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2,886,473

PROCESS FOR TREATING TEXTILE MATERIALS AND RESULTING PRODUCTS

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

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This invention relates to the treatment of textile materials. More particularly, the invention relates to a process for treating cellulosic textile materials to improve their crease and shrink resistance without unduly affecting the strength of the materials.

Specifically, the invention provides a new process for treating cellulosic textile materials to improve their crease and shrink resistance without unduly affecting their strength, which process comprises treating the textile material with an aqueous medium containing a polyether polyepoxide, rubber latex and an epoxy curing agent and heating to effect cure. The invention further provides improved textile materials prepared by the aforedescribed process.

I have recently found that polyether polyepoxides are promising materials for imparting crease and shrink resistance to textile fabrics. When these materials are applied to the fabric in the form of aqueous solutions or dispersions and then cured in the presence of a curing agent, the resulting goods have a soft hand and excellent crease and shrink resistance. The polyether polyepoxides are superior in this application to the crease- and shrink-proofing agents used heretofore, such as urea-aldehyde type resins, in that they tend to give higher wrinkle recovery values, better washability and can be applied to white goods without fear of discoloration after bleaching.

One of the difficulties encountered in the use of the polyepoxides, however, has been the fact that in some cases the polyepoxides, like other crease-proofing agents, cause some loss in tensile strength of the treated material. This is not significant for certain applications, but if the material is to be used in the manufacture of goods, such as shirts and blouses, it would be highly desirable if some way could be found to lessen or eliminate the loss of strength.

It is, therefore, an object of the invention to provide a new process for the treatment of textile materials. It is a further object to provide a process for treating textile materials to improve their crease and shrink resistance without material loss of strength. It is a further object to provide a process for treating cellulosic textile materials with polyether polyepoxides to improve their crease and shrink resistance without unduly affecting their tensile and tear strength. It is a further object to provide a process for treating cellulosic textile materials to improve crease and shrink resistance which has little effect on tear strength as well as tensile strength. It is a further object to provide treated textile materials having improved crease and shrink resistance and good tensile and tear 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 process of the invention which comprises treating the textile material with an aqueous medium containing a polyether polyepoxide, rubber and an epoxy curing agent and heating to effect

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cure. It has been found that the textile materials treated in this manner not only have all of the desired properties previously obtained by the treatment with the polyether polyepoxide, such as high crease and shrink resistance, soft feel and good hand, good washability and non-chlorine retention, but in addition possess far better tensile and tear strength. In addition, in many cases, the crease recovery is also better than that obtained with the polyether polyepoxides alone. Evidence of these unexpected improvements obtained by the above process may be found in the working examples at the end of the specification.

Unless otherwise indicated, the expression "rubber" as used herein refers to natural and synthetic rubber. Representative synthetic rubbery polymers include the "butadiene polymers." Butadiene polymers include those polymers having rubber-like properties which are prepared by polymerizing butadiene alone or with one or more other copolymerizable ethylenically unsaturated compounds, such as styrene, methyl methacrylate, 3,4-dichloro- α -methyl styrene, methyl isopropenyl ketone and acrylonitrile, the butadiene being present in the mixture preferably to the extent of at least 40% and preferably 60-75% of the total polymerizable material. The butadiene-acrylonitrile copolymers are manufactured commercially under such names as "Hycar OR-15" and OR-25. The butadiene-styrene copolymers are produced commercially under such names as GRS-2000 and the like.

Other synthetic rubbers include neoprene rubbers. "Neoprene" is a generic name which is applied to polymers of chloroprene and copolymers of chloroprene with dienes or vinyl compounds in which the chloroprene comprises the predominant monomer. These polymers and copolymers usually made in aqueous emulsions and are available on the market under the names as GR-M, Neoprene Type GN, Neoprene Type E, Neoprene FR and the like.

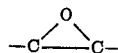
Isobutylene rubbers, such as those known in industry as GR-1 rubbers, may also be used in the process of the invention.

Polyacrylate rubbers, such as those produced from acrylic acid and methacrylic acid esters as ethyl acrylate (Hycar 4021) may also be used.

The foregoing rubber materials, including both natural rubber as well as the various synthetic rubbers may be defined as "rubbery polymers of at least one compound selected from the group consisting of the conjugated diolefins and chloroprene."

The rubbers may be utilized as such or in the form in which they are prepared, such as a latex or dispersion.

The polyepoxides used in preparing the treating compositions used in the process of the invention comprise those compounds having at least two epoxy groups, i.e., at least two



groups. The polyepoxides may be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic and may be substituted if desired with substituents, such as chlorine atoms, hydroxyl groups, ether radicals and the like. They may also be monomeric or polymeric.

