TREATMENT OF TEXTILES WITH AZIRIDINE-
MODIFIED POLYURETHANES


Abstract of the disclosure

Polyurethanes containing isocyanate groups are reacted with alkylene imines to prepare aziridine-modified polyurethanes useful for application to textile materials to improve their properties, e.g., to impart shrink resistance and durable press qualities. Typical example: A polyether polyurethane containing free NCO groups is reacted with ethylene imine to yield an aziridine-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, the latter system being preferred to attain permanent creases.

This is a division of our copending application Ser. No. 675,038, filed Oct. 13, 1967, now Pat. 3,542,505.

A valuable royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

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 aziridine-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.

The prior art discloses that various aziridine derivatives have been proposed for use as shrinkproofing agents for wool. See Tesoro, U.S. Pat. 3,165,375 and 3,279,882, and Textile Research Journal, June 1964, pages 523-532. Among the aziridines tested by said investigator were certain so-called amino-aziridines (those in which the nitrogen atom of the aziridine ring is an amino nitrogen) and amido-aziridines (those in which the nitrogen atom of the aziridine ring is an amido nitrogen). It is reported by this investigator that effectiveness of the aziridines as shrinkproofing agents is related to the basicity of the ring nitrogens, so that the amino-aziridines provide good shrinkproofing results while the amido aziridines do not. In fact, Patent 3,279,882 discloses that effective shrinkproofing results are obtained with the amido aziridines only when they are applied conjointly with a polyamine (i.e., a basic compound). Further disadvantages attributed to the amido aziridines by the said investigator are that they stiffen the treated fabric and cause severe losses in abrasion resistance (Text. Res. Jour., June 1964, p. 529).

We have found that a novel class of aziridine 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 the problems analyzed above. Some of the significant advantages provided by our aziridine derivatives are listed below:

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

They are effective per se; the conjoint application of a polyamine is unnecessary. It may be noted in this connection that application of polyamines to wool is hazardous because if any unreacted polyamine remains on the wool it will cause yellowing and degradation of the fibers.

They do not adversely affect the abrasion resistance of the textile material. In fact, the treated material often exhibits increased abrasion resistance. In contrast, the amido aziridines studied by Tesoro are admitted to cause decrease in abrasion resistance.

They do not cause a stiffening of the fabric. This is in sharp contrast to Tesoro's findings that effective shrinkproofing is coupled with stiffening; indeed, that the degree of stiffening is proportional to shrinkproofing efficiency.

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reaction establishes the desired aziridine-modification of the starting polymer. A typical, but by no means limiting, example of the synthesis is illustrated below:

\[
\begin{align*}
\text{NCO} & \quad \text{Isocyanate-terminated} \\
\text{polyether polyurethane} & \quad \text{polyether polyurethane} \\
\end{align*}
\]

In the above formulae, \( m \) represents the number of tetra-methyleneether repeating units. This may range, for example, about from 5 to 50.

The reaction is carried out at about 10 to 40°C, and under essentially anhydrous conditions to avoid hydrolysis of the isocyanate groups. The alkylene imine is supplied in excess to ensure conversion of all isocyanate groups to aziridine groups. It is evident from the formulae above that modification in the aziridine rings can be effected by selection of the aziridine imine reactant. For example, if propylene imine is used instead of ethylene imine, the aziridine rings will be of the structure

\[
\begin{align*}
\text{Aziridine-modified} & \quad \text{polyether polyurethane} \\
\end{align*}
\]

In other words, in this case \( R'' \) (in Formula I) is methyl.

