having improved dimensional and finish stability.



In accordance with this invention, it has now been discovered that a leveled keratinous fiber containing fabric having improved dimensional and finish stability may be obtained by means of a two step process involving internal stabilization of the keratinous fiber and external stablization of the keratinous fiber, with the internal stabilization preferably being conducted prior to the external stabilization. The phrase "internal stabilization" as employed herein is deemed to include the summation of effects achieved by treatment with a reducing agent followed by leveling and decating, either semi-decating or full-decating, but preferably the latter. The internal stabilization is primarily responsible for imparting durable finish characteristics to a fabric while the external stabilization is primarily responsible for imparting durable dimensional stability to a fabric. It should be understood, however, that there is a unique interaction between the two stabilization treatments which results in a product having an unexpected degree of stability. While the external setting operation may precede the internal setting operation, the preferred sequence is treatment with a reducing agent followed by leveling and full-decating (internal stabilization) and then conducting the external setting operation.

The term "leveling" as employed herein is meant to include any of those finishing operations commonly employed in the textile art to level and flatten the texture of a keratinous fiber containing fabric. More specifically, the type of leveling operation contemplated by this invention is a leveling operation of the type employing heat, pressure and time with or without moisture, an example of such an operation being a simple pressing operation which may be conducted with devices such as, for instance, fixed presses, rotary presses, paper presses, or calenders. In general, leveling pressures of from 50 p.s.i. to 50,000 p.s.i. and leveling temperatures of from 70° F. to 350° F. may be employed, preferably temperatures of from about 100° F. to 350° F. and pressures from 1000 p.s.i. to 50,000 p.s.i. are employed. In the event that leveling operations are conducted by passage of the fabric into the nip of a pair of rolls, it is preferred to refer to pressures in terms of pounds per linear inch. Where a pair of pressure rolls are employed pressures in the range of from about 200 to 3,500 pounds per linear inch and preferably from 500 to 3,000 pounds per linear inch are desired.

A better understanding of the invention may be had from a description of the drawings wherein:

FIGURE 1 is a graph plotting percentage total area shrinkage against washing temperature in degrees Fahrenheit for washed prior art stabilized fabric and washed fabrics stabilized according to this invention.

FIGURE 2 is a graph plotting percentage total area shrinkage against washing temperature in degrees Fahrenheit for washed and tumble dried prior art stabilized fabric and washed and tumble dried fabrics stabilized according to this invention.

Turning to FIGURE 1, all of the fabric samples employed in the preparation of the graph are 100% wool twill weave fabrics having 30 ends per inch and 29 picks per inch prepared from 4.0 run 11 turns per inch "S" twist warp and fill yarns the fabric having a loom width of 74.5 inches and a finished weight of about 10½ ounces per yard. The sample designated by the solid line bearing the legend permanganate stabilized is a fabric treated by a process which is representative of the prior art.

More specifically, this process is known as the SI-RO-NIZE process and is carried out by shrinkproofing the wool fabric with potassium permanganate in concentrated

sodium chloride solution, the manganese dioxide being then removed with sodium bisulphite. The shrinkproofed fabric is then treated with a 1% sodium bisulphite solution so as to result in a pickup of 50% by weight and the treated fabric steamed for 5 minutes on a blowing machine.

The sample designated by the dotted line and bearing the legend post dyed internal and external stabilized is a fabric prepared according to this invention and more specifically prepared according to Example I. The fabric designated by the broken and dotted line bearing the legend pre-dyeing internal and external stabilized is a fabric prepared according to this invention and more specifically prepared according to Example II. As can be seen from FIGURE 1, those fabrics which have undergone internal stabilization prior to external stabilization exhibit stability to washing, the stability being more pronounced in the fabric that was pre-dyed prior to stabilization as opposed to the fabric which was post dyed. Both the internal and external stabilized fabrics were far superior to that fabric which is representative of the prior art. The values necessary in characterizing the stability of the fabrics were obtained by subjecting the fabrics to 10 washing cycles in home automatic washing machines at varying degrees of washing temperatures and then measuring the area shrinkage.

