

1

2,794,754

TREATMENT OF TEXTILE MATERIALS

Carl W. Schroeder, Orinda, Calif., assignor to Shell Development Company, New York, N. Y., a corporation of Delaware

No Drawing. Application April 30, 1956,
Serial No. 581,310

13 Claims. (Cl. 117—139.4)

This invention relates to the treatment of textile materials. More particularly, the invention relates to a method for treating textile materials to render them crease and shrink resistant.

Specifically, the invention provides a new economical process for treating textile materials to render them crease and shrink resistant without affecting feel and without making them chlorine-retentive which comprises impregnating the textile material with an aqueous medium containing a mixture of a compound possessing a plurality of vic-epoxy groups, an organic compound possessing at least one XCH_2OH group wherein X is a member of the group of a nitrogen atom, a carbon atom of an aromatic ring and an aliphatic or cycloaliphatic carbon atom attached to a



group and an epoxy curing agent and then heating the impregnated textile material to a relatively high temperature for a short period. The invention further provides improved textile materials prepared by this process.

This application is a continuation-in-part of patent application Ser. No. 259,504, filed December 1, 1951, now Patent No. 2,752,269.

Many textile fabrics, such as those prepared from cotton and rayon, have poor resilience, i. e., they are easily creased or wrinkled when crushed or otherwise subjected to localized physical force. In addition, many of the fabrics have poor dimensional stability as exemplified by poor resistance to shrinkage. In order to overcome these shortcomings it has been common practice to treat the fabric with materials, such as urea- or melamine-formaldehyde resins or glyoxal, that could be subsequently insolubilized within the fabric fibers. While this method has met with some success with colored fabrics, it has been of little or no use in the treatment of white goods that may be subjected to bleaching. It has been found that during the bleaching process, the added resins retain considerable quantities of chlorine and when the fabric is subsequently exposed to heat as in ironing or hot-air drying, the cloth is charred or discolored and the strength of the material seriously degraded. In addition, many of the fabrics treated with these resins have poor washability, i. e., the resin is easily lost from the fabric after a few washings with soap and water. Furthermore, many of the fabrics treated with these resins have a harsh feel and poor abrasion resistance.

It is an object of the invention, therefore, to provide a new method for treating textile materials. It is a further object to provide a new economical process for rendering textile fabrics crease and shrink resistant without giving a harsh feel and undue stiffness to the fabric. It is a further object to provide a process for rendering fabrics crease and shrink resistant without making them chlorine retentive. It is a further object to provide a method for imparting non-creasing and non-shrinking

2

properties to textiles that will be resistant to washing. It is a further object to provide a new process for treating textiles to make them crease and shrink resistant without having any great effect on other properties, such as tensile strength. Other objects and advantages of the invention will be apparent from the following detailed description thereof.

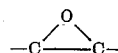
It has now been discovered that these and other objects may be accomplished by the novel process of the invention which comprises impregnating the textile material with an aqueous medium containing a mixture of compound possessing a plurality of vic-epoxy groups, an organic compound possessing at least one XCH_2OH group wherein X is a member of the group consisting of a nitrogen atom, a carbon atom of an aromatic ring and an aliphatic or cycloaliphatic carbon atom attached to a



group and an epoxy curing agent and then heating the impregnated textile material to a relatively high temperature for a short period. Textile materials treated in this manner have been found to have very high crease and shrink resistant values. In fact, the use of the above-noted mixtures of compounds has been found to impart a synergistic action as to crease and shrink resistance, i. e., the combination imparts higher crease and shrink resistant values at the same or lower solids content than the individual components by themselves. Further, the textiles treated in this manner wherein the mixture of treating agents contain at least 50% by weight of the polyepoxide have been found to be non-chlorine retentive, i. e., can be bleached and ironed without causing discoloration of the material. This was very surprising because of the use of many of the materials by themselves make the fabric quite chlorine retentive.

It has been further found that the textile materials treated in the above-described manner have a very soft feel and good hand and excellent abrasion resistance. In addition, the treated materials have been found to have improved washability and can be washed numerous times without danger of losing any substantial amount of the treating resins.

The polyepoxides used in treating the textile materials comprise compounds possessing a plurality of vic-epoxy groups. The expression "vic-epoxy groups" refers to groups having the epoxy oxygen atoms attached to adjacent carbon atoms, such as the group



Examples of the polyepoxides include, among others, vinyl cyclohexane dioxide, butadiene dioxide, 1,4-bis(2,3-epoxypropoxy)benzene, 1,3-bis(2,3-epoxypropoxy)benzene, 1,8-bis(2,3-epoxypropoxy)butane, 1,4-bis(3,4-epoxybutoxy)-2-chlorocyclohexane, diglycidyl ether, diglycidyl thioether, diglycidyl ether of ethylene glycol, diglycidyl ether of diethylene glycol, diglycidyl ether of triethylene glycol, resorcinol diglycidyl ether, 1,2,5,6-diepoxy-hexane, and 1,2,3,4-tetra(2-hydroxy-3,4-epoxybutoxy)butane.

Other examples include the glycidyl polyethers of polyhydric phenols obtained by reacting a polyhydric phenol with an excess, e. g., 4 to 8 mole excess, of a chlorohydrin, such as epichlorohydrin and dichlorohydrin. Thus, Polyether D described hereinafter, which is substantially 2,2-bis(2,3-epoxypropoxyphenyl)-propane, is obtained by reacting bis-phenol-A with an excess of epichlorohydrin in an alkaline medium. Other polyhydric phenols that can be used for this purpose include

3

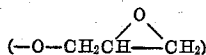
resorcinol, catechol, hydroquinone, methyl resorcinol, or polynuclear phenols, such as 2,2-bis(4-hydroxyphenyl)-butane, 4,4'-dihydroxybenzophenone, bis(4-hydroxyphenyl)ethane, and 1,5-dihydronaphthalene.