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 intermediate 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 castomers. 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 aziridine 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,

\[
\begin{align*}
\text{Polyether polyol} & \quad \text{Polyisocyanate} \\
\end{align*}
\]

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) polyl with a polyisocyanate, using an excess of the latter to ensure provision of free isocyanate groups in the product. A typical, but by no means limiting, example is illustrated below:

\[
\begin{align*}
\text{Isocyanate-terminated} & \quad \text{polyether polyurethane} \\
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\[
\begin{align*}
\text{Polyether polyol} & \quad \text{Polyisocyanate} \\
\end{align*}
\]

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

- toluene-2,4-diisocyanate
- toluene-2,6-diisocyanate
- commercial mixtures of toluene-2,4 and 2,6-diisocyanates
- ethylene diisocyanate
- ethylidene diisocyanate
- propylene-1,2-diisocyanate
- cyclohexylene-1,2-diisocyanate
- cyclohexylene-1,4-diisocyanate
- m-phenylene diisocyanate
- 3,3'-diphenyl-4,4'-biphenylene diisocyanate
- 4,4'-biphenylene diisocyanate
- 3,3'-dichloro-4,4'-biphenylene diisocyanate
- 1,6-hexamethylene diisocyanate
- 1,4-tetramethylene diisocyanate
- 1,10-decamethylene diisocyanate
- 1,5-naphthalenediisocyanate
- cumene-2,4-diisocyanate
- 4-methoxy-1,3-phenylenediisocyanate
- 4-chloro-1,3-phenylenediisocyanate
3,682,556

4-bromo-1,3-phenylenediisocyanate 4-ethoxy-1,3-phenylenediisocyanate 2,4'-diisocyanatodiphenyl ether 5,6-diisocyanato-1,3-phenylenediisocyanate 2,4-diisocyanatotoluene 4,4'-diisocyanatoxylyl 3,3'-dimethyl-4,4'-diisocyanatophenylmethane 2,6-diisocyanatophenyl 2,4-diisocyanatosilane 3,3'-dimethoxy-4,4'-diisocyanatophenyl 1,4-anthrancedisocyanate 2,5-fluorenedisocyanate 1,8-naphthalenedisocyanate 2,6-disocyanatobenzofuran 2,4,6-toluamidrisocyanate, and 2,4'-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 disocyanate, 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—\\(OCH_3)\\— as would be the case with, for example, 4-chloro-1,3-phenylenediisocyanate or 4-methoxy-1,3-phenylenediisocyanate—R' will be the hydrocarbon radical of the reactant and R will be the substituent—chlorine or methoxy in the given examples.

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

Among the polyester 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 either 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 polyester chains in which there are two hydroxyl groups per polymer molecule. When polymerization of the oxide is carried out in the presence of glycerol, trifunctional alcohol, the resulting polyester 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 polyester polyols include:

- propylene glycol
- trimethylene glycol
- 1,2-butanediol
- 1,3-butadiol
- 1,4-butanediol
- 1,5-pentanediol
- 1,6-hexanediol
- 1,10-decanediol
- 1,2-cyclohexanediol
- 2-butene-1,4-diol
- 3-cyclohexene-1,1-dimethanol

3,682,556 5 4-methyl-3-cyclohexene-1,1-dimethanol 3-methylen-1,5-pentanediol diethyle 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-pentylx) 1-propyl-1,3-propanediol 3-oxopropenylphenoxy 1,2-propanediol thiodiglycol

1,2-(thiobis(ethylenoxy)) diethanol polyethyleneether glycol (molecular weight about 200) 2,2'-isopropylidenedi(\(p\)-phenyleneoxy) diethanol 1,2,6-hexanetriol 1,1,1-trimethylolpropane 3-(2-hydroxyethoxy) 1,2-propanediol 2,3-(2-hydroxypropoxy) 1,2-propanediol 1,1,1-tris(2-hydroxyxethoxy) methyl)ethane 1,1,1-tris(2-hydroxypropoxy) methyl)propane triethanolamine 2,3-(2-hydroxyxethoxy)-1-propanol resorcinal pyrogallol phloroglucinol hydroquinone 4,6-di-tertiarybutyl catechol catechol resorcinol 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(2-hydroxyethoxy) ethane 1,1,3-tris-(2-hydroxypropyl) propane.