FIGURE 2 of the drawings is illustrative of the dimensional stability of the same fabrics set forth in FIGURE 1 with the exception that the degree of dimensional stability is evaluated for fabrics undergoing tumble drying as well as washing cycles. It can again be noted that those fabrics which were subjected to internal stabilization operations prior to an external stabilization operation exhibited superior stability to that fabric which is representative of the prior art. It can also be noted that the pre-dyed internal and subsequent external stabilized fabric exhibited a superior dimensional stability over the post dyed sample.

The external setting of the keratinous fiber containing fabrics of the invention is preferably accomplished by means of a polymeric chemical reagent. Typical examples of such setting processes are additive type shrinkproofing 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 other keratinous fiber may also be accomplished by means of coating the fibers with a nonreactive 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 Region 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 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 systems, such as those involving the formation of poly(hexamethylene sebacate) through interfacial polymerization techniques, treatments with reactive terpolymers based on vinyl type monomers, treatments with polyepoxide-polyamine compositions, treatments with reactive polyurethanes and treatments with emulsions of certain acrylic esters such as, for instance, polymethylmethacrylate, polyethylmethacrylate, polypropylmethacrylate and polybutylmethacrylate.

The use of polymeric external stabilizing reagents in combination with reducing agents as set forth herein has many advantages, including better shrinkage control than is feasible with the monomeric reagents. The polymeric reagents, most importantly however, provide better appearance retention, such as more pronounced creases or other configurations, better surface qualities, such as luster, and better flat dry ratings, than are possible with other types of reagents. These compounds also may actually increase, rather than decrease, the strength of the fabrics so treated.

This advantages are particularly evident in the use of isocyanate reaction products, which constitute highly preferred embodiment of the present invention.

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 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 following the isocyanate on the fabric in situ.

Regardless of the system utilized, however, it is preferred that the ratio of isocyanate to active hydrogen compounds in the system be at least about 0.4, but more preferably, greater than 1.0, e.g., from about 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 with a minimum amount of reagent, permitting washing with little or no degradation of hand, or feel, of the fabric. Surprisingly, configurations imparted to such fabrics by prior 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 a stiffening effect on fabrics so treated.

By "pre-polymer" as employed 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 components and particularly the chlorinated hydrocarbons.

When the prepolymer 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.

Among the suitable isocyanates that may be used in accordance with this invention are included aryl diisocyanates such as 2,4-tolylene diisocyanate, 2,6-tolylene 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 - methylphenylene - 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; alicylic 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 aryldiisocyanates are preferred because of their solubility and availability.

Additional isocyanates include polymethylenediisocyanates and diisothiocyanates, and such ethylene diisocy-

anate, 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 diisocyantes 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

$$(C_5H_6CH(NCO)CH_2NCO)$$

diiosocyanates and diisothiocyanates and containing heteroatoms such as $SCNCH_2OCH_2NSC$,

$$SCNCH_2CH_2OCH_2CH_2NSC$$

and $SCN(CH_2)_3—S—(CH_2)_3NSC$; 1,2,3,4 - tetraisocyanatobutane, butane - 1,2,2-triisocyanate, toluylene-2,4,6-triisocyanate, toluylene-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, toluylene-2,4-diisocyanate is preferred.

Any of the above isocyanate-terminated compounds, either in pre-polymer or monomer form (as in the "one-shot" technique) may be blocked if desired, as with phenols or any of the well known blocking agents for isocyanates. The blocking group is activated by heat and driven off to provide available isocyanate groups for reaction with the functional groups of keratin fibers.

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 polyalkylene-aryleneether-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 substitutents may be present, such a 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 radical having a molecular weight of about 500 for each arylene radical 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 polyhydroxy 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; octadecanedioic acid; 8-octadecenedioic acid; ricinoleic acid; 6,8-octadecadienedioic acid; malic; and the like. Other acids include unsaturated acids such as maleic, fumaric, glutaconic, and itaconic; the cycloalkane dicarboxylic acid such 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 or ricinoleic acid, and ricinoleyl alcohol, and mixtures thereof.

Represenative 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, 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.

