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3,814,578

TREATMENT OF TEXTILES WITH GLYCIDOL-MODIFIED POLYURETHANES

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No Drawing. Filed Jan. 14, 1972, Ser. No. 217,963

Int. Cl. D06m 3/08, 15/52

U.S. Cl. 8-127.6

7 Claims

ABSTRACT OF THE DISCLOSURE

Polyurethanes containing isocyanate groups are reacted with glycidol to prepare glycidol-modified polyurethanes useful for application to textile materials to improve their properties, e.g., to impart shrink resistance. Typical example: A polyether polyurethane containing free NCO groups is reacted with glycidol to yield a glycidol-modified polymer which is formed into an emulsion and applied to a textile material. The treated textile may be directly cured or the curing operation may be delayed until the fabric is manufactured into a finished garment.

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DESCRIPTION OF THE INVENTION

This invention relates to and has among its objects the provision of novel processes for treating textile materials and the products of such processes. A special object of the invention is the provision of such treatments involving the use of glycidol-modified polyurethanes whereby to provide such benefits as improved shrinkage resistance and permanent press qualities. Further objects and advantages of the invention will be evident from the following description wherein parts and percentages are by weight unless otherwise specified.

It is well-known in the art that many textile fibers exhibit poor dimensional stability. For example, laundering causes severe shrinkage of woolen textiles. This technical disadvantage seriously restricts the applications of wool in the textile industry and much research has been undertaken in order to modify the natural fibers in order to provide them with resistance to shrinking. Among the procedures advocated for this purpose are those wherein a polyepoxide and a compound containing a plurality of amino groups, typically a polyamine or a polyamino-polyamide, are co-applied to the textile. See U.S. Pats. 2,869,971 and 3,019,076.

We have found that a novel class of glycidol derivatives exhibits an unusual ability to improve the properties of textiles, particularly wool. Our agents are not only chemically distinct from those of the prior art, but also obviate problems inherent in the prior art techniques. Some of the significant advantages provided by our glycidol derivatives are listed below:

They provide effective shrinkproofing even when applied in small proportion to the textile material.

They are effective per se: Conjoint application of a polyamine or polyamino-polyamide is unnecessary. It may

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be noted in this connection that application of polyamines or polyamino-polyamides to wool is hazardous because these reagents tend to cause yellowing of the treated fibers. The compounds of the invention have the advantage that they do not cause yellowing of wool or other textile fibers. They do not adversely affect the resistance of the treated textiles to soils, and they do not adversely affect the ability to remove soil by conventional washing procedures. In contrast, textiles treated with the known epoxide compositions tend to become soiled more readily than the untreated textile, and on washing are subject to soil re-deposition problems.

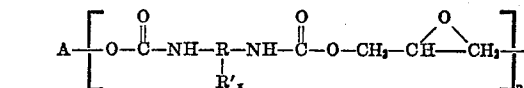
They are useful in applications involving delayed curing, that is, where the glycidol derivative is applied to the fabric, and the treated fabric cured only after a considerable delay, for example, after the treated fabric has been manufactured into a garment. This permits the compounds of the invention to be used in conjunction with agents which provide permanent press qualities to the textile. The particular advantage of the present invention which makes it especially adapted to such use is that our glycidol derivatives do not undergo spontaneous curing; they remain in the uncured state even after long storage of the treated fabric. In contrast, prior art treatments with epoxides and polyamines or polyamino-polyamides cannot be used in delayed curing systems because they undergo spontaneous curing when held at room temperature even a few days.

Dispersions of the compounds of the invention exhibit a long pot-life so that a single batch of the dispersion may be prepared for treating large amounts of textile material. In contrast, prior art formulations of epoxides and polyamines or polyamino-polyamides have a short pot-life in that they tend to gel and become useless in a short time.

They do not affect the intrinsic properties of the fibers such as color, tensile strength, abrasion resistance, flexibility, hand, porosity, etc. so that the treated fibrous materials can be employed in any of the usual textile applications as in fabricating shirts, skirts, trousers, and other garments, blankets, draperies, carpets, etc.

The compounds of the invention may aptly be termed as glycidol-modified polyurethanes, and have the structure:

(Formula I)

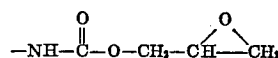


wherein:

A is the residue of a polyether polyol or polyester polyol having a valence of n ,

R is a hydrocarbon radical containing at least two carbon atoms,

R' is hydrogen, halogen, lower alkoxy, or a radical of the structure—



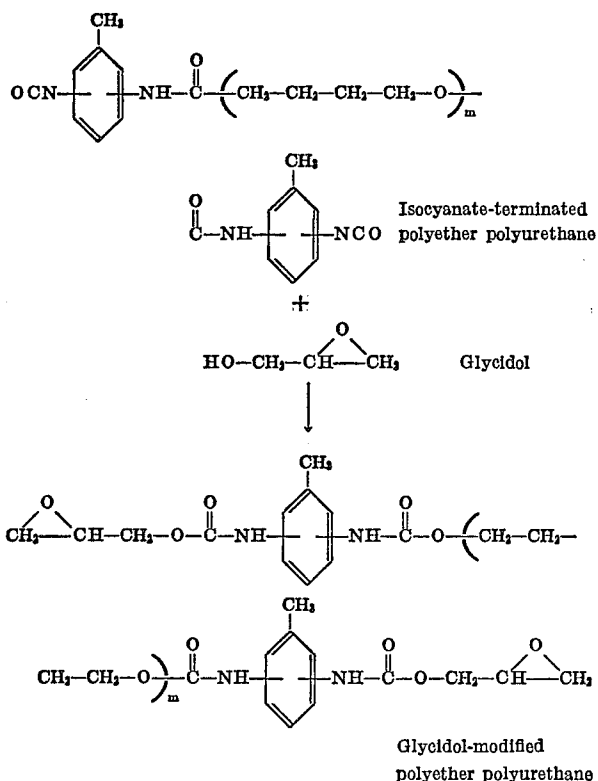
n is an integer from 2 to 4, and

x is an integer from 1 to 2.