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

\[-CH_2-CH_2-CH_2-CH_2-O-\]

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

The polyester polyls which may be employed as precursors for the aziridines 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, glutaric acid, \(\delta\)-hydromuconic acid, \(\gamma\)-hydromuconic acid, \(\alpha\)-buty1-\(\alpha\)-ethylglutaric acid, \(\alpha\,\beta\)-diethyloxycinnamic acid, orthalic acid, isophthalic acid, terephthalic acid, hemimelite acid, trimellitic acid, trimesic acid, melhophanic acid, prehnitic acid, pyromellitic acid, citric acid, benzenepercarboxylic 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-butylen glycol, 1,3-butylen glycol, 1,2-butylen 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, trimethyl propane, 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 polyester units so that they may be considered as condensation polyols or as polyester 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 polyalkyleneether 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, ricinoleic acid, form another category of useful polyester polyols. Typically, one can use esters of ricinoleic acid with ethylene glycol, propylene glycol, glycerol, pentaerythritol, diglycol, 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 AZIRIDINE TO THE TEXTILE

The aziridines of the invention may be applied to the textile in various ways. One technique involves applying the aziridine as such to the textile, using warmings if necessary to make the aziridine flow, and distributing it with calender rolls or the like. A preferred technique involves dissolving the aziridine in an inert solvent and applying the resulting solution to the textile material.

Typical of the solvents which may be used are benzene, toluene, xylene, dioxane, disopropyl 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 naphtha, etc.

Usually it is preferred to use the aziridines in the form of aqueous emulsions. These can be prepared by customary techniques—suspension of the aziridine with water and a conventional emulsifying agent such as an alkyl-phenoxy-poly-(ethylenoxy)ethanol, polyoxyethylene sorbitan monopalmitate, polyoxyethylene lauryl ether, polyoxyethylene-polyoxypropylene stearate, sorbitan monopalmitate, sorbitan monolaurate, and the like. The concentration of the aziridine 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 aziridine, the amount of aziridine to be deposited on the fibers, the viscosity of the dispersion, etc. In general, a practical range of concentration could be from about 1% to about 25%. The dispersion 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 technique 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 aziridine desired. Generally, the amount of aziridine 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 purpose. In treating textiles such as fabrics the amount of aziridine 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 aziridine, the treated textile is cured (heated) to effect an insolubilization of the applied aziridine and to promote bonding of the aziridine to the textile. Although the mechanism of bonding has not been identified, bonding is known to occur and it is believed to involve chemical combination of the aziridine with active radicals present 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 aziridine 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 aziridine, 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 aziridine. In many cases an adequate cure is effected by heating the 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. Generally, the invention is applicable to the treatment of any textile or the like, although it 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 cellulosic fibers, e.g., cotton, linen, hemp, jute, ramie, sisal, cellulose acetate rayons, cellulose acetate-butryate rayons, saponified acetate rayons, viscose rayons, cuprammonium rayons, ethyl cellulose fibers, fibers formed from amylose, algins, 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 albumins, collagen, or keratins, such as feathers, animals' horn. Mixtures of 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, polylvinyl 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-repellency, increasing adhesion or bonding characteristics of the substrates with rubber, polyester resins, etc.

DELAYED CURE SYSTEM

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, no one has been able 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 thioglycollate or sodium bisulphite. Aqueous laundering and the fabrics need ironing for next appearance. Various materials such as melamine-formaldehyde resins, urea-formaldehyde resins, dihydroxyethyl dimethylo 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 aziridines 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 in manufacture—i.e., 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 aziridine is applied to the fabric but curing is delayed until the fabric has been made up into the desired article, which may be, for example, a completed garment. The curing then not only bonds the aziridine 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 aziridine is applied to the fabric using a solution or emulsion of the aziridine, as described hereinabove. The conditions of application may be adjusted to vary the amount of aziridine deposited on the fabric. Usually, it is preferred to deposit about 0.2 to 20% of the aziridine, based on the weight of the fabric. In a preferred modification of the procedure a reducing agent, such as sodium bisulphite, is incorporated in the liquid preparation of the aziridine. However, as hereinafter explained the reducing agent may be applied at a later stage in the process. The treated fabric is then dried to remove the solvent or other carrier in which the aziridine was 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 30°C. However, since curing does not occur immediately, short exposures to higher temperatures are permissible.