For clarity, many of the polyepoxides and particularly those of the polymeric type will be described throughout the specification and claims in terms of epoxy equivalent value. The meaning of this expression is described in U.S. 2,633,458.

If the polyepoxide material consists of a single compound and all of the epoxy groups are intact, the epoxy equivalency will be integers, such as 2, 3, 4 and the like.

3 However, in the case of the polymeric type polyepoxides many of the materials may contain some of the mono-meric monoepoxides or have some of their epoxy groups hydrated or otherwise reacted and/or contain macromolecules of somewhat different molecular weight so the epoxy equivalent values may be quite low and contain fractional values. The polymeric material may, for example, have epoxy equivalent values, such as 1.5, 1.8, 2.5, and the like.

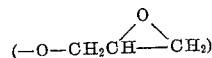
Examples of the polyepoxides include, among others, 10 epoxidized triglycerides as epoxidized glycerol trioleate and epoxidized glycerol trilinoleate, the monoacetate or epoxidized glycerol dioleate, 1,4-bis(2,3-epoxypropoxy) benzene, 1,3-bis(2,3-epoxypropoxy) benzene, 4,4'-bis(2,3-epoxypropoxy) diphenyl ether, 1,8-bis(2,3-epoxypropoxy)- 15 octane, 1,4-bis(2,3-epoxypropoxy) cyclohexane, 4,4'-bis(2-hydroxy-3,4'-epoxybutoxy) diphenyldimethylmethane, 1,3-bis(4,5-epoxypentoxy)-5-chlorobenzene, 1,4-bis(3,4-epoxybutoxy)-2-chlorocyclohexane, 1,3-bis(2-hydroxy-3,4-epoxybutoxy) benzene, 1,4-bis and (2-hydroxy-4,5-epoxy- 20 pentoxy) benzene.

Other polyepoxides comprise the polyepoxide polyethers obtained by reacting, preferably in the presence of an acid-acting compound, such as hydrofluoric acid, one of the afore-described halogen-containing epoxides with a 25 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, hydroxy-ketones, 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-hydroxyethyl 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 mono-glycerides, such as monostearin, monoesters 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.

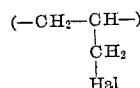
Coming under special consideration are the polyglycidyl polyethers of polyhydric alcohols obtained by reacting the polyhydric alcohol with epichlorohydrin, preferably in the presence of 0.1% to 5% by weight of an acid-acting compound, such as boron trifluoride, hydrofluoric acid, stannic chloride or 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 in general contain at least three non-cyclic ether (—O—) linkages, terminal epoxide-containing ether

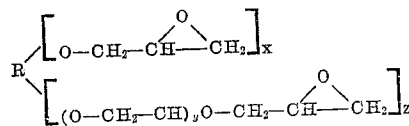


groups and halogen attached to a carbon of an intermediate



group.

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



30 in which R is the residue of the polyhydric alcohol which may contain unreacted hydroxyl group. 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.

40 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.

45 PREPARATION OF GLYCIDYL POLYETHERS OF POLYHYDRIC ALCOHOLS

Polyether A.—About 276 parts (3 moles) of glycerol with mixed with 10 parts of diethyl ether solution containing about 4.5% boron trifluoride and then 832 parts (9 moles) of epichlorohydrin added dropwise. The temperature of this mixture was between 50° C. and 75° C. for about 3 hours. About 370 parts of the resulting glycerol-epichlorohydrin condensate was dissolved in 900 55 parts of dioxane containing about 300 parts of sodium aluminate. While agitating, the reaction mixtures 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 0.671 equivalent per 100 grams and the molecular weight was 324 as measured ebullioscopically in dioxane solution. For convenience, this product will be referred to hereinafter as Polyether A.

Polyether A produced above may be extracted with water to obtain a water soluble fraction referred to hereinafter as Polyether A.

70 *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

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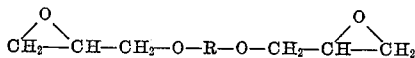
was placed in a reaction kettle and heated to 65–70° C. Sufficient BF₃-ethyl ether complex was added to bring the pH to about 1.0 and then 132 parts of epichlorohydrin added dropwise. After all the epi had been added, the reaction was continued for about 15 minutes to assure complete reaction. This product was then dissolved in benzene and 57 parts of sodium hydroxide were added in 7 equal portions at about 87–89° C. over a period of ¾ hour and then filtered to remove 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.

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 to 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.