The glycidol derivatives of the invention are prepared by reacting glycidol, in the presence of a suitable catalyst, with a polyether (or polyester) polyurethane containing free isocyanate groups. This simple reaction establishes the desired glycidol-modification of the starting polymer.

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A typical, but by no means limiting, example of the synthesis is illustrated below:



(In the above formulas, m represents the number of tetramethylene-ether repeating units. This may range, for example, about from 5 to 50.)

The reaction of the polyurethane and glycidol is carried out at about 50–70° C., and under essentially anhydrous conditions to avoid hydrolysis of the isocyanate groups. The glycidol is supplied in the amount necessary to obtain conversion of all the isocyanate groups to glycidyl groups. The reaction is promoted by the presence of catalysts such as dibutyltin dilaurate or an amine such as piperidine or combinations of these.

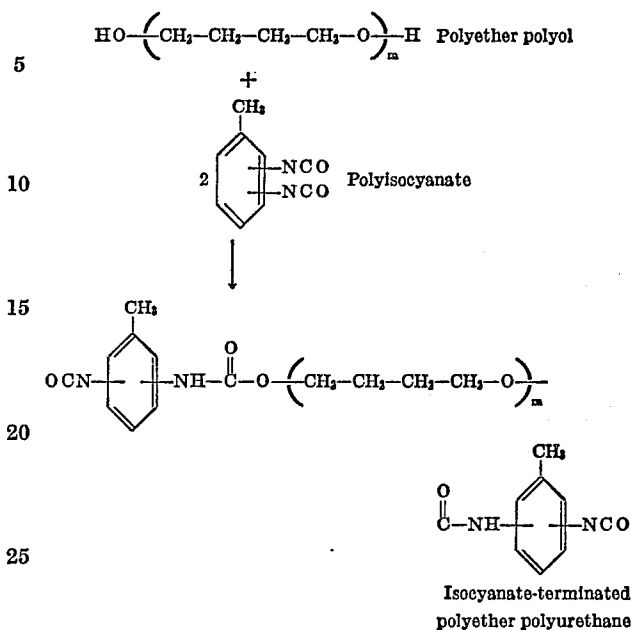
Referring to Formula I, above, it is evident that selection of the polymer intermediate—the polyether or polyester polyurethane containing free isocyanate groups—will determine the values of A , R , R' , n , and x . The preparation of these intermediates is well-known in the art; they are widely used in the production of urethane foams for padding and insulation applications, and in the production of elastomers. Although the preparation of these intermediates forms no part of the present invention, this subject will be explained below to illustrate the wide range of intermediates which may be employed in producing the glycidol derivatives of the invention. Thus, for the purposes of the invention, the intermediate may be any polyether or polyester polyurethane which contains at least two free NCO groups per polymer molecule. Preferred are the polymer intermediates having a molecular weight of at least 500, more preferably those having a molecular weight of at least 1000. Also, it is generally preferred to use the polyether-based polymers, for example, the NCO-containing polyurethanes derived from polyalkylene ether glycols such as polyethylene ether glycols, polytrimethylene ether glycols, polytetramethylene ether glycols, polypropyleneether glycols, and the like.

THE POLYMER INTERMEDIATES

Polyether (or polyester) polyurethanes containing free isocyanate groups useful as intermediates for the present invention may be prepared, as well-known in the art, by reacting a polyether (or polyester) polyol with a polyisocyanate, using an excess of the latter to ensure provision

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of free isocyanate groups in the product. A typical, but by no means limiting, example is illustrated below:



(In the above formulas, m represents the number of tetramethylene-ether repeating units. This may range, for example, about from 5 to 50.)

Representative examples of polyisocyanates which may be employed for reaction with the polyether (or polyester) polyol include:

- 35 toluene-2,4-diisocyanate
- toluene-2,6-diisocyanate
- commercial mixtures of toluene-2,4 and 2,6-diisocyanates
- ethylene diisocyanate
- 40 ethylidene diisocyanate
- propylene-1,2-diisocyanate
- cyclohexylene-1,2-diisocyanate
- cyclohexylene-1,4-diisocyanate
- m-phenylene diisocyanate
- 3,3'-diphenyl-4,4'-biphenylene diisocyanate
- 45 4,4'-biphenylene diisocyanate
- 3,3'-dichloro-4,4'-biphenylene diisocyanate
- 1,6-hexamethylenediisocyanate
- 1,4-tetramethylene-diisocyanate
- 1,10-decamethylenediisocyanate
- 50 1,5-naphthalenediisocyanate
- cumene-2,4-diisocyanate
- 4-methoxy-1,3-phenylenediisocyanate
- 4-chloro-1,3-phenylenediisocyanate
- 4-bromo-1,3-phenylenediisocyanate
- 55 4-ethoxy-1,3-phenylenediisocyanate
- 2,4'-diisocyanatodiphenylether
- 5,6-dimethyl-1,3-phenylenediisocyanate
- 2,4-dimethyl-1,3-phenylenediisocyanate
- 4,4'-diisocyanatodiphenylether
- 60 benzidinediisocyanate
- 4,6-dimethyl-1,3-phenylenediisocyanate
- 9,10-anthracenediisocyanate
- 4,4'-diisocyanatodibenzyl
- 3,3-dimethyl-4,4'-diisocyanatodiphenylmethane
- 65 2,6-dimethyl-4,4'-diisocyanatodiphenyl
- 4,4'-diisocyanatodibenzyl
- 2,4-diisocyanatostilbene
- 3,3'-dimethyl-4,4'-diisocyanatodiphenyl
- 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl
- 70 1,4-anthracenediisocyanate
- 2,5-fluorenediisocyanate
- 1,8-naphthalenediisocyanate
- 2,6-diisocyanatobenzofuran
- 2,4,6-toluenetriisocyanate, and
- 75 p,p',p''-triphenylmethane triisocyanate.