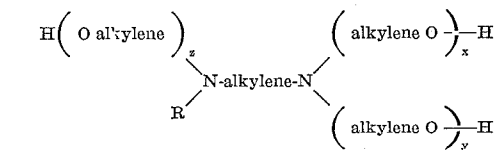
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Additional polyesters include those obtained by reacting one or more of the above acids with a mixture of polyhydric alcohols comprising (1) polyhydric alcohols of the general formula:




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).

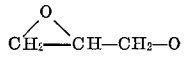
The polyepoxides used in accordance with the invention are organic compounds having at least two epoxy groups per molecule and may be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic and may be substituted with non-interfering substituents such as hydroxyl groups, ether radicals, 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 triflouride 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, epidohydrin, 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; 1,2-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-tetrakis (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 resorcinal and diglycidyl ether, the reaction product of catechol and diglycidyl ether, and the reaction product of 1,4-dihydroxy-cyclohexane and diglycidyl ether.

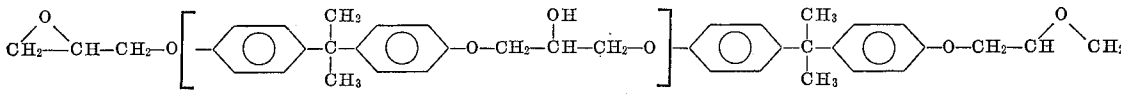
Polyepoxides which do not contain ether groups may

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 of 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' - iminio - 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, betamethyl 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. 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 polyamide, 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'-isopropylidenediphenol with one of the aforementioned alkylene oxides.

Any suitable hydrogenation product of olefins-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 polyfuntional 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 catalyst 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 preferably are applied to the keratinous fiber containing fabric in the form of a solution, the solution employing a non-reactive solvent although aqueous emulsions may be utilized if desired. 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, suf-

ficient components remain reactive with the keratin fibers to provide adequate inhibition of shrinkage and/or setability 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, oxylene, 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, dimethyl sulfoxide, 2,2,4 - trimethyl - pentane and the like. Mixtures of solvents may be used.

The internal setting of the keratinous fibers is preferably accomplished by means of a chemical reagent which has the ability to rupture polymeric linkages, particularly disulfide linkages, within the structure of keratin. These ruptured linkages may be at least partially reformed while holding the keratinous fiber in the desired configuration, thereby setting this configuration durably in the fiber. 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 linkage and reformation of hydrogen bonds and hydrophobic 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 and/or hydrophobic bonding. These changes in location of cystine linkages and changes in hydrogen and/or hydrophobic 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 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 to some extent 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 alkanolamine 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, dimethyl hexanolamine 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, titanous 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 $\beta$-mercapto ethanol; and mixtures of these reducing agents.

Particularly beneficial results are 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, dimethyl sulfoxide, 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 hydroxy 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 accordance with this invention.

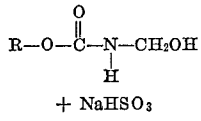
The reducing agent with or without the auxiliary agent or polyhydroxy compound may be applied to the fabric in any desired amount, depending upon the degree of reducing desired. In general, optimum results are obtained when aqueous solutions containing from about 0.01 to about 20% by weight and most 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.

The reducing agent may be applied to the fabric by methods such as, for instance, spraying padding, squeezing, simple immersion, and wetting with blankets saturated with reducing solutions. It is desirable that the reducing agent treated fabric be given time for the reducing agent to distribute and react before the fabric is subjected to lustering operations. After the reducing agent treated fabric has been aged, it is preferably dried, the drying operation being sufficient to reduce the moisture content of the fabric to the point that substantial setting of the fabric is not accomplished prior to the decating operations. In some instances, however, a special finish may be imparted by allowing sufficient moisture to remain in the fabric to accomplish partial setting of the fabric in a leveling operation, the complete permanent setting preferably being accomplished by a full-decating operation. The preferred leveling operation is a calendering operation.