The fabric containing the aziridine 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 a reducing agent was not co-applied with the aziridine, then a reducing agent 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 the reducing agent may be sprayed on the textile, particularly in those areas where it is intended to form creases or pleats. Enough of the solution is usually applied so there is about 0.1 to 2% of the reducing agent, based on the weight of fabric. It is to be particularly emphasized that the production of the creases need not follow directly after the aziridine treatment of the fabric. Indeed, the fabric containing the uncured aziridine can be held for long periods without danger of spontaneous curing. The aziridines 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 garments, for example, in treating articles) there is no danger of spontaneous curing.

The garment or other textile article is then subjected to a curing operation to insolubilize the aziridine 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 above for a time sufficient to cause the desired curing of the applied aziridine. 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 musiness so that they are truly press-free, i.e., no pressing is needed even after repeated washings.

As noted hereinabove, where permanent crease qualities are desired, a reducing agent is preferably applied to the textile, concomitantly with application of the aziridine or in a later step but prior to curing. Representative examples of reducing agents include: Inorganic sulphides such as alkali metal, alkaline earth metal, ammonium, etc., sulphides and hydrosulphides. Organic sulphides, for example, containing a thiol group, as, for example, thioglycollic acid, or its salts such as the alkali metal or ammonium salts; thioanisole, ethanol; thioformamide; thio-sulphate; thiourea; thioesters; etc. Formamidine sulphonic acid, also known as iminomaminomethane sulphonic acid betaine. Formaldehyde sulphoxylates, generally used in the form of their alkali metal, zinc, or ammonium salts. Alkali metal or ammonium sulphites, bisulphites and hydrosulphites. Aldehyde or ketone addition products with sulphites or bisulphites, e.g., formaldehyde bisulphite, sodium acetone bisulphite, etc. Generally, the reducing agents used in accordance with the invention may be defined as sulphur-containing, reductive, disulphide-splitting agents because of the fact that they all contain sulphur in their structures and because they have the ability to open the disulphide (cystine) linkage in the wool molecule, generally converting a single disulphide (—S—S—) bond into two thiol (—SH) groups.

The amount of reducing agent is not critical and may be varied depending on such circumstances as the efficacy of the agent selected, the durability of set desired in the product, the character of the fibers being treated, etc. Even minute amounts of the reducing agent will provide some degree of improvement. Usually, the reducing agent is used in an amount from about 0.1 to about 2%, based on the weight of the textile substrate being treated. It is, of course, obvious that the reducing agent should not be applied in such a high proportion as would degrade the textile substrate.

Although the use of a reducing agent in conjunction with our aziridines is primarily of advantage in treatments where the substrate is to be provided with durable creases or other configurations, it is within the broad ambit to employ the reducing agent in other procedures, e.g., ones wherein creasing is not involved. The advantage of the reducing agent is that it enhances bonding of the aziridine to the textile substrate. Thus, generally, the invention includes in its broad compass any textile-treating procedure wherein the reducing component is contained in conjunction with our aziridines, and is applied to the textile concomitantly with the aziridine or at any earlier or later stage, prior to the curing step.

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 wash-
ing 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 aziridine-modified polytetramethylene-ether polyurethane

The starting material for this synthesis was a commercial liquid polyurethane having a molecular weight of about 2000 and an isocyanate (—NCO) content of 4.1%. It is believed to have the structure

\[
\text{CH}_3\text{O} - \text{NH} - \text{O} - \text{A'} - \text{O} - \text{C} - \text{NH} - \text{NCO}
\]

wherein A’ represents the residue of a polytetramethylene-ether glycol containing about twenty-five units.

In Example 2, the emulsion was prepared as described above in Example 1 was diluted with water (to levels indicated below) and applied to swatches of wool. In some instances, measured amounts of NaHSO₃ were added to the emulsions.