It is evident that the selection of the polyisocyanate reactant will determine the values of R and R' in Formula I. For example, where the reactant is a hydrocarbon diisocyanate, R will be a hydrocarbon radical and R' will represent a hydrogen atom forming part of said hydrocarbon radical. Where the reactant contains a substituent such as chlorine or methoxy—as would be the case with, for example, 4-chloro-1,3-phenylene diisocyanate or 4-methoxy-1,3-phenylene diisocyanate—R will be the hydrocarbon residue of the reactant and R' will be the substituent—chlorine or methoxy in the given examples.

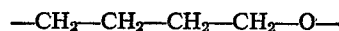
The polymer intermediates useful for the purposes of the invention may, in turn, be derived from any of a wide variety of polyether polyols and polyester polyols, and representative examples of these polyols are described below:

Among the polyether polyols which may be so used are those prepared by reaction of an alkylene oxide with an initiator containing active hydrogen groups, a typical example of the initiator being a polyhydric alcohol such as ethylene glycol. The reaction is usually carried out in the presence of either an acidic or basic catalyst. Examples of alkylene oxides which may be employed in the synthesis include ethylene oxide, propylene oxide, any of the isomeric butylene oxides, and mixtures of two or more different alkylene oxides such as mixtures of ethylene and propylene oxides. The resulting polymers contain a polyether backbone and are terminated by hydroxyl groups. The number of hydroxyl groups per polymer molecule is determined by the functionality of the active hydrogen initiator. For example, a difunctional alcohol such as ethylene glycol (as the active hydrogen initiator) leads to polyether chains in which there are two hydroxyl groups per polymer molecule. When polymerization of the oxide is carried out in the presence of glycerol, a trifunctional alcohol, the resulting polyether molecules contain an average of three hydroxyl groups per molecule. Even higher functionality—more hydroxyl groups—is obtained when the oxide is polymerized in the presence of such polyols as pentaerythritol, sorbitol, dipentaerythritol, and the like. In addition to those listed above, other examples of polyhydric alcohols which may be reacted with alkylene oxides to produce useful polyether polyols include:

propylene glycol
trimethylene glycol
1,2-butylene glycol
1,3-butanediol
1,4-butanediol
1,5-pentanediol
1,2-hexylene glycol
1,10-decanediol
1,2-cyclohexanediol
2-butene-1,4-diol
3-cyclohexene-1,1-dimethanol
4-methyl-3-cyclohexene-1,1-dimethanol
3-methylene-1,5-pentanediol
diethylene glycol
(2-hydroxyethoxy)-1-propanol
4-(2-hydroxyethoxy)-1-butanol
5-(2-hydroxypropoxy)-1-pentanol
1-(2-hydroxymethoxy)-2-hexanol
1-(2-hydroxypropoxy)-2-octanol
3-allyloxy-1,5-pentanediol
2-allyloxymethyl-2-methyl-1,3-propanediol
[(4-pentyloxy)methyl]-1,3-propanediol
3-(o-propenylphenoxy)-1,2-propanediol
thiodiglycol
2,2'-(thiobis(ethyleneoxy))diethanol
polyethyleneether glycol (molecular weight about 200)
2,2'-isopropylidenebis(p-phenyleneoxy)diethanol
1,2,6-hexanetriol
1,1,1-trimethylolpropane
3-(2-hydroxyethoxy)-1,2-propanediol
3-(2-hydroxypropoxy)-1,2-propanediol

2,4-dimethyl-2-(2-hydroxyethoxy)methylpentanediol-1,5
1,1,1-tris[(2-hydroxyethoxy)methyl]ethane
1,1,1-tris[(2-hydroxypropoxy)methyl]propane
triethanolamine
triisopropanolamine
resorcinol
pyrogallol
phloroglucinol
hydroquinone
4,6-di-tertiarybutyl catechol
catechol
orcinol
methylphloroglucinol
hexylresorcinol
3-hydroxy-2-naphthol
2-hydroxy-1-naphthol
2,5-dihydroxy-1-naphthol
bis-phenols such as 2,2-bis(p-hydroxyphenyl)propane
and bis-(p-hydroxyphenyl)methane
1,1,2-tris-(hydroxyphenyl)ethane
1,1,3-tris-(hydroxyphenyl)propane.

An especially useful category of polyether polyols are the polytetramethylene glycols. They are prepared by the ring-opening polymerization of tetrahydrofuran, and contain the repeating unit



in the polymer backbone. Termination of the polymer chains is by hydroxyl groups.