Still a further group of polyepoxides comprises the polyepoxy polyethers obtained by reacting, preferably in the presence of an acid-acting compound, such as hydrofluoric acid, one of the aforescribed halogen-containing epoxides with a polyhydric alcohol, and subsequently treating the resulting product with an alkaline component. As used herein and in the claims, the expression "polyhydric alcohol" is meant to include those compounds having at least two free alcoholic OH groups and includes the polyhydric alcohols and their ethers and esters, hydroxy-aldehydes, hydroxyketones, halogenated polyhydric alcohols, and the like. Polyhydric alcohols that may be used for this purpose may be exemplified by glycerol, propylene glycol, ethylene glycol, diethylene glycol, butylene glycol, hexanetriol, sorbitol, mannitol, pentaerythritol, polyallyl alcohol, polyvinyl alcohol, inositol, trimethylolpropane, bis(4-hydroxycyclohexyl)dimethylmethane, 1,4-dimethylolbenzene, 4,4'-dimethyloldiphenyl, dimethyloltoluenes, and the like. The polyhydric ether alcohols include, among others, diglycerol, triglycerol, dipentaerythritol, tripentaerythritol, dimethylolanisoles, beta-hydroxyethyl ethers of polyhydric alcohols, such as diethylene glycol, polyethylene glycols, bis(beta-hydroxyethyl ether) of hydroquinone, bis(beta-hydroxyethyl ether) of bisphenol, beta-hydroxy-ethyl ethers of glycerol, pentaerythritol, sorbitol, mannitol, etc., condensates of alkylene oxides, such as ethylene oxide, propylene oxide, butylene oxide, isobutylene oxide, glycidyl, epichlorohydrin, glycidyl ethers, etc., with polyhydric alcohols, such as the foregoing and with polyhydric thioethers, such as 2,2'-dihydroxydiethyl sulfide, 2,2'-3,3'-tetrahydroxy dipropyl sulfide, etc. The hydroxyaldehydes and ketones may be exemplified by dextrose, fructose, maltose, glyceraldehyde. The mercapto (thiol) alcohols may be exemplified by alpha-monothioglycerol, alpha,alpha-dithioglycerol, etc. The polyhydric alcohol esters may be exemplified by monoglycerides, such as monostearin, mono-esters of pentaerythritol and acetic acid, butyric acid, pentanoic acid, and the like. The halogenated polyhydric alcohols may be exemplified by the monochloride of pentaerythritol, monochloride of sorbitol, monochloride of mannitol, monochloride of glycerol, and the like.

A further group of the polyepoxides comprise the polyepoxy polyesters obtained by esterifying a polycarboxylic acid with an epoxy-containing alcohol, such as, for example, the diglycidyl esters of polycarboxylic acids as diglycidyl phthalate, diglycidyl maleate, diglycidyl adipate and the like.

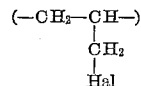
Coming under special consideration are the polyglycidyl polyethers of polyhydric alcohols obtained by reacting the polyhydric alcohol with epichlorohydrin, preferably in the presence of 0.1% to 5% by weight of an acid-acting compound, such as boron trifluoride, hydrofluoric acid, stannic chloride or stannic acid. This reaction is effected at about 50° C. to 125° C. with the proportions of reactants being such that there is about one mole of epichlorohydrin for every equivalent of hydroxyl group in the polyhydric alcohol. The resulting chlorohydrin ether is then dehydrochlorinated by heating at about 50° C. to 125° C. with a small, e. g., 10% stoichiometrical excess of a base, such as sodium aluminate.

The products obtained by the method shown in the preceding paragraph may be described as polyether polyepoxide reaction products which is general contain at least three non-cyclic ether (—O—) linkages, terminal epoxide-containing ether



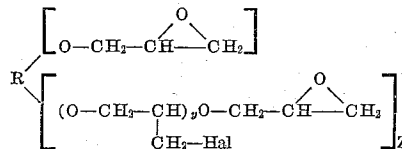
4

groups and halogen attached to a carbon of an intermediate



group.

These halogen-containing polyether polyepoxide reaction products obtainable by partial dehydrohalogenation of polyhalohydrin alcohols may be considered to have the following general formula



in which R is the residue of the polyhydric alcohol which may contain unreacted hydroxyl groups, X indicates one or more of the epoxy ether groups attached to the alcohol residue, y may be one or may vary in different reaction products of the reaction mixture from zero to more than one, and Z is one or more, and X+Z, in the case of products derived from polyhydric alcohols containing three or more hydroxyl groups, averages around two or more so that the reaction product contains on the average two or more than two terminal epoxide groups per molecule.

The preparation of one of these preferred polyglycidyl ethers of polyhydric alcohols may be illustrated by the following example showing the preparation of a glycidyl polyether of glycerol.