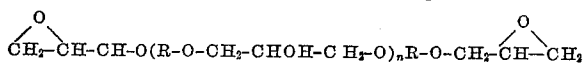
Particularly preferred members of this group comprise the glycidyl polyethers of aliphatic polyhydric alcohols containing from 2 to 10 carbon atoms and having from 2 to 6 hydroxyl groups and more preferably the alkane polyols containing from 2 to 8 carbon atoms and having from 2 to 6 hydroxyl groups. 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.

Other examples include the epoxy polyethers of polyhydric phenols obtained by reacting a polyhydric phenol with a halogen-containing epoxide or dihalohydrin in the presence of an alkaline medium. Polyhydric phenols that can be used for this purpose include among others resorcinol, catechol, hydroquinone, methyl resorcinol, or polynuclear phenols, such as 2,2-bis(4-hydroxyphenyl) propane (Bisphenol A), 2,2-bis(4-hydroxyphenyl) butane), 4,4'-dihydroxybenzophenone, bis(4-hydroxyphenyl) ethane, 2,2-bis(4-hydroxyphenyl) pentane, and 1,5-dihydroxynaphthalene. The halogen-containing epoxides may be further exemplified by 3-chloro-1,2-epoxybutane, 3-bromo-1,2-epoxyhexane, 3-chloro-1,2-epoxyoctane, and the like.

The monomer products produced by this method from dihydric phenols and epichlorohydrin may be represented by the general formula



wherein R represents a divalent hydrocarbon radical of the dihydric phenol. The polymeric products will generally not be a single simple molecule but will be a complex mixture of glycidyl polyethers of the general formula



wherein R is a divalent hydrocarbon radical of the dihydric phenol and *n* is an integer of the series 0, 1, 2, 3, etc. While for any single molecule of the polyether, *n* is an integer, the fact that the obtained polyether is a mixture of compounds causes the determined value for *n* to be an average which is not necessarily zero or a whole number. The polyethers may in some cases contain a very small amount of material with one or both of the terminal glycidyl radicals in hydrated form.

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 alka-

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linity 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 dihydric phenols will be illustrated below. Unless otherwise specified, parts indicated are parts by weight.

PREPARATION OF GLYCIDYL POLYETHERS OF DIHYDRIC PHENOLS

Polyether D.—About 2 moles of 2,2-bis(4-hydroxyphenyl) propane 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 quantity by weight 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 eq./100 g. of 0.50 so the epoxy equivalency was 1.75.

Polyether E.—A solution consisting of 11.7 parts of water, 1.22 parts of sodium hydroxide, and 13.38 parts of 2,2-bis(4-hydroxyphenyl) propane was prepared by heating the mixture of ingredients to 70° C. and then cooling to 46° C. at which temperature 14.06 parts of epichlorohydrin was added while agitating the mixture. After 25 minutes had elapsed, there was added during an additional 15 minutes' time a solution consisting of 5.62 parts of sodium hydroxide in 11.7 parts of water. This caused the temperature to rise to 63° C. Washing with water at a temperature of 20° C. to 30° C. was started 30 minutes later and continued for 4½ hours. The product was dried by heating to a final temperature of 140° C. in 80 minutes, and cooled rapidly. At room temperature, the product was an extremely viscous semi-solid having a melting point of 27° C. by Durran's mercury method and a molecular weight of 483. The product had an epoxy value eq./100 g. of 0.40.

Polyether F.—About 228 parts of 2,2-bis(4-hydroxyphenyl) propane and 84 parts sodium hydroxide as a 10% aqueous solution were combined and heated to about 45° C. whereupon 177 parts of epichlorohydrin was added rapidly. The temperature increased and remained at about 95° C. for 80 minutes. The mixture separated into a two-phase system and the aqueous layer is drawn off. The resinous layer that remained is washed with hot water and then drained and dried at a temperature of 130° C. The Durran's mercury method melting point of the resulting product is 52° C. and the molecular weight is about 710. The product has an epoxy value of 0.27 eq./100 g.