The polyester polyols which may be employed as precursors for the compounds of the invention are most readily prepared by condensation polymerization of a polyol with a polybasic acid. The polyol and acid reactants are used in such proportion that essentially all the acid groups are esterified and the resulting chain of ester units is terminated by hydroxyl groups. Representative examples of polybasic acids for producing these polymers are oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, brassylic acid, thapsic acid, maleic acid, fumaric acid, glutaconic acid, α -hydromuconic acid, β -hydromuconic acid, α -butyl- α -ethylglutaric acid, α,β -diethylsuccinic acid, o-phthalic acid, isophthalic acid, terephthalic acid, hemimellitic acid, trimellitic acid, trimesic acid, mellophanic acid, prehnitic acid, pyromellitic acid, citric acid, benzenepentacarboxylic acid, 1,4-cyclohexanedicarboxylic acid, diglycollic acid, thiodiglycollic acid, dimerized oleic acid, dimerized linoleic acid, and the like. Representative examples of polyols for forming these polymers includes ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 1,4-butylene glycol, 1,3-butylene glycol, 1,2-butylene glycol, butene-1,4-diol, 1,5-pentane diol, 1,4-pentane diol, 1,3-pentane diol, 1,6-hexane diol, hexene-1,6-diol, 1,7-heptane diol, diethylene glycol, glycerine, trimethylolpropane, 1,3,6-hexanetriol, triethanolamine, pentaerythritol, sorbitol, and any of the other polyols listed hereinabove in connection with the preparation of polyether polyols.

An interesting class of polyester polyols are those which include polyether units so that they may be considered as polyester polyols or as polyether polyols, depending on whether the ester or the ether groups are in majority. The compounds may be produced by the condensation polymerization of any of the above-mentioned polybasic carboxylic acids with a polyalkyleneether glycol—typically, a polyethyleneether glycol having a molecular weight of about 200 to 2000—using the glycol in the required proportion to assure termination by hydroxyl.

Esters of the hydroxyl-containing acid, ricinoleic acid, form another category of useful polyester polyols. Typically, one can use esters of ricinoleic acid with ethylene glycol, propylene glycol, glycerol, pentaerythritol, diglycerol, dipentaerythritol, polyalkyleneether glycols, and the like. Representative of this category of polyester polyols

is castor oil which is composed mainly of the tri-glyceride of ricinoleic acid.

APPLICATION OF THE GLYCIDOL DERIVATIVES TO THE TEXTILE

The compounds of the invention may be applied to the textile in various ways. One technique involves dissolving the compound in an inert, volatile solvent and applying the resulting solution to the textile material. Typical of the solvents which may be used are benzene, toluene, xylene, dioxane, diisopropyl ether, dibutyl ether, butyl acetate, chlorinated hydrocarbons such as chloroform, carbon tetrachloride, ethylene dichloride, trichloroethylene, 1,3-dichlorobenzene, fluorohydrocarbons such as benzotrifluoride, 1,3-bis-(trifluoromethyl)benzene, etc., petroleum distillates such as petroleum naphthas, etc. Usually it is preferred to apply the compounds in the form of aqueous emulsions. These can be prepared by customary techniques—agitation of the glycidol derivative with water and a conventional emulsifying agent such as an alkylphenoxypoly-(ethyleneoxy)ethanol, polyoxyethylene sorbitan monopalmitate, polyoxyethylene lauryl ether, polyoxyethylene - polyoxypropylene stearate, sorbitan monopalmitate, sorbitan monolaurate, and the like. The concentration of the glycidol derivative in the dispersion—this last term being herein employed in a generic sense to include solutions and emulsions—is not critical and may be varied depending on such circumstances as the solubility characteristics of the derivative, the amount thereof to be deposited on the fibers, the viscosity of the dispersion, etc. In general, a practical range of concentration would be from about 1% to about 25%.

The dispersion of the glycidol derivative will also contain a catalyst, whereby to promote curing (in a subsequent step) of the glycidol derivative to form an insoluble product *in situ* on the textile fibers. As the curing catalyst we prefer to use an acid or an acid-acting agent, that is, a substance not usually classified as an acid but which acts as such. Typical examples of curing catalysts are citric acid, acetic acid, acetic acid anhydride, butyric acid, caproic acid, phthalic acid, phthalic acid anhydride, tartaric acid, aconitic acid, oxalic acid, succinic acid, succinic acid anhydride, lactic acid, maleic acid, maleic acid anhydride, fumaric acid, glutaric acid, malonic acid, acetoacetic acid, naphthalic acid, trimellitic acid, phosphoric acid, sulfuric acid, boric acid, perchloric acid, persulfuric acid, and p-toluenesulfonic acid; metal salts, such as zinc fluoroborate, magnesium perchlorate, copper fluoroborate, zinc sulfate, zinc persulfate, zinc phosphate, ferrous perchlorate, nickel fluoroborate, manganese phosphate and strontium fluoroborate. Boron trifluoride is also a useful agent for the purpose, and is particularly preferred in the form of its adduct with piperidine, this adduct being soluble in organic solvents. In addition to the above-named substances, one can use any of the acid or acid-acting agents known in the art to promote the insolubilization of epoxides. The curing catalyst is generally employed in a proportion of about 1 to 20%, based on the weight of glycidol derivative in the dispersion.

The dispersions containing the ingredients described above may be distributed on the textile material by any of the usual methods, for example, by spraying, brushing, padding, dipping, etc. A preferred technique involves immersing the textile in the dispersion and then passing it through squeeze rolls to remove the excess of liquid. Such techniques as blowing air through the treated textile may be employed to reduce the amount of liquid which exists in interstices between fibrous elements. In any case, the conditions of application are so adjusted that the textile material contains the proportion of glycidol derivative desired. Generally, this amount is about from 0.5 to 20%, based on the weight of the textile material but it is obvious that higher proportions may be used for special purposes. In treating textiles such as fabrics the amount of glycidol derivative is usually limited to a range of about

0.5 to 10% to attain the desired end such as shrink resistance without interference with the hand of the textile.