PREPARATION OF GLYCIDYL POLYETHERS OF POLYHYDRIC ALCOHOLS

Polyether A

About 276 parts (3 moles) of glycerol was mixed with 832 parts (9 moles) of epichlorohydrin. To this reaction mixture was added 10 parts of diethyl ether solution containing about 4.5% boron trifluoride. The temperature of this mixture was between 50° C. and 75° C. for about 3 hours. About 370 parts of the resulting glycerolepichlorohydrin condensate was dissolved in 900 parts of dioxane containing about 300 parts of sodium aluminate. While agitating, the reaction mixture was heated and refluxed at 93° C. for 9 hours. After cooling to atmospheric temperature, the insoluble material was filtered from the reaction mixture and low boiling substances removed by distillation to a temperature of about 150° C. at 20 mm. pressure. The polyglycidyl ether, in amount of 261 parts, was a pale yellow viscous liquid. It had an epoxide value of 9.671 equivalent per 100 grams and the molecular weight was 324 as measured ebullioscopically in dioxane solution. The epoxy equivalency of this product was 2.13. For convenience, this product will be referred to hereinafter as Polyether A.

Polyether B

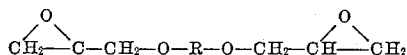
10.5 moles of ethylene oxide was bubbled through 3.5 moles glycerine containing an acid catalyst at 40–50° C. The resulting product had a molecular weight of 224 and a hydroxyl value of 1.417 eq./100 g. 101 parts of this ethylene oxide glycerine condensate was placed in a reaction kettle and heated to 65–70° C. Sufficient BF₃-ethyl ether complex was added to bring the pH to about 1.0 and then 132 parts of epichlorohydrin added dropwise. After all the epi had been added, the reaction was continued for about 15 minutes to assure complete reaction. This product was then dissolved in benzene and 57 parts of sodium hydroxide were added in 7 equal portions. This product was then dissolved in benzene and then filtered to remove the salt. The solvent and light ends were then removed by stripping at a low vacuum. The resulting product had a molecular weight of 455, and an epoxy value of .524 eq./100 g. For convenience, this polyether will be referred to herein as Polyether B.

5 Polyether C

One equivalent of 1,2,6-hexanetriol was placed in a reaction kettle and heated to 65–70° C. Sufficient BF₃-ethyl ether complex was added to bring the pH to about 1.0 and then 1 equivalent of epichlorohydrin added dropwise. After all the epi had been added, the reaction was continued for about 15 minutes to assure complete reaction. This product was then dissolved in acetone and sodium orthosilicate was added at about 65° C. over a period of 0.5 hour and then filtered to remove the salt. The solvent and light ends were then removed by stripping at a low vacuum. The resulting product had a molecular weight of 325 and an epoxy value of .600 eq./100 g. For convenience, this polyether will be referred to herein as Polyether C.

Particularly preferred members of this group comprise the glycidyl polyethers of aliphatic polyhydric alcohols containing from 2 to 10 carbon atoms and having from 2 to 6 hydroxyl groups and more preferably the alkane polyols containing from 2 to 8 carbon atoms and having from 2 to 6 hydroxyl groups. Such products preferably have an epoxy equivalency greater than 1.0, and still more preferably between 1.1 and 4 and a molecular weight between 300 and 1000.

Also of importance are the monomeric polyethers of dihydric phenols obtained by reacting epichlorohydrin with a dihydric phenol in an alkaline medium. These products may be represented by the general formula



wherein R represents a divalent hydrocarbon radical of the dihydric phenol.

The aforescribed preferred glycidyl polyethers of the dihydric phenols may be prepared by reacting the required proportions of the dihydric phenol and the epichlorohydrin in an alkaline medium. The desired alkalinity is obtained by adding basic substances, such as sodium or potassium hydroxide, preferably in stoichiometric excess to the epichlorohydrin. The reaction is preferably accomplished at temperatures within the range of from 50° C. to 150° C. The heating is continued for several hours to effect the reaction and the product is then washed free of salt and base.

The preparation of some of the glycidyl polyethers of the dihydric phenols will be illustrated below.

PREPARATION OF GLYCIDYL POLYETHERS OF DIHYDRIC PHENOLS

Polyether D

About 2 moles of bis-phenol was dissolved in 10 moles of epichlorohydrin and 1% to 2% water added to the resulting mixture. The mixture was then brought to 80° C. and 4 moles of solid sodium hydroxide added in small portions over a period of about 1 hour. During the addition, the temperature of the mixture was held at about 90° C. to 110° C. After the sodium hydroxide had been added, the water formed in the reaction and most of the epichlorohydrin was distilled off. The residue that remained was combined with an approximately equal amount of benzene and the mixture filtered to remove the salt. The benzene was then removed to yield a viscous liquid having a viscosity of about 150 poises at 25° C. and a molecular weight of about 350 (measured ebullioscopically in ethylene dichloride). The product had an epoxy value of 0.50 eq./100 g., and an epoxy equivalency of 1.75. For convenience, this product will be referred to hereinafter as Polyether D.

Particularly preferred members of the above-described group are the glycidyl polyethers of the dihydric phenols, and especially 2,2-bis(4'-hydroxyphenyl) propane, having an epoxy equivalency between 1.1 and 2.0 and a molecular weight between 300 and 900. Particularly preferred are those having a Durrans' Mercury Method softening point below about 60° C.

6

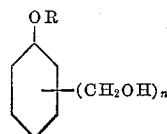
The glycidyl polyethers of polyhydric phenols obtained by condensing the polyhydric phenols with epichlorohydrin are also referred to as "ethoxyline" resins. See Chemical Week, vol. 69, page 27, for September 8, 1951.

Of particular value in the process of the invention are the monomeric polyepoxides containing elements selected from the group consisting of carbon, hydrogen, oxygen and halogen atoms. By "monomeric" is meant compounds which possess only one structure unit as distinguished from polymers which are made up by a repetition of the same structural unit.