The treatments in each case were as follows: Wool swatches were immersed in the emulsion bath until completely wet-out, then the swatches were run through a squeeze roll to attain a wet pick-up of 80-100%, based on the weight of the fabric. The damp fabrics were dried in air at room temperature.

Next, the dried fabrics were creased: Each swatch was moistened by spraying with water, folded, and then subjected to steam and pressing on a tailor’s hot-head press. The fabrics were steamed for 10-20 seconds, then pressure (60-80 p.s.i.) and heat (ca. 140-150°F C.) applied for 20 seconds. The creased swatches were then cured in a forced draft oven at 300°F for 20 minutes.

The cured swatches were then given three 75-minute washes (as described above) and tumble-dried after each wash. The swatches were measured for shrinkage and examined for crease retention and overall appearance after each tumbler drying (following each wash).

In a first series of runs, applied to an undyed woolen fabric, the following results were obtained:

<table>
<thead>
<tr>
<th>Cone. of aziridine in treating emulsion, percent</th>
<th>1st washing and drying</th>
<th>2nd washing and drying</th>
<th>3rd washing and drying</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Area shrinkage, percent</td>
<td>Appearance</td>
<td>Area shrinkage, percent</td>
</tr>
<tr>
<td>4</td>
<td>2.9 E</td>
<td>0.5 E</td>
<td>0.5 E</td>
</tr>
<tr>
<td>3</td>
<td>2.6 E</td>
<td>1.0 E</td>
<td>1.0 E</td>
</tr>
<tr>
<td>2</td>
<td>2.2 E</td>
<td>1.5 E</td>
<td>1.5 E</td>
</tr>
<tr>
<td>2 (plus 1% NaHSO₃)</td>
<td>2.2 E</td>
<td>2.0 E</td>
<td>2.0 E</td>
</tr>
<tr>
<td>None (untreated wool)</td>
<td>16.1</td>
<td>26.3</td>
<td>26.3</td>
</tr>
</tbody>
</table>

1 Fabric appearance was rated as follows: Excellent (E)—sharp crease, fabric flat and in no need of ironing. Good (G)—sharp crease, fabric flat but could use slight tacking up with the iron. Fair (F)—crease still visible but not sharp, some wrinkling, needs definite ironing. Poor (P)—no crease visible, badly wrinkled.

(A) Two hundred grams (0.1 mole) of the polyurethane were dissolved in 300 grams of toluene. While stirring the solution, 8 grams (0.2 mole) of ethylene imine were added dropwise. During the addition, the temperature of the solution was not allowed to exceed approxi-

mately 40°C. At the end of the addition, an infra-red spectrum of the solution revealed no residual NCO group. This indicated the presence of the desired aziridine derivative.

(B) To a 100-gram sample of the aziridine solution, prepared as described above, was added 4 grams of a commercial oil-soluble emulsifying agent, an alkylphenoxypoly(ethyleneoxy)ethanol. The mixture was stirred rapidly and 50 cc. of water were slowly added. The thick water-in-oil emulsion was transferred to a blender and an additional 200 cc. of water was added while stirring at high speed. The resulting oil-in-water emulsion of the aziridine was used as a stock supply and diluted with water as needed.

In a second series of runs, the treatments and tests were applied to an undyed worsted (wool) fabric which in other tests was found to be considerably more difficult to stabilize than the woolen fabric of the first series. The results with the worsted fabric are given below:

<table>
<thead>
<tr>
<th>Cone. of aziridine in treating emulsion, percent</th>
<th>1st washing and drying</th>
<th>2nd washing and drying</th>
<th>3rd washing and drying</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Area shrinkage, percent</td>
<td>Appearance</td>
<td>Area shrinkage, percent</td>
</tr>
<tr>
<td>4</td>
<td>2.6 E</td>
<td>1.5 E</td>
<td>2.2 E</td>
</tr>
<tr>
<td>3</td>
<td>2.2 E</td>
<td>2.0 E</td>
<td>2.0 E</td>
</tr>
<tr>
<td>2 (plus 1% NaHSO₃)</td>
<td>1.0 E</td>
<td>1.0 E</td>
<td>1.0 E</td>
</tr>
<tr>
<td>None (untreated wool)</td>
<td>46.6</td>
<td>58.7</td>
<td>58.7</td>
</tr>
</tbody>
</table>