After application of the glycidol derivative, the treated textile is cured (heated) to effect an insolubilization of the applied compound and to promote bonding thereof to the textile. Although the mechanism of bonding has not been identified, it is believed to involve chemical combination between the epoxy group of the glycidol moiety with active radicals in the textile substrate, these active radicals including carboxyl, hydroxyl, amino, and thiol groups. Such groups are, of course, present in many textile materials including wool, animal hair, leather, and other proteinaceous materials; cotton, rayon, linen, and other cellulosic fibers; nylon, polyurethanes, and many other synthetic fibers.

In cases where the glycidol derivative is applied as a dispersion, that is, a solution, emulsion, or suspension, the solvent or other volatile dispersing medium is preferably evaporated prior to the curing operation. Such prior evaporation is not a critical step and the evaporation may be simply effected as part of the curing step. The temperature applied in the curing step is not critical and usually is within the range from about 50° C. to about 150° C. It is obvious that the time required for the curing will vary with such factors as the reactivity of the selected glycidol derivative, the type of textile material, and particularly the temperature so that a lower curing temperature will require a longer curing time and vice versa. It will be further obvious to those skilled in the art that in any particular case the temperature of curing should not be so high as to cause degradation of the textile or the glycidol derivative. In many cases an adequate cure is effected by heating the treated textile in an oven at about 100° C. for about 5 to 60 minutes.

Although the present invention is of particular advantage in its application to wool, this is by no means the only type of fiber which comes into the ambit of the invention. Generically, the invention is applicable to the treatment of any textile material and this material may be in any physical form, e.g., bulk fibers, filaments, yarns, threads, slivers, roving, top, webbing, cord, tapes, woven or knitted fabrics, felts or other non-woven fabrics, garments or garment parts. Illustrative examples of textile materials to which the invention may be applied are: Polysaccharide-containing textiles, for instance, those formed of or containing cellulose or regenerated celluloses, e.g., cotton, linen, hemp, jute, ramie, sisal, cellulose acetate rayons, cellulose acetate-butyrate rayons, saponified acetate rayons, viscose rayons, cuprammonium rayons, ethyl cellulose, fibers prepared from amylose, algin, or pectins; mixtures of two or more of such polysaccharide-containing textiles. Protein-containing textiles, for instance, those formed of or containing wool, silk, animal hair, mohair, leather, fur, regenerated protein fibers such as those prepared from casein, soybeans, peanut protein, zein, gluten, egg albumin, collagen, or keratins, such as feathers, animal hoof or horn. Mixtures of any two or more protein-containing textiles. Mixtures of polysaccharide-containing textiles and protein-containing textiles, e.g., blends of wool and cotton; wool and viscose, etc. Textiles formed of or containing synthetic resins, e.g., alkyd resins, polyvinyl alcohol, partially esterified or partially etherified polyvinyl alcohol, nylon, polyurethanes, polyethylene glycol terephthalate, polyacrylonitrile, polyethylene, polypropylene, polyvinyl chloride, and polyvinylidene chloride. Blends of natural fibers such as cotton or wool with synthetic fibers such as nylon, polyethylene-glycol terephthalate, acrylonitrile, etc. Inorganic fibers such as asbestos and glass fibers. The applications of the teachings of the invention may be for the purposes of obtaining functional or decorative effects such as shrinkproofing, developing permanent crease qualities, sizing, finishing, increasing abrasion resistance, increasing gloss or transparency, increasing water-, oil-, and soil-repel-

lency, increasing adhesion or bonding characteristics of the substrates with rubber, polyester resins, etc.

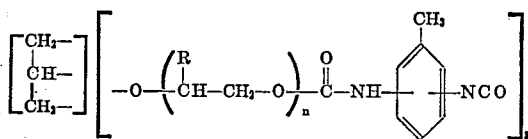
EXAMPLES

The invention is further demonstrated by the following illustrative examples.

Washing procedure for shrinkage tests: The samples were washed in a reversing agitator-type household washing machine, using a three-pound load, a water temperature of 105° F., and a low-sudsing detergent in a concentration of 0.1% in the wash liquor. The wash cycle itself was for 75 minutes, followed by the usual rinses and spin-drying. The damp material from the washer was then tumble-dried in a household-type clothes dryer. The dried samples were measured to determine their length and width and the shrinkage calculated from the original dimensions.

Example 1.—Preparation of Polymer A

The starting material for this synthesis was a commercial liquid polyurethane derived from a polyalkyleneether triol, having a molecular weight of about 3000 and an isocyanate (—NCO) content of 4%. It is believed to have the structure—

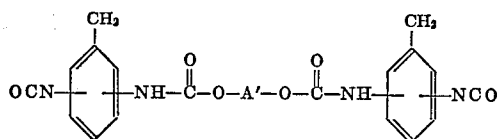


wherein R is CH₃ or H and *n* is about 18.

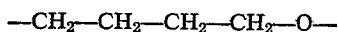
The polyurethane (200 g., providing approximately 0.2 mole of NCO) was dissolved in 300 g. of toluene. To this solution was added 15 grams (0.2 mole) of glycidol, followed by 5 drops of dibutyltin laurate and 100 mg. of triethylene diamine. The solution was heated at 65° C. overnight. At the end of this time, an infrared spectrum of the solution revealed no residual NCO groups. This indicated that the desired glycidol derivative had been achieved.