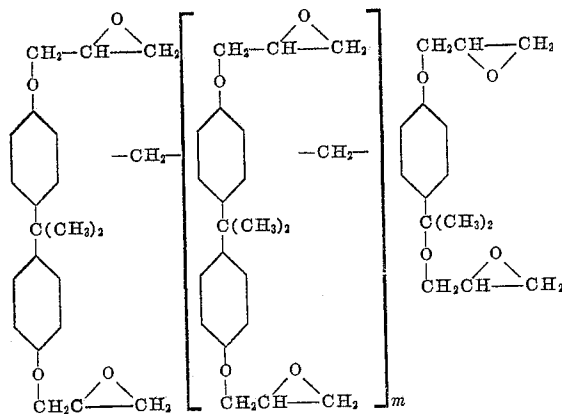
Polyether G.—By using a smaller ratio of epichlorohydrin to 2,2-bis(4-hydroxyphenyl) propane a glycidyl polyether of higher melting point was obtained. Thus, polyether D was obtained in the same manner as polyether C except that for every mole of 2,2-bis(4-hydroxyphenyl) propane, there was used 1.57 moles of epichlorohydrin and 1.88 moles of sodium hydroxide. This provided a product having a melting point of about 70° C., a molecular weight of 900 and an epoxide value of 0.20 eq./100 g.

Preferred members of the above-described group of polyepoxides are the glycidyl polyethers of the dihydric

phenols, and especially 2,2-bis(4-hydroxyphenyl) propane, having an epoxy equivalency between 1.0 and 2.0 and a molecular weight between 300 and 900. Particularly preferred are those having a Durran's mercury method softening point no greater than 60° C.

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

Another group of polyepoxides that may be used to prepare the adducts comprise the glycidyl ethers of novolac resins which resins are obtained by condensing an aldehyde with a polyhydric phenol. A typical member of this class is the epoxy resin from formaldehyde 2,2-bis(5-hydroxyphenol) propane novolac resin which contains as predominant constituent the substance represented by the formula



wherein m is a value of at least 1.0. For the nature and preparation of novolac resins, see the book by T. S. Carswell, Phenoplasts, 1947, page 29, et seq.

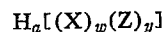
Another group of polyepoxides include the glycidyl polyethers of a polyhydric phenol which has two hydroxyaryl groups separated by an aliphatic chain of at least six carbon atoms in the chain and with the chain being attached by carbon-to-carbon bonding to a nuclear carbon atom of the hydroxyl aryl groups. Suitable phenols used for preparing these resins comprise those obtained by condensing phenol with a phenol having an aliphatic side chain with one or more olefinic double bonds positioned in the chain so the required separating atoms are present between two hydroxyphenol groups of the resulting polyhydric phenol. Cardanol, obtainable in known manner from cashew nut shell liquid, is a convenient source of phenols containing such side chain. Mixed grades of cardanol containing about equal amounts of m -(8-pentadecenyl) phenol and a phenol with a 15 carbon atom side chain having two double bonds similarly removed from the aromatic nucleus are available from the Irvington Varnish and Insulator Co.

Another group of polyepoxides include the epoxy esters of polybasic acids, such as diglycidyl phthalate and diglycidyl adipate, diglycidyl tetrahydrophthalate, diglycidyl maleate, epoxidized dimethylallyl phthalate and epoxidized dicrotyl phthalate.

The epoxy curing agent employed in the impregnating solution may be any alkaline, neutral or acidic material which acts to effect cure of the polyepoxide to form an insoluble product. The epoxy curing agent is preferably neutral or alkaline. Use of acidic curing agents requires special procedure in preparation of the rubber latex as indicated hereinafter. Examples of curing agents include, among others, alkalis 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

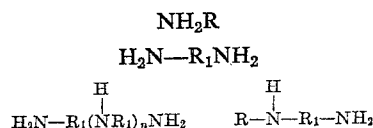
chloride or boron trifluoride as well as complexes thereof with ethers, acid anhydrides, ketones, diazonium salts, etc.; salts, such as zinc fluoborate, magnesium perchlorate and zinc fluosilicate; phosphoric acid and partial esters thereof including n -butyl orthophosphate, diethyl orthophosphate and hexethyl tetraphosphate; amino compounds, such as, for example, diethylene triamine, triethylene tetraamine, dicyandiamide, melamine, pyridine, cyclohexylamine, benzyldimethylamine, benzylamine, diethylaniline, triethanolamine, piperidine, tetramethylpiperazine, 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, diolelamine, dicyclohexylamine, methylethylamine, ethylcyclohexylamine, o -tolylaminophthylamine, pyrrolidine, 2-methylpyrrolidine, tetrahydropyridine, 2-methylpiperidine, 2,6-dimethylpiperidine, diaminopyridine, tetraethylene pentamine, metaphenylene 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 curing agents to be employed are the poly-carboxylic acids and their anhydrides, the primary and secondary aliphatic and aromatic amines and salts of metals having an atomic weight between 24 and 210, and preferably in groups I to IV and VIII of the periodic table of elements and inorganic acids 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 gains 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 a equals the valency of the radical $(X)_w(Z)_y$, such as sulfuric acid, fluoboric acid, fluosilicic acid, persulfuric acid, phosphoric acid and the like.