The materials to be used in combination with the above-described polyepoxides in the treating of the textile materials comprise those organic compounds substituted with one or more —XCH₂OH groups wherein X is a nitrogen atom, a carbon atom of an aromatic ring or an aliphatic or cycloaliphatic carbon atom attached to a



group. These materials include, among others, the methylol-containing urea-formaldehyde resins, methylol-substituted ureas and melamine compounds, such as dimethylol urea, dimethylol ethylene urea, di- and trimethylol melamine, dimethyl trimethylol melamine, dimethylol thiourea and the lower alkyl ethers of the above, such as the lower alkyl ethers of dimethylol urea, lower alkyl ethers of tetramethylol melamine, and the like. Other examples include the methylol-substituted aromatic compounds, such as methylol-containing phenol-aldehyde resins, 1-hydroxy-2,4,6-tri(hydroxymethyl)benzene, 1-butyloxy-2,4,6-tri(hydroxymethyl)benzene, 1-allyloxy-2,4,6-tri(hydroxymethyl)benzene, 1-hydroxy-2,4,6-tri(hydroxymethyl)-3,5-dimethylbenzene, 1-hydroxy-2,6-di(hydroxymethyl)benzene, chloroallyloxy-2,4,6-tri(hydroxymethyl)benzene, 1-hydroxy-2,6-di(hydroxymethyl)-3,5-diisopropylbenzene, and the like, and mixtures thereof. Particularly preferred methylol-substituted aromatic compounds to be used comprise those of the formula



wherein R is hydrogen or an aliphatic, cycloaliphatic or aromatic hydrocarbon radical and their halogen-substituted derivatives and *n* is an integer equal to from 2 to 3. Ethers of these compounds obtained by etherifying one or more of the —CH₂OH groups with aliphatic monohydric alcohols, such as butanol, pentanol, hexanol, octanol, and the like, are also particularly preferred.

Other examples of alkylol-substituted compounds include the reaction products of ketones and formaldehyde, such as compounds of the formula



wherein R is an aliphatic hydrocarbon radical or combines with the number 2 carbon atom to form a cycloaliphatic hydrocarbon radical, such as, for example, 1-hydroxy-3-butanone, 1-hydroxy-3-hexanone, 1-hydroxy-3-octanone, 2-hydroxymethyl-1-cyclohexanone, 1-hydroxy-3,6-butanedione, and 1-hydroxy-3,5-octanedione.

The ratio in which the polyepoxide and the methylol-substituted compound are combined in the mixture may vary within certain limits. At least 15% by weight and preferably from 15% to 90% by weight of the mixture should be made up of the polyepoxide and the remainder being the methylol-substituted compound. The highest wrinkle and shrink resistance, however, are generally obtained when the polyepoxide varies from 30% to 70% by weight and the remainder being the methylol-substituted compound.

The polyepoxide and the methylol-substituted com-

ound are applied to the textile material in the form of an aqueous solution. Many of the polyepoxides and methylol-substituted compounds are water soluble and the aqueous solutions may be prepared by merely adding the mixture of materials to the water. In other cases, it may be helpful to add solvents, such as acetone, ethyl alcohol and dioxane, to the water, or to employ emulsifying agents to assist in the formation of the water solution. Emulsifying agents may also be employed in preparing the solutions. Examples of suitable emulsifying agents include, among others, monooleate of sorbitan polyoxyethylene, the trioleate of sorbitan polyoxyethylene, sorbitan tristearate, sorbitan monolaurate, polyoxyethylene ethers of alkyl-phenols, carboxymethyl-cellulose, starch, gum arabic, polyvinyl alcohol, aryl and alkylated aryl sulfonates, such as cetyl sulfonate, oleyl sulfonate, sulfonated mineral oils, copolymers of vinyl methyl ether, maleic anhydride and the like, and mixtures thereof. The emulsifying agents are generally employed in amounts varying from 0.1% to 10% by weight and more preferably from 1% to 5% by weight.

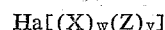
The amount of the mixture of polyepoxide and methylol-substituted compounds to be employed in the impregnating solution will vary depending chiefly on the amount of the mixture to be deposited on the textile material and this in turn will depend upon the number of applications and the pick-up allowed per application. As indicated hereinafter, the amount of the mixture to be applied to the textile material will generally vary from about 3% to about 20%. If a 100% pick-up is allowed and the solution is applied but once, the impregnating solution should contain the mixture of materials in amounts varying from 3% to 20% in order to apply these same percentages to the textile material. On the other hand, if say only a 50% pick-up is allowed and the solution applied but once, the impregnating solution should contain the material in amounts varying from 6% to 40% in order to apply the material in the preferred amounts of 3% to 20%. In general applications, solution is usually applied but once with pick-ups varying from 55% to 100%.