The calendering operation is preferably carried out at elevated temperatures, that is from about 100° F. to about 350° F. and most preferably from about 250° F. to 300° F. Calendering pressures are in the range of from about ½ ton per linear inch to about 2 tons per linear inch and preferably from about 1 ton per linear inch to about 1½ tons per linear inch. The upper limit for calendering pressures may be higher, the only real limitation imposed is the maximum pressure which may be obtained from calendering apparatus. It should be understood that the calendering operation is always carried out under conditions which will produce chiefly a temporary setting with little or no permanent setting of the keratinous fibers of the fabric. The calendered fabric is then sent into the preferred full-decating operation, the full-decating operation employing a steam interval of from about 1 minute

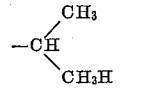
utes to about 6 minutes and a vacuum interval of from about 2 minutes to about 60 minutes and preferably from about 10 minutes to about 30 minutes. The steaming operation is carried out at autoclave pressures of from about 1 p.s.i. to about 100 p.s.i. gauge and preferably from about 15 p.s.i. gauge to about 40 p.s.i. gauge. The steam pressures, of course, will also determine the temperatures employed.

It is preferred that the stabilized fabric of this invention be subjected to an aldehyde treatment in order to enhance still further the durability of the finished product. The aldehyde may be present in the reducing agent both in the form of an organic compound which releases aldehyde on thermal decomposition at temperatures such as are encountered in full-decating operations or may be applied as a separate operation subsequent to the reducing agent treatment. The fabric must, however, be in its preferred configuration 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 thruogh 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:



+ $NaHSO_3$

wherein R is a member selected from the group consisting of (1) $-CH_3$ (2) $-C_2H_5$

(3) 

(4) —n-butyl (5) —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 degraded compound. For this reason, it is preferred that inorganic reducing agents be employed in conjunction with the thermally degradable compound.

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, propiolaldehyde, 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-chlorobenzaldehyde, o-nitrobenzaldehyde, m-nitrobenzaldehyde, p-nitrobenzaldehyde, salicylaldehyde, anisaldehyde, vanillin, veratraldehyde, piperonal, α-naphthaldehyde, antraldehyde 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

$HO(CH_2O)_n.H$

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 ethers, 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 solutions.

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 of aralkyl. These compounds hydrolyze to formaldehyde and the parent alcohol. Preferred formals include methylol and 1,3-dioxolane. The latter compound hydrolyzed 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-methylolacrylamide 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 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, cellulosic fiber and the like, or with synthetic fibers, such as synthetic cellulosic fibers including acetylated cellulose, for example, the cellulose acetates, acetylated rayon, rayon per se and the like; polyamides, particularly nylon, both 6 and 66 types; polyesters, such as polyethylene terephthalate and the like; polyolefins, 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 fibers, for example at least about 20%, preferably at least about 40%, by weight be present in the substrates being treated.

The following examples of the preparation of the internally and externally stabilized fabric 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

An all wool twill weave fabric (10.5 oz./linear yard—60 inches wide) which has been preconditioned to remove excess residual oils, sizes and vegetable matter and which has been prepared by mechanical wet finish techniques to impart desired bulking or other properties is padded with a solution of 2.6% sodium bisulfite, 2.85% diammonium phosphate and 0.25% Syn-O-Wet HR (anionic surface active agent marketed by Syn-Chem Corporation) to 70% wet pickup and dried at 225° F. to approximately 10% moisture regain. The fabric is then calendered in a conventional roll calender at 80 tons

pressure across 72 inch roll-face and at a roll temperature of 280° F. This flattened fabric is then placed in a full decater package and autoclaved at 12 p.s.i. gauge steam using a cycle of 5½ minutes penetration followed by 2½ minutes outside to inside steam flow and 2½ minutes inside to outside steam flow. The entire autoclave package is then subjected to vacuum pumping for 20 minutes.

A polymeric coating composition is then prepared as follows: Into a jacketed stainless steel reactor is poured 225 pounds of polypropylene glycol adduct of glycerin having a molecular weight of about 5000. 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 pounds 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 pre-polymer solution has a color of from colorless to a very pale straw color.