1 Fabric appearance was rated as described in Table I.

EXAMPLE 3
Examination of treated fabrics at intervals for delayed-cure features

The emulsion prepared as described in Example 1 was diluted to an aziridine concentration of 2%. In one of the runs, the diluted emulsion per se was used; in a second run 2% of NaHSO₃ was added.

Wool fabric was treated as follows: Swatches of the wool were wet-out in the emulsion bath, pressed to 80-100% wet pick-up, and air-dried at room temperature. The dried fabrics were then stored at room temperature, and after certain times of storage (3, 8, 15, and 30 days) were creased and cured as described in Example 2. The
swatches were then subjected to four 75-minute washes with tumble-drying after each wash. The results are tabulated below:

<table>
<thead>
<tr>
<th>Time of storage before setting and curing, days</th>
<th>Emulsion in emulsion bath</th>
<th>Area shrinkage, percent</th>
<th>Appearance ¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Yes</td>
<td>2.1 E</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>No</td>
<td>2.1 E</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Yes</td>
<td>2.2 E</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>No</td>
<td>2.0 E</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Yes</td>
<td>1.8 E</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>No</td>
<td>2.0 E</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>Yes</td>
<td>2.2 E</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>No</td>
<td>2.3 E</td>
<td></td>
</tr>
<tr>
<td>Control (unstressed wool)</td>
<td></td>
<td>23.3</td>
<td></td>
</tr>
</tbody>
</table>

¹ Appearance was rated as described in Table I.
² In this run, the remoistening of the fabric (part of the creasing operation) was accomplished by spraying with an aqueous solution containing 6% Na₂SO₄.
³ After 3 washes.

### Table III

<table>
<thead>
<tr>
<th>Concentration of aziridine-modified polyurethane in emulsion, percent:</th>
<th>Area shrinkage (Accelerator test), percent:</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>1.5</td>
<td>2</td>
</tr>
<tr>
<td>0.4</td>
<td>3</td>
</tr>
<tr>
<td>None (control)</td>
<td>42</td>
</tr>
</tbody>
</table>

### Example 5

The starting material for the synthesis was a commercial liquid polyether polyurethane having a molecular weight of about 1300 and an isocyanate (—NCO) content of 6.5%. It is believed to have the structure

![Structure](structure.png)

### Example 4

The starting material for this synthesis was a commercial liquid polyether polyurethane having a molecular weight of about 850 and an isocyanate (—NCO) content of about 9.5%. It is believed to have the structure

![Structure](structure.png)

wherein A' represents the residue of a polytetramethylene-ether glycol containing about seven

[—CH₂—CH₂—CH₂—CH₂—O—]

units.

One hundred grams (0.12 mole) of the liquid polyurethane was dissolved in 300 ml. of dry benzene. While stirring, 13 ml. (0.26 mole) of ethylene imine was added at a rate slow enough so that the reaction temperature did not rise above 40° C.

An emulsion containing 3% of the aziridine-modified polyurethane was prepared as follows: To 47 grams of the solution of the aziridine polymer, prepared as described above, was added 1 gram of a commercial emulsifier, Tris(polyoxyethylene)sorbitan monopalmitate, and 450 ml. of water and applying rapid agitation in a blender. More dilute emulsions were prepared by incorporating water in this stock emulsion.

Samples of wool flannel were treated with the emulsions by padding with the emulsion, squeezing through rollers to remove excess liquid, and then curing in an oven for 20 minutes at 300° F.