The curing agent added to the impregnating solution may be any alkaline, neutral or acidic material which acts to effect cure of the polyepoxide to form an insoluble product. Examples include, among others, alkalies like sodium or potassium hydroxides; alkali phenoxides like sodium phenoxide; carboxylic acids or anhydrides, such as formic acid, oxalic acid or phthalic anhydride; Friedel-Crafts metal halides like aluminum chloride, zinc chloride, ferric chloride or boron trifluoride as well as complexes thereof with ethers, acid anhydrides, ketones, diazonium salts, etc; salts, such as zinc fluoborate, magnesium perchlorate and zinc fluosilicate; phosphoric acid and partial esters thereof including n-butyl ortho-phosphate, diethyl ortho-phosphate and hexaethyl tetraphosphate; amino compounds, such as, for example, diethylene triamine, triethylene tetraamine, dicyandiamide, melamine, pyridine, cyclohexylamine, benzyltrimethylamine, benzylamine, diethylaniline, triethanolamine, piperidine, tetramethyl piperazine, N,N-dibutyl-1,3-propane diamine, N,N-diethyl-1,3-propane diamine, 1,2-diamino-2-methylpropane, 2,3-diamino-2-methylbutane, 2,4-diamino-2-methylpentane, 2,4-diamino-2,6-dimethyloctane, dibutylamine, dioctylamine, dinonylamine, distearylamine, diallylamine, dioleylamine, dicyclohexylamine, methylethylamine, ethyl-cyclohexylamine, o-tolyl-naphthylamine, pyrrolidine, 2-methyl-pyrrolidine, tetrahydropyridine, 2-methylpiperidine, 2,6-dimethyl-piperidine, diaminopyridine, tetraethylene pentamine, meta-phenylene diamine, and the like; and soluble adducts of amines and polyepoxides and their salts, such as described in U. S. 2,651,589 and U. S. 2,640,037. Preferred agents to be used are the acid-acting agents. This includes acids as well as those materials not classified as acids but which act as such. These agents include, among others, organic

and inorganic acids and their anhydrides, such as 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, actetoacetic acid, naphthalic acid, trimellitic acid, phosphoric acid, sulfuric acid, boric acid, sulfonic 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; and amine hydrochlorides, such as hydrochlorides of aniline, benzylidene, n-propylamine, di-n-butyl amine, di-benzylamine, triethylamine, alpha-phenylethylamine, alpha-naphthyl-ethylamine, beta-aminoanthraquinone, 1,3-diamino-anthraquinone, piperidine, pyridine, quinoline, morpholine, pyrrole and guanidine, and hydrochlorides of hydroxyamines as 2-amino-2-methyl propanol and isobutanol amine.

Particularly preferred curing agents to be employed are the organic and inorganic acids containing no more than 12 carbon atoms, the salts of metal having an atomic weight between 24 and 210 and inorganic acid the anion portion of which contains at least two dissimilar elements having an atomic weight above 2, such as, for example, oxalic acid, citric acid, succinic acid, zinc fluoroborate, copper perchlorate, magnesium perchlorate, barium persulfate, iron perchlorate, and the like.

Coming under special consideration, particularly because of the excellent color and exceptionally fine crease proofing properties obtained therewith, are the salts of metals of groups I to IV and VIII of the periodic table of elements and inorganic acid the anion portion of which contains at least two dissimilar elements having an atomic weight above 2, and particularly inorganic acids of the formula



wherein X is a non-metal having an atomic weight above 2, Z is an element which tends to gain from 1 to 2 electrons in its outer orbit, such as oxygen and fluorine, w is an integer, y is an integer greater than 1 and α equals the valency of the radical $(\text{X})_w(\text{Z})_y$, such as sulfuric acid, fluoboric acid, fluosilicic acid, persulfuric acid, phosphoric acid and the like.

The amount of the curing agent employed will vary depending upon the type of agent selected. In general, the amount of the curing agent will vary from about 0.5% to 30% by weight of the mixture of polyepoxide and methylol compound. The inorganic acids and tertiary amines are preferably employed in amounts varying from about 0.5% to 20%, the metal salts are preferably employed in amounts varying from about 1% to 15%, and the amine hydrochlorides are preferably employed in amounts varying from about 1% to 20%. The primary and secondary amines and anhydrides are preferably used in equivalent amounts, i. e., an amount required to furnish one amino hydrogen or anhydride group, per epoxy group.

The solution employed in the treatment of the textile materials according to the process of the invention may also contain plasticizers to improve the flexibility of the textiles, although these should not be present in such proportions as to render the finished materials soft or sticky at temperatures and humidities to which they may be exposed. It is found, however, that the substances employed in the present invention yield products which are sufficiently flexible for most purposes without the use of plasticizers. Among plasticizers that may be used according to the present invention may be mentioned organic and inorganic derivatives of phenols, for example, diphenylol propane and triphenyl and tricresyl phosphates, sulphonamides, alkyl phthalates, glycol phthalates, derivatives of polyhydric alcohols, such as mono- di- and

triacetin and products obtained by condensing polyhydric alcohols with themselves or with aldehydes or ketones. The compositions may also contain natural resins, e. g., shellac, and other natural resins and synthetic or semi-synthetic resins, e. g., ester gum and poly-hydroxypolybasic acid resins.

Textile softening agents may also be added in varying amounts to improve the feel of the treated fabrics. Examples of these agents include, among others pentadecyl phenol, octadecyl succinic acid, octadecenyl succinic acid, sulfonated waxes and sulfonated alcohols, dimerized long-chain unsaturated acids, non-ionic fatty acid esters of higher polyglycerols. Preferred softeners are the epoxidized di- and triglycerides.

The application of the aqueous solution containing the polyeptides and methylol-substituted compounds to the textile fabric may be effected in any suitable manner, the method selected depending upon the results desired. If it is desired to apply the solution only to one surface of the material, as, for example, when it is desired to treat the back only of a fabric having a face of artificial or natural silk and a cotton back, the application may be effected by spraying or by means of rollers, or the composition may be spread upon the surface by means of a doctor blade. When, however, it is desired to coat both surfaces of the material, or if the material is to be thoroughly impregnated with it, the fabric may be simply dipped in the solution or run through conventional-type padding rollers. The solutions may also be applied locally to the material, for example, by means of printing rollers or by stencilling.

