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## TREATMENT OF WOOL CONTAINING TEXTILES

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This invention relates to the treatment of wool containing textiles. More particularly, the invention relates to a process for treating wool containing textiles to reduce their tendency to shrink and to improve their water repellancy.

Specifically, the invention provides a new and particularly efficient process for treating wool containing textile fabrics to reduce their tendency to shrink and to improve their water repellancy which comprises impregnating the wool-containing fabric with an aqueous medium containing a polyether polyepoxide and an amine catalyst and subjecting the impregnated fabric to an elevated temperature to cure the polyether polyepoxide in the fibers of the fabric. The invention further provides improved fabrics prepared by the afore-described process.

Wool containing materials have poor dimensional stability and tend to shrink when subjected to ordinary washing conditions. These materials also tend to mat together and lose shape when they are agitated while damp. Numerous methods have been employed in the past to correct these defects and provide wool containing fabrics having improved shrink resistance and better water repellancy, but the results obtained have not been too satisfactory. Many of the methods suggested, for example, have imparted a harsh feel and considerable stiffness to the fabric. Other methods have employed ingredients which have damaged the fiber and reduced the wearing qualities of the fabric. Still other methods have given only a temporary improvement and the increase in shrink resistance and water repellancy is lost after several launderings.

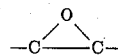
It is an object of the invention, therefore, to provide a new and improved method for treating wool containing fabrics. It is a further object to provide a new process for rendering wool containing fabrics shrink resistant. It is a further object to provide a method for improving the water repellancy of wool containing fabrics. It is a further object to provide a method for rendering wool containing fabrics more shrink resistant and more water repellent without giving a harsh feel and undue stiffness to the fabric. It is a further object to provide a process for rendering wool containing fabrics shrink resistant which has little, if any, detrimental effect on the other desired properties of the fabric. It is a further object to provide a method for treating wool containing fabrics which makes the fabric more crease resistant as well as more shrink resistant. It is a further object to provide wool containing fabrics having these and other improved properties. 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 wool containing fabric with an aqueous medium containing a polyether polyepoxide, and particularly a glycidyl polyether of a polyhydric alcohol, and an amine catalyst and subjecting

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the impregnated fabric to an elevated temperature to cure the polyether polyepoxide in the fibers of the fabric. It has been found that wool containing fabrics treated in this manner, even with relatively small amounts of the polyether polyepoxide, have outstanding shrink resistance and good water repellancy. Wool flannel cloth treated with the preferred glycidyl polyethers of the polyhydric alcohols and the amine catalysts, for example, show only a shrinkage of from .5% to 2% after five launderings while an untreated flannel after five launderings shows a shrinkage of up to 35%. Cloth treated in this manner also has a soft feel and good hand and can be used for many applications for which the wool treated with many of the known shrink proofing agents would be entirely unsuited. Surprisingly, these properties are also obtained with little, if any, loss of other desired properties, such as tear and tensile strength, which loss generally occurs with the addition of many of the conventional shrink proofing agents.

The polyether polyepoxides to be used in the process of the invention comprise those compounds possessing at least two ether linkages (i. e., —O— linkages) and a plurality of 1,2-epoxy groups (i. e.,



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

For clarity, many of the polyether polyepoxides and particularly those of the polymeric type will be described throughout the specification and claims in terms of an epoxy equivalency. The term "epoxy equivalency" as used herein refers to the average number of epoxy groups contained in the average molecule. This value is obtained by dividing the average molecular weight of the polyepoxide by the epoxide equivalent weight. The epoxide equivalent weight is determined by heating a one-gram sample of the polyepoxide with an excess of pyridinium chloride dissolved in pyridine. The excess pyridinium chloride is then back titrated with 0.1 N sodium hydroxide to phenolphthalein end point. The epoxide value is calculated by considering one HCl as equivalent to one epoxide group. This method is used to obtain all epoxide values reported herein.

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

Polyether polyepoxides to be used in the process of the invention may be exemplified by 1,4-bis(2,3-epoxypropoxy)benzene, 1,3-bis(2,3-epoxypropoxy)benzene, 4,4'-bis(2,3-epoxypropoxy)diphenyl ether, 1,3-bis(2,3-epoxypropoxy)octane, 1,4-bis(2,3-epoxypropoxy)cyclohexane, 4,4'-bis(2-hydroxy-3,4-epoxybutoxy)diphenyl dimethylmethane, 1,3-bis(4,5-epoxypentoxy)-5-chlorobenzene, 1,4-bis(3,4-epoxybutoxy)2-chlorocyclohexane, ethylene glycol diglycidyl ether, resorcinol diglycidyl ether, 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 (2,2-bis(4'-hydroxyphenyl)propane) with an excess of epichlorohydrin in an alkaline medium. Other polyhydric phenols that can be used for this purpose include 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 the polyether 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, 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, sorbitol, mannitol, inositol, trimethylolpropane, bis(4-hydroxycyclohexyl)dimethylmethane, 1,4-dimethylolbenzene, 4,4'-dimethyldiphenyl, dimethylol toluenes, and the like. The polyhydric ether alcohols include, among others, diglycerol, triglycerol, dipentaerythritol, tripentaerythritol, dimethylolanes, beta hydroxyethyl ethers of polyhydric alcohols, such as diethylene glycol, polyethylene glycols, bi(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 hydroxy-aldehydes 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, 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.