Coming under special consideration are the mono- and polyamines, such as those of the formulae



wherein R is a monovalent hydrocarbon radical and R_1 is a bivalent hydrocarbon radical, containing no more than 18 carbon atoms and n is an integer, preferably from 1 to 8.

Also coming under special consideration are the adducts of the above-described preferred amines and polyepoxides, such as obtained when one utilizes from 1.5 to 3 moles of the polyamine per epoxide equivalent weight of the polyepoxide. Only about one mole of the amine actually reacts and chemically combines with one epoxy equivalent weight of the polyepoxide. The unreacted excess amine is then preferably separated and removed from the reaction product as completely as possible by usual methods, such as distillation or extraction. Salts of these adducts and organic or inorganic acids and particularly their neutral fatty acid salts are also preferred as curing agents.

The above-described components are applied to the fibrous material in the form of an aqueous medium. The medium may be a water solution or an aqueous emulsion or dispersion. All three components may be added as such directly to an aqueous medium or one or more of the components may be added separately in the form of an aqueous dispersion or emulsion. In most cases, it is preferred to add the polyepoxide and epoxy curing agent to an aqueous rubber latex such as may be ob-

tained by the conventional rubber polymerization techniques. If the polyepoxide has limited solubility, it is usually preferred to add the polyepoxide to the rubber dispersion in the form of an aqueous emulsion.

Preferred emulsifying agents that may be utilized in the formation of the treating composition or in the preparation of emulsions of the various components include, among others, monooleate of sorbitan polyoxyethylene, the trioleate of sorbitan polyoxyethylene, sorbitan tristearate, sorbitan monolaurate, polyoxyethylene esters of alkyl phenols, carbomethylcellulose, starch, gum arabic, polyvinyl alcohol, aryl and alkylated aryl sulfonates, such as cetyl sulfonate, oleylatezulfonate, 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 polyether polyepoxide in the impregnating solution may vary over a considerable range depending chiefly on the amount of resin to be deposited on the fabric and this, in turn, will depend on the number of applications and the pick-up allowed per application. When the solution is applied but once, with a 65% to 100% pick-up by weight of the fabric in the dry state, a concentration ranging from 3% to 25% by weight will ordinarily suffice. If less than 65% pick-up is permitted, the concentration may in some cases go as high as 30% to 50%.

The rubber is added to the impregnating solution in amounts varying from about 5 parts to 70 parts per 100 parts of the polyether polyepoxide, and more preferably in amounts varying from 10 to 60 parts per 100 parts of the polyether polyepoxide.

The amount of curing agent used may vary over a wide range depending on the particular type utilized. The amount of agent preferably varies from 0.5% to 40% by weight of the polyepoxide and more preferably from about 5% to 30% by weight of the polyepoxide. If the curing agent is an acid anhydride, it is preferably utilized in equivalent amounts, i.e., an anhydride group for every epoxy group.

If the epoxy curing agent is an acidic material and the rubber is employed as a dispersion, it is necessary to take steps to stabilize the dispersion. This is preferably accomplished by adding a small amount of ammonium caseinate, remove the ammoniate from the latex by addition of the required amount of formaldehyde. The acid curing agent then may be added to the stabilized latex with stirring.

The treating solution is preferably prepared by combining the components as indicated above and then stirring to effect thorough mixing. This may be accomplished by use of stirrers or by other mechanical means.

The aqueous medium employed to treat the textile materials may also contain other materials. The aqueous medium may contain, for example, polyaldehydes, such as glutaraldehyde, to assist in the crease and shrink-proofing of the cloth.

The medium may also contain plasticizers to improve their flexibility, 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 would be so 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, sulphoamides, alkyl phthalates, for example, diethyl phthalate and glycol phthalates, diethyl tartarate, derivatives of polyhydric alcohols, for example, mono-, di- and tri-acetin, and products obtained by condensing polyhydric alcohols with themselves or with aldehydes or

ketones. The compositions may also contain natural resins, e.g., shellac, resin, and other natural resins and synthetic or semi-synthetic resins, e.g., ester gum, polyhydroxy-polybasic alkyd resins, phenol aldehyde and urea-aldehyde 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, epoxidized glycerides, such as epoxidized soybean oil, glycidyl octadecyl ether, 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 polyglycols. Preferred softeners are the epoxidized tri- and diglycerides.