The amount of the mixture of polyeptide and methylol-substituted compounds to be deposited on the fabric will vary over a wide range depending upon the degree of wrinkle resistance and shrink resistance desired in the finished material. If the fabric is to have a soft feel, such as that intended for use for dresses, shirts, etc., the amount of mixture deposited will generally vary from 3% to 20% by weight of the fabric. If stiffer materials are required such as for the shoe fabrics, draperies and the like, still higher amounts of the mixture, such as of the order of 25% to 50% by weight may be deposited.

If the desired amount of mixture of polyeptide and methylol-substituted compound deposited in the fabric is not obtained in one application, the solution can be applied again or as many times as desired in order to bring the amount of the mixture up to the desired level.

After the desired amount of solution has been applied to the fabric, the treated fabric is preferably dried for a short period to remove some or all of the dispersing liquid, such as water, and the like. This is generally accomplished by exposing the wet sheets to hot gas either slack or framed to dimension at temperatures ranging up to 120° C. The period of drying will depend largely on the amount of pick-up permitted during the application of the solution, and the concentration of the mixture of polyeptide and methylol-substituted compounds. In most instances, the drying periods of from 1 to 30 minutes should be sufficient.

The dried fabric is then exposed to relatively high temperatures to accelerate cure. Temperatures used for this purpose generally range from 100° C. to 200° C., and more preferably from 130° C. to 190° C. At these preferred temperature ranges the cure can generally be accomplished in from 1 to 10 minutes. Exposures of less than 3 minutes, e. g. 1 minute, may probably be used in continuous, commercial processing.

The process of the invention may be applied to the treatment of any textile fabric, colored or white. Such materials include the natural or artificial textile materials, such as cotton, linen, natural silk and artificial silk, such as the artificial silk obtained from cellulose acetate or other organic esters or ethers of cellulose and the regenerated cellulosic type of artificial silk obtained by the viscose, cuprammonium or nitrocellulose process, jute,

hemp, rayon, animal fibers, such as wool, hair, mohair, synthetic fibers including the fibers from polyesters, such as for example the ethylene glycolterephthalic acid polyesters (Dacron), the acrylic polyvinyls, such as for example the acrylonitrile polymers (Orlon), the polyethylenes, polyurethans (Perluran), polyvinyl alcohol proteins (Caslen), Alginic (Alginate rayon), non-acrylic polyvinyls as vinyl chloride and vinylidene polymers (Vinyon), mineral fibers (Fiberglas) polyamides, such as the aliphatic dicarboxylic acid-polyamides reaction products (nylon).

The terms "textile" and "textile material" as used generally herein and in the appended claims include within their meaning all types of textile materials, such as filaments, fibers, cords, threads, yarns, twisted yarns, rovings, etc., as such are in woven, felted or otherwise formed fabrics, sheets, cloths and the like.

The materials treated according to the process of the invention will have excellent crease resistance and improved dimensional stability and may be used for a wide variety of important applications. The woven cotton, rayon and wool fabrics, both colored and white, containing conventional amounts of resin, e. g., from 3% to 25% by weight, may be used, for example, in the preparation of soft goods, such as dresses, shirts, coats, sheets, and the like, while the fabrics containing much larger amounts of the resin, e. g., 25% to 50% may be used in other applications demanding more crispness and fullness such as the preparation of rugs, carpets, drapes, upholsteries, shoe fabrics, and the like.

To illustrate the manner in which the invention may be carried out, the following examples are given. It is to be understood, however, that the examples are for the purpose of illustration and the invention is not to be regarded as limited to any of the specific materials or conditions recited therein.

The wrinkle recovery values reported in some of the examples were determined by the Monsanto Recovery Method. The tests were carried out at 65% relative humidity and 70° F.

EXAMPLE I

This example illustrates the superior results obtained by using a mixture of Polyether A and dimethylol urea in the treatment of cotton.

(A) 100 parts of a mixture of resins as indicated in the table below was added to a 25/75 mixture of isopropyl alcohol and water. 6 parts of BF₃-ammonia complex was added to this mixture. Sufficient water was added to make the solution a 15% solution based on the resin solids.

Cotton cloth (80 x 80 print-unmercerized) was then impregnated with the above-described solution by means of a Butterworth-3-Roll laboratory padder. There was approximately 65% wet pick-up. The cloth was then dried at 60° C. for 5 minutes and cured at 160° C. for 5 minutes. The finished product was washed and rinsed three times in warm water to remove any soluble material.

The cloth treated in the above described manner with the mixture of Polyether A and dimethylol urea had excellent crease and shrink resistance, soft feel, good color and excellent washability. The cloth treated with the resin mixture containing at least 50% of Polyether A also had good non-chlorine retentive properties.

The results of the tests as to crease recovery are shown in the following table:

Mixture of Resin		Cease Recovery
75% Polyether A	25% Dimethylol urea	131
50% Polyether A	50% Dimethylol urea	
25% Polyether A	75% Dimethylol urea	132
75% Polyether A	25% Dimethylol urea	128
50% Polyether A	50% Dimethylol urea	

11

(B) The above high crease recovery values are much higher than could be expected from the results obtained by using Polyether A and dimethylol urea alone. This is shown by the following experiment. 100 parts of Polyether A and dimethylol urea were added to separate solutions of isopropyl alcohol and water (25/75 mixtures) and 6 parts of acid curing agents added thereto. Sufficient water was added to make a 15% solution on resin solids. Cotton cloth was impregnated with these solutions and the cloth dried at 60° C. for 5 minutes and cured at 160° C. for 5 minutes. The treated cloth was washed and rinsed three times in warm water to remove any soluble material.

The crease recovery value of the cloth treated with the 15% Polyether A solution was 121 and the crease recovery value of the cloth treated with the 15% dimethylol urea solution was 126.