Example 2.—Preparation of Polymer B

The starting material for this synthesis was a commercial liquid polyurethane having a molecular weight of about 2000 and an isocyanate content of 6.5%. It is believed to have the structure—



wherein A' represents the residue of a polytetramethyleneether glycol containing about thirteen

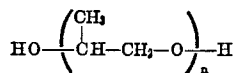


units.

The polyurethane (200 g., providing approximately 0.31 mole of NCO) was dissolved in 300 g. of toluene. To this solution there was added 23 g. (0.31 mole) of glycidol, followed by 5 drops of dibutyltin laurate and 100 mg. of triethylene diamine. The solution was heated at 65° C. overnight. At the end of that time, examination of the solution by infrared analysis revealed that all of the available —NCO had reacted with the hydroxy group of the glycidol.

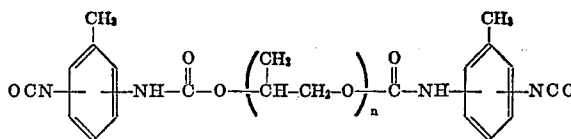
Example 3.—Preparation of Polymer C

The starting material for this synthesis was a polypropylene-ether glycol of molecular weight about 6000, and having the structure—



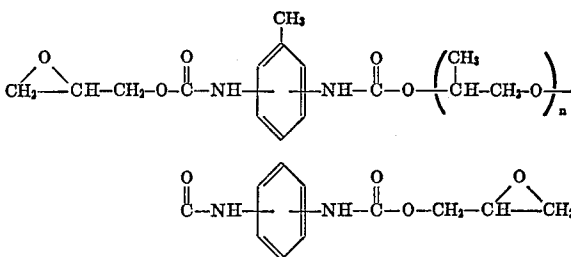
wherein *n* is about 100.

The glycol was reacted with toluene diisocyanate in conventional manner to produce an isocyanate-terminated polyurethane



wherein *n* is about 100.

The polyurethane intermediate was then reacted with glycidol in the same manner as described in Example 2 to yield the glycidol-modified polyurethane of the structure



wherein *n* is about 100.

Example 4.—Preparation of Polymer D

The starting material for this synthesis was a commercial polyester-based polyurethane having a molecular weight of 1900 to 2200, a viscosity of 90,000 cps. at 73° F., and an isocyanate content of 4%.

The polyurethane was reacted with glycidol in a manner similar to that used in Example 1 to produce the desired glycidol-modified polyurethane.

Example 5.—Preparation of Polymer Emulsion

This example illustrates the preparation of emulsions of the glycidol-modified polyurethanes.

To a 100-gram sample of a solution containing 40 g. of glycidol-modified polyurethane and 60 g. of toluene, there was added 2 g. of a commercial oil-soluble emulsifying agent—an alkylphenoxy poly(ethyleneoxy)ethanol. The mixture was stirred rapidly and 50 ml. of water were slowly added. The thick water-in-oil emulsion was transferred to a blender and, while stirring at high speed, there was added 200 ml. of water containing 2 g. of a water-soluble emulsifier—an alkylphenoxy poly(ethyleneoxy)ethanol. The resulting oil-in-water emulsion of the glycidol-modified polyurethane was used as a stock supply and diluted with water as necessary.

Example 6.—Application of Glycidol-Modified Polyurethanes to Fabrics

A brown-dyed worsted, 100% wool fabric was employed to test the effectiveness of various glycidol-modified polyurethanes. These polymers were applied either as solutions in an organic solvent or as aqueous emulsions. A catalyst (as indicated below) was added to the polymer solutions or emulsions. Samples of the fabric were wet-out with the polymer solution or emulsion, run through squeeze rolls to remove excess liquid and leave a wet pick-up of 50–80%. The fabrics were air-dried, then cured in an oven at 300° F. for 20 minutes. The treated fabrics were then washed in the manner detailed above and the shrinkage determined.

The materials used and the results obtained are summarized in the following table.

Solvent	Catalyst and amount thereof, percent based on weight of polymer	Add-on of polymer, percent based on weight of fabric	Area shrinkage after two 75-min. washes, percent
Polymer:			
A.....	CH ₃ -CCl ₃ ... BF ₃ .piperidine..	20	3
A.....	CH ₃ -CH ₂ OH... do.....	20	1
A.....	Aq. emulsion. Mg fluoborate...	20	3
A.....	do..... Zn fluoborate...	10	1
B.....	do..... Mg fluoborate...	20	2
C.....	CH ₃ -CCl ₃ ... BF ₃ .piperidine..	15	3
D.....	CH ₃ -CCl ₃ ... do.....	20	1
None (control).....			32

Example 7

An aqueous emulsion was prepared containing 3% of Polymer A and 0.6% of magnesium fluoroborate.

The emulsion was padded onto samples of worsted, 100% wool fabric which were then squeezed through rolls to a wet pick-up of 70%. After air-drying at room temperature, the fabrics were stored at 22° C. for one month.

At the end of this time, one sample of the treated fabric was at 310° F. for 20 minutes, then subjected to two 75-minute washes as above described. The area shrinkage was found to be 2%.

Another sample of the treated fabric, without any curing step, was subjected to the washing test. It was found that this uncured sample shrank 25% in area. This indicated that the applied polymer had remained inactive during the storage period.