The application of the treating solution to the textile materials may be effected in any suitable manner. It is generally preferred to apply the solution by simply dipping the fibrous material, loose or under tension, into the solution and running it through conventional-type padding rollers. The solution can also be applied by spraying, brushing or other conventional methods. If the desired amount of rubber and polyepoxide 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 rubber and polyepoxide to the desired level. Wet-pick up per pass preferably varies from 20% to 100% and more preferably from 30% to 80%.

The amount of the polyepoxides to be deposited on the fabric will vary over a wide range depending upon the degree of crease 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 polyether polyepoxide deposited will generally vary from 3% to 20% by weight of the fabric. If stiffer materials are required such as for shoe fabrics, draperies, etc., still higher amounts of resins, such as of the order of 25% to 50% by weight may be deposited.

After the desired amount of solution has been applied, the treated fibrous material is preferably dried for a short period to remove some or all of the dispersing liquid, such as the water. This is preferably accomplished by maintaining the material at its original dimensions and exposing the framed product to elevated temperatures for a few minutes. Drying time will depend largely on the amount of pick-up permitted during the application of the solution and the concentration of the solution. In most cases, drying periods of from 1 to 30 minutes at temperatures ranging from about 100° C. to 200° C. should be sufficient. Water content of the treated fibrous material is preferably reduced below 10% and more preferably below 5%. Drying may be accomplished by exposure to infrared rays for a few seconds.

The framed fabric is then exposed to relatively high temperatures to accelerate the cure of the polyepoxides. 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 cellulosic textile material. The textile material may be of any type, such as woven, knitted, or netted and may be white or colored. Examples of these materials include, among others textile materials made of cotton, linen, regenerated cellulose, cellulose esters as cellulose acetate, such as obtained by the viscose, cuprammonium or nitrocellulose process, and blends of these materials with other fiber-forming materials such as jute, hemp, wool, animal fibers, hair, mohair, synthetic fibers, such as polyesters as the ethylene glycol phthalic acid polyesters (Dacron), the acrylic polyvinyls, such as the acrylonitrile polymers (Orlon), the polyethylenes, polyurethans (Perluran), polyvinyl alcohol fibers, pro-

teins, alginic (alginate rayon), non-acrylic polyvinyls as vinyl chloride and vinylidene polymers (Vinyon), mineral fibers (Fiberglas), polyamides, such as the aliphatic dicarboxylic acid-polyamide reaction products (nylon).

The materials treated according to the process of the invention will have excellent crease and shrink resistance and good strength and are suited for preparing a great variety of different type articles. The woven 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 skirts, dresses, shirts, coats, 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 as in the preparation of rugs and carpets.

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 wrinkle recovery method, and the tear strength values were determined by the trapezoid method ASTM-D-39-49. All tests were carried out at 65% relative humidity and 70° F.

Unless otherwise indicated, parts disclosed in the examples are parts by weight.

Example I

This example illustrates the unexpected improvement in strength that is obtained by treating a cotton fabric with an aqueous medium containing Polyether A and Hycar rubber (butadiene-acrylonitrile copolymer) with zinc fluoborate as the curing agent.

An impregnating solution was prepared as follows: 100 parts of Polyether A and 10.0 parts of a polyethylene glycol monostearate were mixed together. To this mixture was added 75 parts of a 5% aqueous solution of polyvinyl alcohol (Elvanol 32/70), 100 parts of an aqueous solution containing 7.23 parts of zinc fluoborate and 50 parts of Hycar OR-15 (now Hycar 1001-60% butadiene-40% acrylonitrile) rubber latex (40% solids). Additional water was added to make the solution 12% Polyether A solution.

Similar impregnating solutions were prepared containing 75 parts of the Hycar rubber latex, 100 parts of the rubber latex and 125 parts of the rubber latex.

Pieces of cotton cloth were then impregnated with each of the above solutions by means of a Butterworth 3-roll laboratory padder. The sheets after padding showed a 65% wet pick-up. The impregnated sheets were then dried at 90° C. for 5 minutes and cured at 160° C. for 5 minutes. The finished sheets were then washed in a 0.1% solution of Ivory Flakes and 0.065% Na₂CO₃ solution at 70° C. for 12 minutes and then rinsed three times in water.

The sheets treated in the above-described manner had the same color as before the treatment, had a soft feel, good hand, good crease and shrink resistance and improved strength.