EXAMPLE II

Example I was repeated with the exception that the solution containing Polyether A and dimethylol urea was a 10% solution instead of a 15% solution. The crease recovery values obtained in this case are shown in the table below:

Mixture of Resin	Crease Recovery
75% Polyether A.....	113
25% Dimethylol urea.....	
50% Polyether A.....	
50% Dimethylol urea.....	
25% Polyether A.....	
75% Dimethylol urea.....	108

The above results were quite surprising in view of the fact that the cloth treated with a 10% Polyether A solution had a crease recovery value of 98, and the cloth treated with a 10% dimethylolurea solution had a crease recovery value of 108.

The cloth treated with mixtures containing at least 50% by weight of the Polyether A also has good non-chlorine retentive properties.

EXAMPLE III

Example I was repeated with the exception that the solution containing Polyether A and dimethylol urea was a 5% solution instead of a 15% solution. The crease recovery values obtained in this case are shown in the table below:

Mixture of Resin	Crease Recovery
75% Polyether A.....	106
25% Dimethylol urea.....	
50% Polyether A.....	
50% Dimethylol urea.....	
25% Polyether A.....	
75% Dimethylol urea.....	100

The above results are quite surprising in view of the fact that the cloth treated with a 5% Polyether A solution alone had a crease recovery value of 90, and the cloth treated with a 5% dimethylol urea solution had a crease recovery value of 102.

EXAMPLE IV

This example illustrates the superior results obtained by using a mixture of Polyether A and dimethylol ethylene urea in the treatment of cotton.

100 parts of a mixture of resins as indicated in the table below was combined with 20 parts of epoxidized triglyceride, 50 parts of a 10% aqueous polyvinyl alcohol (85% hydrolyzed polyvinyl acetate) and sufficient water was added to make a 10% solution on resin solids. 8 parts of zinc fluoborate was added to the mixture as the curing agent.

Cotton fabric was then impregnated with the above-

12

described solution by means of a Butterworth-3-Roll laboratory padder. The cloth was then dried at 60° C. for 5 minutes and cured at 160° C. for 5 minutes. The finished product was washed and rinsed three times in warm water to remove any soluble material.

The cloth treated in the above-described manner with the mixture of Polyether A and dimethylol ethylene urea had excellent crease and shrink resistance, soft feel, good color and excellent washability. The cloth treated with the resin mixture containing at least 50% of Polyether A also had good non-chlorine retentive properties.

The results of the tests as to crease recovery are shown in the following table:

Mixture of Resins	Crease Recovery
75% Polyether A.....	123
25% Dimethylol ethylene urea.....	
50% Polyether A.....	
50% Dimethylol ethylene urea.....	
25% Polyether A.....	
75% Dimethylol ethylene urea.....	138

The above results are surprising in view of the fact that the cloth treated with the Polyether A solution by itself had a crease recovery value of 115, and the cloth treated with dimethylol ethylene urea by itself had a crease recovery value of 142.

EXAMPLE V

This example illustrates the superior results obtained by using a mixture of Polyether A and trimethylol melamine in the treatment of cotton fabric.

100 parts of a mixture of resins made up of 75 parts of Polyether A and 25 parts of trimethylol melamine was combined with 20 parts of epoxidized triglyceride, 50 parts of 10% aqueous solution of 85% hydrolyzed polyvinyl acetate and sufficient water to bring the total weight up to 800 parts. 8 parts of magnesium perchlorate was then added to this mixture.

Cotton cloth was then impregnated with the above-described solution by means of a Butterworth-3-Roll laboratory padder. The cloth was then dried at 60° C. for 5 minutes and cured at 160° C. for 5 minutes.

The cloth treated in the above-described manner with the mixture of Polyether A and dimethylol melamine had excellent crease and shrink resistance and no chlorine retention. The cloth also had a soft feel, good color and excellent washability.

EXAMPLE VI

This example illustrates the superior results obtained by using a mixture of Polyether A and dimethylol ethylene urea in the treatment of rayon.

100 parts of a mixture of Polyether A (50 parts) and dimethylol ethylene urea (50 parts) was combined with 20 parts of epoxidized triglyceride, 50 parts of 10% aqueous solution of 77% hydrolyzed and polyvinyl acetate and sufficient water was added to bring the total weight up to 800 parts. 8 parts of zinc fluoborate was then added to the mixture.

Rayon cloth was then impregnated with the above-described solution by means of a Butterworth-3-Roll laboratory padder. The cloth was then dried at 60° C. for 5 minutes and cured at 160° C. for 5 minutes. The finished product was washed and rinsed three times in warm water to remove any soluble material.

The cloth treated in the above-described manner had excellent crease and shrink resistance and no chlorine retention. The cloth also had a soft feel, good color and excellent washability.

EXAMPLE VII

This example illustrates the improved results obtained by using a mixture of Polyether A and 1-hydroxy-2,4,6-tri(hydroxymethyl) benzene in the treatment of cotton.

100 parts of a mixture of Polyether A (75 parts) and

13

14

1-hydroxy-2,4,6-tri(hydromethyl)benzene was combined with 20 parts of epoxidized triglyceride, 50 parts of 10% aqueous solutions of 85% hydrolyzed polyvinyl acetate and sufficient water was added to bring the total weight up to 800 parts. Phosphoric acid was then added to the mixture as curing agent.

Cotton cloth was then impregnated with the above-described solution by means of a Butterworth-3-Roll laboratory padder. The cloth showed a 65% wet pick-up. The cloth was then dried at 60° C. for 5 minutes and cured at 160° C. for 5 minutes. The finished product was washed and rinsed three times in warm water to remove any soluble material.