The treated samples were then tested for shrink resistance, using the Accelerator method. In this test the fabric samples are rolled at 1700 r.p.m. for 2 minutes at 40–42° C. in an Accelerator with aqueous sodium oleate (0.5%) solution, using a liquor-to-wool ratio of 50 to 1. After this washing operation, the samples were measured to determine their area and the shrinkage calculated from the original area. This is a very severe test which applied to untreated wool samples gives an area shrinkage of 40–50%. The Accelerator is described in American Dyestuff Reporter, vol. 45, p. 685, Sept. 10, 1956.

The results obtained are tabulated below:

<table>
<thead>
<tr>
<th>Concentration of aziridine-modified polyurethane in emulsion, percent:</th>
<th>Area shrinkage (Accelerator test), percent:</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>1.5</td>
<td>2</td>
</tr>
<tr>
<td>0.4</td>
<td>3</td>
</tr>
<tr>
<td>None (control)</td>
<td>42</td>
</tr>
</tbody>
</table>

### Example 6

A polypropyleneether glycol of molecular weight about 6000 was reacted with toluene diisocyanate in conventional manner to form an isocyanate-terminated polyurethane. This, in turn, was reacted with propylene imine to form an aziridine modified polyurethane with terminal groups of the structure

![Structure](structure.png)

Fifty grams of the aziridine-modified polymer—having a molecular weight of 6300–6800 and containing 0.36 to 0.38 milliequivalent of imine per gram of polymer—was dissolved in 30 grams of benzene and 2 grams of a commercial emulsifier, a polyoxyethylene-polyoxypropylene monostearate, was added. While stirring the solution in a blender, water was gradually added to make 1000 grams of an emulsion.
A sample of wool flannel was immersed in the emulsion for 1 minute, then passed through squeeze rollers, and then dried in air. From the increase in weight of the fabric, the uptake of polymer was found to be 4%. The treated fabric was cured (300° F., 10 minutes), then tested for shrinkage by the Accelerator method described above. Area shrinkage was found to be 1%. A sample of the same fabric but untreated shrank 39.7% in area by the same test.

**EXAMPLE 7**

A series of experiments were carried out to compare the effectiveness of the aziridine derivatives of the invention with that of various commercial products recommended for shrinkproofing applications. The various products tested were:

(A) The aziridine-modified polyalkyleneether polyurethane described above in Example 1: It was applied in the form of 2% emulsion to which had been added sodium bisulphite (1%).

(B) A polyamide modified by reaction with epichlorhydrin: This material is commercially available as a water-soluble resin (“Kynene” manufactured by Hercules Co.) and contains epoxide linkages available for reaction with wool and for crosslinking. This product was applied in a form of 2.5% solution in water, and to which was added sodium bisulphite (1%).

(C) A polyacrylate containing methylol groups (—CH₂OH) which can cross-link and/or react with hydroxyl groups in wool by elimination of water: The main component of the polymer is a soft acrylate, polybutyl acrylate. It is sold under the name “HA-8” by Rohm and Haas Co. for wool shrinkproofing and other uses. It was used with an acid catalyst, ZnNO₃, in accordance with the manufacturer’s recommendation. It was applied in the form of a 4% emulsion, to which was added sodium bisulphite (1%).

(D) A urea-formaldehyde condensation product, consisting basically of dihydroxyethylene dimethylol urea:

\[ \text{HOCH₂N—CO—CH₂OH} \]

It is widely used in applications to cotton and other cellulosic textiles to impart permanent press qualities. It was used, following the manufacturer’s recommendation in conjunction with an acid catalyst, ZnNO₃. It was applied in the form of 10% aqueous solution to which was also added 1% sodium bisulphite.

Samples of a wool fabric were treated with the various agents described above, using the following technique in each case. The fabric was wet-out in the aqueous solution or emulsion of the agent, put through squeeze rolls to 80-100% wet pick-up, and dried in air overnight. The next day the samples were moistened by spraying with water and were creased by folding and application of steam and pressure. The creased samples were then cured in an oven —310° F. for 20 minutes.