The tensile and tear strengths and wrinkle recovery values for each of the sheets are shown below in comparison to the values obtained with untreated sheets and sheets treated only with Polyether A:

Conc. Pol. A	Conc. of Rubber—PH-PA ¹	Wrinkle Recovery	Tensile Strength, lbs./in.	Tear Strength
12%-----	0	124	42.9	1.04
12%-----	20	128	47.8	1.18
12%-----	30	136	51.1	1.27
12%-----	40	133	45.3	1.31
12%-----	50	134	52.1	1.50

¹ Parts per hundred of Polyether A.

Similar results are obtained by replacing the Hycar OR-15 with an equal amount of Hycar OR-25 (1002), (67% butadiene, 33% acrylonitrile).

Example II

This example illustrates the unexpected improvement in strength that is obtained by treating cotton fabric with an aqueous medium containing Polyether A and Hycar OR-15 rubber latex with magnesium perchlorate as the curing agent.

An impregnating solution was prepared as follows: 100 parts of Polyether A and 10.0 parts of a polyethylene glycol monostearate were mixed together. To this mixture was added 75 parts of a 5% solution of polyvinyl alcohol (32/70), 100 parts of an aqueous solution containing 7.5 parts of magnesium perchlorate and 50 parts of Hycar rubber latex (40% solids). Additional water was added to make the solution at 12% Polyether A solution.

Similar impregnating solutions were prepared containing 75 parts of the Hycar OR-15 rubber latex, 100 parts of the rubber latex and 125 parts of the rubber latex.

Pieces of cotton cloth were then impregnated with each of the above solutions by means of a Butterworth 3-roll laboratory padder. The sheets after padding showed a 65% wet pick-up. The impregnated sheets were then dried at 90° C. for 5 minutes and cured at 160° C. for 5 minutes. The finished sheets were then washed in a 0.1% solution of Ivory Flakes and 0.065% Na₂CO₃ solution at 70° C. for 12 minutes and then rinsed three times in water.

The sheets treated in the above-described manner had the same color as before the treatment, had a soft feel, good hand, good crease and shrink resistance and improved strength.

The tensile and tear strengths for each of the sheets are shown below in comparison to values obtained with the sheet treated only with Polyether A. The wrinkle recovery values in each case were about the same.

Conc. Polyether A	Conc. of Rubber—PH-PA	Tensile Strength, lbs./in.	Tear Strength
12%-----	0	41.2	0.94
12%-----	20	57.3	1.54
12%-----	30	57.1	1.74
12%-----	40	59.1	1.65

Example III

This example illustrates the unexpected improvement in strength that is obtained by treating rayon fabric with an aqueous medium containing Polyether A, glutaraldehyde and Hycar OR-15 rubber latex with zinc fluoborate as the curing agent.

An impregnating solution was prepared as follows: 100 parts of Polyether A was combined with 5 parts of polyethylene oxide condensation product of sorbitan monopalmitate and 50 parts of a 5% solution of polyvinyl alcohol and the mixture stirred. 150 parts of 30% aqueous glutaraldehyde, 11.2 parts of zinc fluoborate and 50 parts of Hycar OR-15 (40% solids) were then stirred into the above mixture and sufficient water added to bring the total to 1000 parts (giving 15% solution of polyepoxide and polyaldehyde).

Rayon cloth was then impregnated with the above-described solutions 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 good wrinkle and shrink resistance, good hand and a soft feel and improved strength. The tensile strength of the cloth was 71.0 as compared to 63.0 for cloth

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treated only with Polyether A and glutaraldehyde and a tear strength of 1.52 as compared to a value of 0.94 for cloth treated only with Polyether A and glutaraldehyde.

Similar results are obtained by replacing Polyether A in the above process with equivalent amounts of each of the following: Polyether B, Polyether C and Polyether D.

Example IV

100 parts of Polyether A and 10 parts of a polyethylene glycol monostearate are mixed together at 100° C. 100 parts of a 5% aqueous solution of polyvinyl alcohol (77% hydrolyzed polyvinyl acetate) are slowly added thereto with stirring. 100 parts of a GR-S 2000 (44-48% styrene, 56-42% butadiene) latex (33.1% solids) and 7.5 parts of zinc fluoborate are added with additional water to make the solution into a 10% Polyether A solution.

Cotton gingham cloth (5.6 yd./lb. 80-70 count) is impregnated with the above aqueous medium 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 is then washed and rinsed three times in warm water to remove any soluble material.

The cloth treated in the above-described manner has good wrinkle and shrink resistance, good hand and soft feel and has higher tensile and tear strength values than similar cloth treated with a solution containing only Polyether A.

Similar results are obtained by replacing the GR-S 2000 latex in the above process with equal amounts of each of the following: natural rubber latex, GR-S 2101 (21-24.5% styrene and 79-74% butadiene) and neoprene latex.