Permanent Press

A particular embodiment of this invention is concerned with the production of wool products which exhibit not only shrink resistance but also permanent press qualities. Heretofore, it has been difficult to impart this combination of useful properties to wool. Existing wool shrinkproofing treatments do lead to dimensionally-stable fabrics; however, when the fabrics are washed or dry-cleaned they have a mussy appearance and must be pressed. Creases have been set in woolen garments by, for example, treatment with reducing agents such as ammonium thioglycolate or sodium bisulphite. The creases, however, do not withstand aqueous laundering nor generally more than 1 or 2 dry-cleanings. Of course, no shrinkproofing is attained with these creasing procedures. Attempts to combine wool shrinkage treatments with creasing treatments have not been successful in that although shrinkage can be controlled, creases are lost after aqueous laundering and the fabrics need ironing for neat appearance. Various materials such as melamine-formaldehyde resins, urea-formaldehyde resins, dihydroxy-ethylene dimethylol urea, or alkyl carbamates, which are commercially used in producing permanently creased garments of cotton or cotton-synthetic blends have proved entirely unsuccessful when applied to wool.

However, these problems are obviated by the present invention. By application of our glycidol derivatives to wool fabrics one attains resistance to shrinkage, a smooth wrinkle-free appearance after washing or dry-cleaning so that no ironing is required, and creases and pleats imparted to the fabric are permanent—they withstand repeated aqueous laundering or non-aqueous dry-cleaning.

This embodiment of the invention is most profitably practiced in a system which incorporates a delayed cure, that is, the glycidol derivative is applied to the fabric but curing is delayed until the fabric has been made up into the desired product which may be, for example, a completed garment. The curing then not only bonds the glycidol derivative to the fabric, but also renders permanent the creases or pleats which have been imparted to the fabric. Typical ways of practicing this embodiment of the invention are described in detail below:

The glycidol derivative is applied to the fabric, preferably using an emulsion of the glycidol derivative, as de-

scribed hereinabove. The conditions of application may be adjusted to vary the amount of glycidol derivative deposited on the fabric. Usually, it is preferred to deposit about 0.2 to 20%, based on the weight of the fabric. In a preferred modification of the invention, N-methylol acrylamide (hereinafter referred to as NMA) and an aldehyde-bisulphite is incorporated in the emulsion. However, as hereinafter explained, the NMA and aldehyde-bisulphite may be added at a later stage in the process. The treated fabric is then dried to remove the water in which the glycidol derivative and other agents were dispersed for the application step. The drying may be in air at ordinary (room) temperature, or, warm air may be applied to increase the rate of evaporation. To avoid premature curing, the temperature of the treated fabric should be kept below about 50° C. However, since curing does not occur immediately, short exposures to higher temperatures are permissible.

The fabric containing the glycidol derivative in its uncured state is then made up into the desired product. This may be, for example, a garment, in which case the fabric would be subjected to the usual garment-making operations of cutting, sewing, and pressing. Included in these operations would be formation of creases or pleats in selected areas by the usual pressing methods employed by the tailor. In the event that the NMA and aldehyde-bisulphite were not co-applied with the glycidol derivative, these agents may be applied to the textile during the moistening step which commonly forms a part of the pressing operation. For example, an aqueous solution of NMA and aldehyde-bisulphite may be sprayed onto the textile, particularly in those areas where it is intended to form creases or pleats. Enough of the solution is usually applied to furnish the following amounts (based on the weight of fabric): NMA—about 2 to 20%, preferably about 2 to 10%; aldehyde-bisulphite—about 0.5 to 10%, preferably about 2 to 4%. It is to be particularly emphasized that production of garments need not follow directly after application of the glycidol derivative to the fabric. Indeed, the fabric containing the uncured glycidol derivative can be held for long periods without danger of spontaneous curing. The glycidol derivatives of the invention are particularly characterized by their stability, i.e., their ability to remain in an uncured state for long periods of time. Moreover, their stability is not affected by moisture. If moisture is applied (as necessary in certain garment fabricating steps) there is no danger of premature curing.

The garment or other textile article is then subjected to a curing operation to insolubilize the glycidol derivative and bond it to the wool fibers. Typically, the curing is accomplished by placing the garments in an oven where they are maintained at a temperature and for a time sufficient to cause the desired curing effect. In general, temperatures of at least 50° C., preferably about 100–150° C., are applied for a period of about 5–60 minutes. The product after removal from the oven is now ready for use or for sale and, as previously noted, exhibits not only resistance to shrinkage when washed but also retains its pleats, creases, or other conformations imparted to the garment. Also, when washed, the products retain a neat appearance free from wrinkling or mussiness so

that they are truly press-free, i.e., no pressing is needed even after repeated washings.

The aldehyde-bisulphites used in accordance with the invention are known substances prepared by reacting an aldehyde with an alkali metal bisulphite, usually sodium bisulphite. Many different aldehydes may be used (in the form of their bisulphites), as for example: saturated aliphatic aldehydes such as formaldehyde, 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, 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, anthraldehyde, and the like; and aromatic aldehydes wherein the aldehyde group is not attached to a ring, such as phenylacetaldehyde, cinnamaldehyde, and the like; and heterocyclic aldehyde, such as α -formylthiophene, α -formylfurfural, furfural, tetrahydrofurfural, and the like. In general, we prefer to use glyoxal bisulphite.

Below are listed, by way of example, alternative techniques for practicing this embodiment of the invention.

Technique A:

1. Apply glycidol derivative to fabric.
2. Dry treated fabric and make up garment therefrom.
3. Spray garment with aqueous solution of NMA and aldehyde-bisulphite, for example, to an approximately 40-50% wet pick-up, using an aqueous solution containing about 5 to 10% of NMA and about 1 to 3% of aldehyde-bisulphite.
4. Steam-press garment to desired configuration.
5. Oven cure garment.