The cured samples were then subjected to three 75-minute washes with tumble drying after each wash. After this the samples were measured for shrinkage and assayed for retention of creases and general appearance. The results obtained are tabulated below:

<table>
<thead>
<tr>
<th>Run</th>
<th>Agent applied</th>
<th>Area shrinkage, percent</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Aziridine-modified polyalkyleneether polyurethane.</td>
<td>1.8 E.</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>Epichlorhydrin-modified polyamide.</td>
<td>10.3 F to P.</td>
<td>2</td>
</tr>
<tr>
<td>C</td>
<td>Polyacrylate containing methylol groups.</td>
<td>28.4 P.</td>
<td>3</td>
</tr>
<tr>
<td>D</td>
<td>Urea-formaldehyde cond. product.</td>
<td>39.4</td>
<td>4</td>
</tr>
</tbody>
</table>

1 Appearance was rated as described in Table I.

**EXAMPLE 8**

Experiments were carried out to compare the effectiveness of the process of the invention with one wherein a commercially-employed shrinkproofing treatment was followed by treatment with sodium bisulphite.

A sample of undyed worsted (wool) fabric was given a shrinkproofing treatment by application of polyhexamethylene sebacamide through interfacial polymerization, as disclosed in Patent 3,078,138. In particular, the fabric was first immersed in an aqueous solution of hexamethylene diamine (1.5%) and sodium carbonate (1.5%), run through squeeze rolls, then immersed in a solution of sebacoyl chloride (2.0%) in a volatile petroleum hydrocarbon solvent, run through squeeze rolls, and washed in water to remove unreacted materials, and dried. The fabric was then wet-out with an aqueous 2% solution of sodium bisulphite and creased by folding an application of steam and pressure, as described in Example 2. The treated fabric was then subjected to a 75-minute wash, as described above, and tumble dried. It was observed that the crease had disappeared. In contrast, a sample of the same fabric treated as described in Example 2 with a 2% emulsion of the aziridine-modified polyurethane and 1% sodium bisulphite, retained its creases even after four 75-minute washes (each followed by tumble drying). This unusual durability of the creases plainly indicates that our process involves a synergistic effect between the aziridine-modified polyurethane and the bisulphite.

**EXAMPLE 9**

A hydroxy-terminated polyethylene adipate of molecular weight approximately 6500 was end-capped by reaction with an excess of toluene diisocyanate to produce a polyether polyurethane with terminal NCO groups. One mole of this polymer was then reacted with two moles of ethylene imine to produce an aziridine-terminated polyether polyurethane. A 2% emulsion of this aziridine-modified polymer was prepared as in Example 1, part B, and wool fabric was treated with the emulsion as described in Example 2. After four 75-minute washes the treated fabric showed 3% shrinkage in the warp and 2% shrinkage in the fill directions, while the control (untreated wool fabric) had shrunk 30% in the warp and 24% in the fill under the same washing conditions.

Having thus described our invention, we claim:

1. A dispersion, in a liquid carrier, of (a) an aziridine-modified polyurethane of the structure

\[ \text{A} \]

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 alkyl, or a radical of the structure

\[ \text{CHR''} \]

where:

- \( \text{CHR''} \) is hydrogen or a lower alkyl radical,
- \( n \) is an integer from 2 to 10, and
- \( x \) is an integer from 1 to 2, and

Properties after three 75-min. washes

<table>
<thead>
<tr>
<th>Run</th>
<th>Agent applied</th>
<th>Area shrinkage, percent</th>
<th>Appearance</th>
</tr>
</thead>
</table>

- A... Aziridine-modified polyalkyleneether polyurethane. 1.8 E.
- B... Epichlorhydrin-modified polyamide. 10.3 F to P.
- C... Polyacrylate containing methylol groups. 28.4 P.
- D... Urea-formaldehyde cond. product. 39.4.
(b) a sulphur-containing reductive disulphide-splitting agent.
2. The dispersion of claim 1 wherein the said agent is an alkali metal bisulphite.

References Cited
UNITED STATES PATENTS