A 3% solution is then prepared from a 70% solution of pre-polymer by dilution with trichloroethylene and the fabric padded to a wet pickup of 100%, the pad bath containing Quadrol (N,N,N',N'-tetrakis 2-hydroxy propyl ethylene diamine marketed by Wyandotte Chemical Corporation), the fabric being dried at about 160° F. and cured at about 260° F. The fabric thus treated is allowed to set for 16 hours. scoured in a cascade washer and then placed in a dyebeck for dyeing. After dyeing with normal wash-fast wool dyeing techniques, the fabric is then dried, padded with a 5.5% solution of formalin (2.0% formaldehyde) to approximately 70% wet pickup and dried at 225° F. to a moisture regain of 10%. After drying the fabric is full decated at 12 p.s.i. for 3 minutes, pumped for 10 minutes and inspected. The resulting fabric has excellent dimensional stability and finish stability to home laundering at 140° F. in a Kenmore Model 600 washing machine less than 1 year old, set at the Normal cycle and containing 10 grams of Tide detergent.

## EXAMPLE II

The procedure of Example I was again repeated with the exception that the fabric was dyed prior to application of the solution of 2.6% sodium bisulfite. The finished product is found to have excellent dimensional stability and finish stability to home laundering at 140° F. in a Kenmore Model 600 washing machine less than 1 year old, set at the Normal cycle and containing 10 grams of Tide detergent.

## EXAMPLE III

The procedure of Example I is again repeated with the exception that the application of the 5.5% solution formalin is omitted. The resulting fabric is found to have good dimensional stability and finish stability to home laundering at 140° F. in a Kenmore Model 600 washing machine less than 1 year old, set at the Normal cycle and containing 10 grams of Tide detergent.

## EXAMPLE IV

The procedure of Example II is again repeated with the exception that the application of the 5.5% solution of formalin is omitted. The resulting fabric is found to have good dimensional stability and finish stability to home laundering operations at 140° F. in a Kenmore Model 600 washing machine less than 1 year old, set at the Normal cycle and containing 10 grams of Tide detergent.

## EXAMPLE V

A 55% Acrilan (acrylic fiber marketed by Chemstrand Division of Monsanto Co.)/45% woolen flannel fabric which has been preconditioned to remove excess residual oils, sizes and vegetable matter and which has been prepared by mechanical wet finish techniques to impart desired bulk and then placed in a dyeing beck for dyeing with normal wash-fast wool dyeing steps. The fabric is then padded, dried and cured with the urethane polymer according to procedure set forth in Example I. The fabric is allowed to stand for 11 hours and then scoured in a cascade washer. The fabric is then padded with a solution of 6.4% monoisopropanolamine sulfite, 2.85% diammonium phosphate and 0.25% Syn-O-Wet HR to 70% wet pickup and dried at 225° F. to approximately 10% moisture regain. The fabric is then calendered in a conventional roll calender at 80 tons pressure across 72 inches roll face and at a roll temperature of 280° F. The flattened fabric is then pressed in a full decater package autoclaved at 12 p.s.i. gauge steam using a cycle of 5 minutes penetration followed by 2 minutes outside to inside steam flow and 2 minutes inside to outside steam. The entire autoclave package is then subjected to vacuum pumping for 20 minutes. The final product is found to have good dimensional and finish stability to home laundering at 140° F. in a Kenmore Model 600 washing machine less than 1 year old, set at the Normal cycle and containing 10 grams of Tide detergent.

## EXAMPLE VI

The procedure of Example V was again repeated with the exception that the fabric was dyed as a final operation subsequent to the full-decating operation. The final product is found to have good dimensional and finish stability to home laundering at 140° F. in a Kenmore Model 600 washing machine less than 1 year old, set at the Normal cycle and containing 10 grams of Tide detergent.

## EXAMPLE VII

The procedure of Example V was again repeated with the exception that prior to full-decating the fabric is dried, padded to 5.5% wet pickup with formalin (2.0% formaldehyde) and dried at 225° F. to a moisture regain of 10%. The final product is found to have excellent dimensional and finish stability to home laundering at 140° F. in a Kenmore Model 600 washing machine less than 1 year old, set at the Normal cycle and containing 10 grams of Tide detergent.