Technique B (preferred):

1. Apply to fabric an aqueous emulsion containing the glycidol derivative, NMA, and aldehyde-bisulphite. Typically, this emulsion will contain about 1 to 4% of the glycidol derivative, about 5 to 10% of NMA, and about 1 to 3% of aldehyde-bisulphite. To inhibit premature polymerization, it is preferred to add to the emulsion about 5 to 10% of a water-soluble alcohol such as methanol, ethanol, isopropanol, or the like.
2. Dry treated fabric and make up garment therefrom.
3. Spray garment with water, for example, to about 40-50% wet pick-up.
4. Steam-press garment to desired configuration.
5. Oven cure garment.

Technique B' (preferred):

1. Apply to fabric an aqueous emulsion containing the glycidol derivative and NMA. Typically, this emulsion will contain about 1 to 4% of the glycidol derivative and about 5 to 10% NMA.
2. Dry treated fabric and make up garment therefrom.
3. Spray garment with water containing about 1 to 4% aldehyde-bisulphite, to about 40-50% wet pick-up.
4. Steam-press garment to desired configuration.
5. Oven cure garment.

Technique C:

1. Prepare garment from fabric.
2. Apply to garment an aqueous emulsion containing the glycidol-derivative, NMA, and aldehyde-bisulphite.

3. Steam press garment while still damp from application of the emulsion.
4. Oven cure garment.

This embodiment of the invention is further demonstrated by the following illustrative example.

Example 8

An aqueous emulsion of 3.5% Polymer A was prepared as described in Example 5. This stock emulsion was then used to prepare a series of emulsions containing different aldehyde-bisulphites (as indicated in the following table) plus other ingredients, the same in each. Thus, each emulsion contained 3.5% of Polymer A (described in Example 1), 0.7% of zinc fluoroborate, 8% NMA, 2% aldehyde-bisulphite, and 10% (by volume) of ethanol.

A piece of worsted 100% wool slack fabric was cut into samples which were treated with the emulsions, using the following procedure in each case. The emulsion was padded onto the fabric which was then squeezed through rolls to a wet pick-up of 50%. While still damp, the fabrics were creased, using a tailor's hot-head press. The creased samples were then cured in an oven at 310° F. for 20 minutes.

The cured samples were then subjected to a series of washes (as described above) and tumble-dried after each wash. The samples were evaluated for smoothness and crease retention after one or more cycles of washing and tumble-drying.

Smoothness and crease retention were determined in accordance with AATCC Methods 88A-II-C and 88C-II-C, respectively. In these tests the evaluation is done by comparison with photographic standards and ratings are given from 1 to 5 with a rating of 1 being very poor and 5 being excellent.

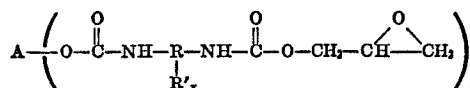
The results obtained are tabulated below.

Aldehyde-bisulphite used	No. of wash-dry cycles	Smoothness	Crease retention
Glutaraldehyde-bisulphite.....	1	4.2	4.8
Do.....	3	3.9	4.6
Do.....	5	3.6	4.6
Propionaldehyde-bisulphite.....	1	4.4	4.8
Do.....	3	3.6	4.6
Do.....	5	3.8	4.0
Furfural-bisulphite.....	10	4.2	3.6
Do.....	1	4.1	4.3
Do.....	3	3.8	4.0
Do.....	5	3.9	3.7
Do.....	10	4.0	4.1
Benzaldehyde-bisulphite.....	1	3.7	4.7
Do.....	3	3.7	4.5
Do.....	5	3.6	3.8
Do.....	10	4.4	3.8
Glyoxal-bisulphite.....	1	4.6	5.0
Do.....	3	4.4	4.7
Do.....	5	4.0	4.7
Do.....	10	4.6	4.9

Having thus described our invention, we claim:

1. A process of treating proteinaceous textile material to improve its properties, which comprises—

- (a) depositing on the textile material an aqueous emulsion containing about 5 to 10% of N-methylol acrylamide, about 1 to 3% of an aldehyde-bisulphite, and about 1 to 4% of a glycidol-modified polyurethane of the structure



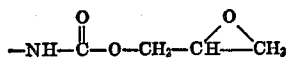
wherein:

A is the residue of a polyether polyol or polyester polyol having a valence of n ,

R is a hydrocarbon radical containing at least two carbon atoms,

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R' is hydrogen, halogen, lower alkoxy, or a radical of the structure



n is an integer from 2 to 4, and

x is an integer from 1 to 2,

(b) and curing the so-treated textile material by heating it at about 50 to 150° C.

2. The process of claim 1 wherein A is the residue of a polyalkyleneether glycol and n is 2.

3. The process of claim 1 wherein A is the residue of a polyalkyleneether triol and n is 3.

4. The process of claim 1 wherein the sole constituents of A are carbon, hydrogen, and oxygen.

5. The process of claim 1 wherein



is the tolylene radical.

6. The process of claim 1 wherein the textile material is wool.

7. The process of claim 1 wherein the treated textile

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material from Step (a) is subjected to garment-fabricating operations including cutting, sewing, and pressing, prior to curing the textile according to Step (b).

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HERBERT B. GUYNN, Primary Examiner

U.S. Cl. X.R.

8—115.5, 128 A, 184, 196; 117—138.8 A, 138.8 N, 139.4, 141; 260—77.5 AP