The cloth treated in the above-described manner had good crease and shrink resistance and no chlorine retention. The cloth also had a soft feel, good color and excellent washability. The crease recovery was better than could have been expected by the use of the components alone.

Related results are obtained by replacing the cotton fabric with rayon fabric and with a fabric made up of a mixture of cotton and rayon.

EXAMPLE VIII

This example illustrates the superior results obtained by using a mixture of Polyether A and 1-hydroxy-3-butanone in the treatment of cotton.

100 parts of a mixture of Polyether A (50 parts) and 1-hydroxy-3-butanone (50 parts) was combined with 20 parts of epoxidized triglyceride, 50 parts of a 10% aqueous solution of 77% hydrolyzed polyvinyl acetate and sufficient water was added to bring the total weight up to 800 parts. 8 parts of zinc fluoroborate was then added to the mixture.

Cotton fabric was impregnated with the above-described solutions and the cloth showed a 65% wet pick-up. The treated cloth was then dried at 60° C. for 6 minutes and cured at 160° C. for 5 minutes. The finished product was washed and rinsed three times in warm water to remove any soluble material.

The cloth treated in the above-described manner had good crease and shrink resistance and no chlorine retention. The cloth also had a soft feel, good color and excellent washability.

Related results are obtained by replacing the 1-hydroxy-3-butanone in the above treatment process with equal amounts of each of the following: 1-hydroxy-3-hexanone, 1-hydroxy-3-octanone and 1-hydroxy-3,6-butanedione.

EXAMPLE IX

This example illustrates the superior results obtained by using a mixture of Polyether C and dimethylol urea in the treatment of cotton fabric.

100 parts of a mixture made up of Polyether C (65 parts) and dimethylol urea (35 parts) was combined with 20 parts of epoxidized triglyceride, 50 parts of 10% aqueous solution of polyvinyl alcohol and sufficient water was added to bring the total weight to 800 parts. 8 parts of citric acid was then added to this mixture.

Cotton cloth was then impregnated with the above-described solution and the cloth dried at 60° C. for 5 minutes and cured at 160° C. for 5 minutes. The finished product was washed and rinsed three times in warm water to remove any soluble material.

The cloth treated in the above-described manner had excellent crease and shrink resistance and no chlorine retention. The cloth also had a soft feel, good color and excellent washability.

Related results are obtained by replacing Polyether C in the above process with an equal amount of each of

the following: Polyether A, Polyether B, vinyl cyclohexene dioxide and epoxidized tetrahydrobenzyl tetrahydrobenzoate.

I claim as my invention:

1. A process for treating textile materials which comprises impregnating the material with an aqueous medium containing a mixture of a polyepoxide having at least two vic-epoxy groups and an organic compound containing at least one $-XCH_2OH$ group wherein X is a member of the group consisting of nitrogen, carbon atoms in an aromatic ring, aliphatic and cycloaliphatic carbon atoms joined to a keto-substituted carbon atom, said polyepoxide making up from 15% to 90% by weight of the mixture of polyepoxide and compound containing at least one $-XCH_2OH$ group, and an epoxy curing agent and heating the resulting impregnated material.
2. A process as in claim 1 wherein the textile material is cotton fabric.
3. A process as in claim 1 wherein the textile material is rayon fabric.
4. A process as in claim 1 wherein the curing agent is zinc fluoroborate.
5. A process for treating textile fabrics to render them crease and shrink resistant which comprises impregnating the textile fabric with an aqueous medium containing a saturated monomeric polyepoxide having an epoxy equivalency per 100 grams between .4 and 2.0, a polymethylol-substituted nitrogen compound, said polyepoxide making up from 15% to 90% by weight of the mixture of polyepoxide and polymethylol-substituted nitrogen compound, an acid-acting epoxy curing agent, and heating the resulting impregnated fabric to a temperature above 100° C. for a short period.
6. A process as in claim 5 wherein the curing agent is zinc fluoroborate.
7. A process as in claim 5 wherein the curing agent is magnesium perchlorate.
8. A process as in claim 5 wherein the polyepoxide is a polyglycidyl ether of glycerol and the polymethyl-substituted compound is dimethylol urea.
9. A process as in claim 5 wherein the polyepoxide is a polyglycidyl ether of glycerol and the polymethyl-substituted compound is a polymethylol melamine.
10. A process as in claim 5 wherein the polyepoxide is vinyl cyclohexene dioxide and the polymethyl-substituted compound is dimethylol ethylene urea.
11. A process as in claim 5 wherein the polyepoxide is diglycidyl ether of diethylene glycol.
12. A process for treating textile fabrics to render them crease and shrink resistant which comprises impregnating the textile fabric with an aqueous medium containing a saturated monomeric polyepoxide having an epoxy equivalency per 100 grams between .4 and 2.0, a polymethylol-substituted phenolic compound, said polyepoxide making up from 15% to 90% by weight of the mixture of polyepoxide and polymethylol-substituted phenolic compound, an acid-acting epoxy curing agent, and heating the resulting impregnated fabric to a temperature above 100° C. for a short period.
13. A process as in claim 12 wherein the polyepoxide is a polyglycidyl ether of glycerol.

References Cited in the file of this patent

UNITED STATES PATENTS

2,512,996	Bixler	June 27, 1950
2,541,027	Bradley	Feb. 13, 1951
2,606,810	Erickson	Aug. 12, 1952
2,681,901	Wiles	June 22, 1954
2,752,269	Condo	June 26, 1956