Example V

100 parts of Polyether A and 10 parts of a polyethylene glycol monostearate are mixed together at 100° C. 100 parts of a 5% aqueous solution of polyvinyl alcohol are slowly added thereto with stirring. 100 parts of a vinyl pyridine-butadiene copolymer (41.1% solids) and 7 parts of magnesium perchlorate are added with additional water to make the solution into a 10% Polyether A solution.

Cotton gingham cloth is impregnated with the above aqueous medium by means of a Butterworth-3-roll laboratory padder. The cloth is then dried at 60° C. for 5 minutes and cured at 160° C. for 5 minutes. The finished product is washed and rinsed three times in warm water to remove any soluble material.

The cloth treated in the above-described manner has good wrinkle and shrink resistance, good hand and a soft feel and good strength. The tensile and tear strength of the cloth is higher than that of cloth treated only with Polyether A.

Similar results are obtained by replacing Polyether A in the above process with equivalent amounts of each of the following: Polyether C, Polyether D and Polyether F.

Example VI

100 parts of Polyether A and 10 parts of a polyethylene glycol monostearate are mixed together at 100° C. 100 parts of a 5% aqueous solution of polyvinyl alcohol are added thereto with stirring. 100 parts of a butadiene-acrylonitrile copolymer latex (40% solids) and 16 parts of diethylene triamine are added with additional water to make the solution into a 10% Polyether A solution.

Cotton gingham cloth is impregnated with the above aqueous medium by means of a Butterworth-3-roll laboratory padder. The cloth is then dried at 60° C. for 5 minutes and cured at 160° C. for 5 minutes. The finished product is washed and rinsed three times in warm water to remove any soluble material.

The cloth treated in the above-described manner has good wrinkle and shrink resistance, good hand, a soft feel and improved strength.

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Similar results are obtained by replacing the diethylene triamine with equal amounts of each of the following: triethylene tetraamine, soluble adduct of Polyether D and diethylene triamine and ethylene diamine.

Example VII

100 parts of Polyether A and 10 parts of a polyethylene glycol monostearate are mixed together at 100° C. 100 parts of a 5% aqueous solution of polyvinyl alcohol (77% hydrolyzed polyvinyl acetate) are slowly added thereto with stirring. 100 parts of Hycar 4021 (polyacrylate rubber) latex and 7.5 parts of zinc fluoborate are added with additional water to make the solution into a 10% Polyether A solution.

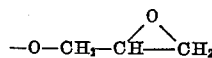
Cotton gingham cloth is impregnated with the above aqueous medium by means of a Butterworth-3-roll laboratory padder, dried and cured as in the preceding example. The cloth treated in this manner has good wrinkle and shrink resistance, good hand and soft feel and has higher tensile and tear strength values than similar cloth treated with a solution containing only Polyether A.

I claim as my invention:

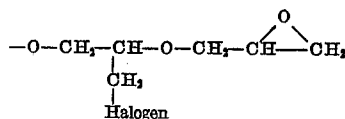
1. A process for preparing polyepoxide-treated cellulosic fabrics having improved tensile strength which comprises impregnating a cellulosic textile material with a 3% to 50% aqueous solution of a polyether polyepoxide containing 5 parts to 60 parts per 100 parts of polyether polyepoxide of a rubber selected from the group consisting of a butadiene-styrene copolymers, butadiene-acrylonitrile copolymers and butadiene-vinylpyridine copolymers, and 0.5% to 40% of an epoxy resin curing agent and heating at a temperature between 100° C. and 200° C. to cure the polyether polyepoxide.

2. A process for preparing polyepoxide-treated cotton-containing fabric having improved tensile strength which comprises impregnating a cotton-containing fabric with a 3% to 50% aqueous emulsion of a polyglycidyl ether of glycerol-containing 5 parts to 60 parts per 100 parts of polyglycidyl ether of a butadiene-acrylonitrile copolymer, and 0.5% to 40% of an acid epoxy curing agent and then heating between 100° C. and 200° C. to cure the polyglycidyl ether of glycerol.

3. A process as in claim 1 wherein the polyether polyepoxide is a halogen-containing polyether polyepoxide composition which composition is a mixture of ethers of polyhydric alcohols, the polyhydric alcohols having from 2 to 5 hydroxyl groups with at least two of the hydroxyl groups replaced in part by the group



and in part by the group



and any hydroxyl groups which are not so replaced being unchanged hydroxyl groups.

4. A process as in claim 1 wherein the fabric is cotton.

5. A process as in claim 1 wherein the fabric is regenerated cellulose.

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