## EXAMPLE VIII

A 55% polyester/45% wool worsted fabric is padded with 2.6% sodium bisulfite, 2.8% diammonium phosphate and 0.25% Syn-O-Wet HR. This fabric is dried at 225° F. to 8% moisture regain, calendered at 50 tons pressure across 72 inch face rolls, placed in a full decater package and autoclaved for 5 minutes. The package is subsequently pumped for 15 minutes. The fabric is then treated with the urethane polymer as in Example I, scoured and dyed with normal wash-fast polyester and wool dyeing techniques and dyestuffs. After dyeing and drying the fabric is padded with a solution of 5% available formaldehyde in the form of a 25% solution of N-methylol methylcarbamate, dried at 200° F. to 8% moisture regain, placed in a full decater

package and autoclaved for 5 minutes after penetration. The fabric shows excellent dimensional and finish stability to washing in a Kenmore Model 600 washing machine less than 1 year old, set at the Normal cycle and containing 10 grams of Tide detergent and tumble drying at 180° F. in a Kenmore Model 600 dryer.

## EXAMPLE IX

The procedure of Example VIII is again repeated with the exception that in place of treatment with the urethane polymer, the fabric is immersed in a 3.3% aqueous solution of polyaminocaproic acid diethyl amino ethynol 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., cured at 130° C. for 15 minutes, scoured and dyed. After undergoing the remaining portion of the treatment, the fabric is found to have excellent dimensional and finish stability to washing in a Kenmore Model 600 washing machine less than 1 year old, set at the Normal cycle and containing 10 grams of Tide detergent and tumble drying at 180° F. in a Kenmore Model 600 dryer.

## EXAMPLE X

The procedure of Example VIII is again repeated with the exception that in place of treatment with the urethane polymer, the fabric is 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-epoxypropoxy phenyl) propane was 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 methylether 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 fabric 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., scoured and dyed. After undergoing the remaining portion of the treatment, the fabric is found to have excellent dimensional and finish stability to washing in a Kenmore Model 600 washing machine less than 1 year old, set at the Normal cycle and containing 10 grams of Tide detergent, and tumble drying at 180° F. in a Kenmore Model 600 dryer.

## EXAMPLE XI

An all wool, twill weave, dyed fabric is treated as in Example I with the reactive polyurethane thereof, except that the pretreatment with the sodium bisulfite solution and post-treatment with formalin is eliminated, but wherein all other procedures, including calendering, steaming and decating are utilized. This fabric is designated Fabric A in Table I below.

The procedures utilized in producing Fabric A are repeated on an additional sample of fabric, except that the formalin post-treatment technique of Example I, including decating, is utilized. The fabric so produced is designated Fabric B in Table I below.

An additional sample of the all wool twill weave fabric is treated with a sodium bisulfite solution and calendered and steamed as set forth in Example I. No pre-polymer or formalin treatments are conducted. This fabric is designated Fabric C in Table I below.

The procedures utilized to produce Fabric C are repeated on an additional fabric sample except that the formalin post-treatment, including decating, is utilized. This fabric is designated Fabric D in Table I.

On additional samples of the all wool fabric, the procedures of Example I are reproduced, with and without the formalin post-treatment. These fabrics are designated Fabrics E and F, respectively, in Table I.

The procedures of Example I are repeated on additional samples of fabric except that the reactive polymer treatment is conducted prior to the levelling and reducing agent treatments, and with and without the formalin post-treatment. These fabrics are designated Fabrics G and H in Table I.

The procedures of Example I are repeated on another sample of the all wool fabric, except that a 3% solution of Zeset TP (believed to be the terpolymer of ethylene, vinyl acetate and methacroyl chloride) is substituted for the pre-polymer solution, and except that the formalin post-treatment is not conducted. This fabric is designated Fabric I in Table I.

Samples of each of the above fabrics are washed ten (10) times under the conditions of Example I, after which the Flat Dry rating for spin performance is measured by the standard appearance test using overhead lighting on vertically hanging fabrics. The fabrics are rated from 1.0 (poorest) to 6.0 (best). The shrinkage of these samples in both warp and filling directions also is measured.

Additional samples of each fabric are subjected to ten (10) washing and drying cycles, the washing being performed as in Example I and drying as in Example VIII. The Tumble and Flat Dry rating and shrinkage are measured after these cycles. Furthermore, the fabrics are rated by objective observers to determine the degrees to which the initial lustrous appearance of the fabric is retained.

All the above measurements are set forth in Table I.

TABLE I

| Fabric | Flat dry | | Washing shrinkage | | Washing and tumble drying shrinkage | | Luster retained, percent |
|---|---|---|---|---|---|---|---|
| | Spin | Tumble | Warp | Fill | Warp | Fill | |
| Fabric A-Reactive pre-polymer, no reducing agent, no HCHO | 4.0 | 5.0 | 3.0 | 2.3 | 4.2 | 3.1 | None |
| Fabric B—Reactive pre-polymer, no reducing agent, with HCHO | 4.2 | 5.0 | 3.8 | 2.1 | 4.2 | 3.1 | None |
| Fabric C—Reducing agent, no prepolymer, no HCHO | 4.9 | 5.0 | 36.0 | 27.0 | 40.0 | 25.0 | None |
| Fabric D—Reducing agent, no pre-polymer, with HCHO | 4.9 | 5.0 | 36.1 | 27.0 | 39.5 | 25.5 | None |
| Fabric E—Reducing agent, reactive pre-polymer, HCHO | 4.5 | 5.0 | 1.8 | 1.0 | 2.0 | 1.8 | 90 |
| Fabric F-Reducing agent, reactive pre-polymer, no HCHO | 4.5 | 5.0 | 1.0 | 0.6 | 3.0 | 4.8 | 60 |
| Fabric G—Reactive pre-polymer, reducing agent, HCHO | 4.4 | 5.0 | 4.5 | 0.8 | 5.2 | 1.2 | 90 |
| Fabric H—Reactive pre-polymer, reducing agent, no HCHO | 4.5 | 5.0 | 1.0 | 0.7 | 3.9 | 4.1 | 70 |
| Fabric I—Reducing agent, Zeset TP, no HCHO | 4.8 | 5.0 | 3.8 | −1.3 | 5.2 | −0.6 | 90 |

The minus values of shrinkage of Fabric I indicates that the fabric stretched to the levels shown.

## EXAMPLE XII

An all will twill weave fabric is impregnated with an aqueous solution containing 1% hexamethylene diamine, 2% sodium metasilicate and 0.05% Triton X–100 (isooctylphenol reacted with 9 to 10 ethoxy groups) to a wet pickup level of 70%. The wet fabric is then immersed in a 3% solution of sebacoyl chloride in Solvesso 100 (a

mixture of aromatic hydrocarbons) to an additional wet pickup of 20%.

After scouring for 15 minutes at 120° F. with a 1% solution of formic acid containing 0.1% Triton X–100, the fabric is rinsed in clear water for 5 minutes at 120° F. and dried.

The externally stabilized fabric is then padded to 20% wet pickup with an aqueous solution containing 2% sodium bisulfite and 0.1% Syn-O-Wet HR. After drying at 200° F., the fabric is full-decated according to the conditions of Example I, then washed, tumble dried and tested as in Example XI. After washing ten (10) times, the shrinkage values in the warp and filling directions are 2.6 and 5.2, respectively. Corresponding values after washing and tumble drying ten (10) times are 5.6 and 7.4, respectively. The Spin and Tumble Flat Dry ratings are, respectively, 4.3 and 4.9. Visual observation indicated about 60% of the lustrous finish was retained.

Having thus disclosed the invention, what is claimed is:

**1.** A process for imparting laundry durable dimensional and finish stability to fabrics containing at least some keratinous fibers, 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 fabric with a reducing agent capable of rupturing the cystine linkages of the keratin fiber,

(c) leveling the reducing agent treated fabric at a temperature and pressure insufficient to permanently set the fibers, and

(d) decating the leveled fabric.

**2.** The process of claim **1** wherein the reducing agent treatment precedes the polymer treatment.

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

**4.** The process of claim **3** wherein the urethane polymer contains free isocyanate groups.

**5.** The process of claim **1** wherein the polymer is a reactive polyethylene.

**6.** The process of claim **1** wherein the leveling is produced by a calendering operation.

**7.** The process of claim **6** wherein the calendering is conducted at a temperature between about 100° and 350° F. at a surface pressure of from about 0.5 ton to 1.5 tons per linear inch.

**8.** The process of claim **1** wherein the decated fabric is subsequently treated with an aldehyde.

**9.** The process of claim **8** wherein the aldehyde is formaldehyde.

**10.** A fabric obtained by the process of claim **1**.

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