Other polyether polyepoxides include the polyepoxy-polyhydroxy polyethers obtained by reacting, preferably in an alkaline medium, a polyhydric alcohol or polyhydric phenol with a polyepoxide, such as the reaction product of a glycidyl ether of a polyhydric phenol with the same or different polyhydric phenol, the reaction product of glycerol and bis(2,3-epoxypropyl) ether, the reaction product of sorbitol and bis(2,3-epoxy-2-methylpropyl) ether, the reaction product of pentaerythritol and 1,2-epoxy-4,5-epoxypentane, and the reaction product of bis-phenol and bis(2,3-epoxy-2-methylpropyl) ether, the reaction product of resorcinol and bis(2,3-epoxypropyl) ether, and the reaction product of catechol and bis(2,3-epoxypropyl) ether.

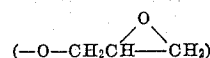
A group of polymeric-type polyether polyepoxides comprises the hydroxy-substituted polyepoxide polyethers obtained by reacting, preferably in an alkaline medium,

a slight excess, e. g., .5 to 3 mole excess, of a halogen-containing epoxide, such as epichlorohydrin, with any of the aforescribed polyhydric phenols, such as resorcinol, catechol, 2,2-bis(4'-hydroxyphenyl)propane, bis[4-(2'-hydroxynaphth-1-yl)-2,2-hydroxynaph-1-yl]methane, and the like.

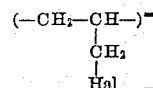
Other polymeric polyether polyepoxides include the polymers and copolymers of the allylic ether of epoxy-containing alcohols. When this type of monomer is polymerized in the substantial absence of alkaline or acidic catalysts, such as in the presence of heat, oxygen, peroxy compounds, actinic light, and the like, they undergo additional polymerization at the multiple bond leaving the epoxy group unaffected. These allylic ethers may be polymerized with themselves or with other ethylenically unsaturated monomers, such as styrene, vinyl acetate, methacrylonitrile, acrylonitrile, vinyl chloride, vinylidene chloride, methyl acrylate, methyl methacrylate, diallyl phthalate, vinyl allyl phthalate, divinyl adipate, 2-chloroallyl acetate, and vinyl methallyl pimelate. Illustrative examples of these polymers include poly(allyl 2,3-epoxypropyl ether), allyl 2,3-epoxypropyl ether-styrene copolymer, methallyl 3,4-epoxybutyl ether-allyl benzoate copolymer, poly(vinyl 2,3-epoxypropyl) ether and an allyl glycidyl ether-vinyl acetate copolymer.

Coming under special consideration, particularly because of the exceptionally fine shrink resistance obtained therewith, 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

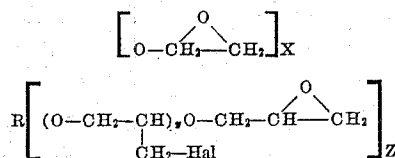


groups and halogen attached to a carbon of an intermediate



group.

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



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 glycerol-epichlorohydrin 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 0.671 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.

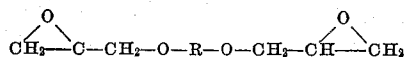
**Polyether B.**—10.5 moles of ethylene oxide was bubbled through 3.5 moles glycerine containing an acid catalyst at 40–50° C. The resulting product had a molecular weight of 224 and a hydroxyl value of 1.417 eq./100 g. 101 parts of this ethylene oxide glycerine condensate was placed in a reaction kettle and heated to 65–70° C. Sufficient BF<sub>3</sub>-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 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.

**Polyether C.**—One equivalent of 1,2,6-hexanetriol was placed in a reaction kettle and heated to 65–70° C. Sufficient BF<sub>3</sub>-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.

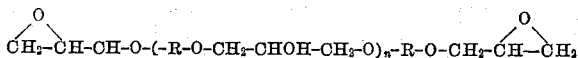
Particularly preferred members of this group comprise the glycidyl polyethers of aliphatic polyhydric alcohols containing from 2 to 10 carbon atoms and having from 2 to 6 hydroxyl groups and more preferably the alkane polyols containing from 2 to 8 carbon atoms and having from 2 to 6 hydroxyl groups. 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 and polymeric glycidyl polyethers of dihydric phenols obtained by reacting epichlorohydrin with a dihydric phenol in an alka-

line medium. The monomeric products of this type 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 of *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 aforedescribed 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.

**Polyether E.**—A solution consisting of 11.7 parts of water, 1.22 parts of sodium hydroxide, and 13.38 parts of bis-phenol 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 20° C. to 30° C. temperature 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 Durrans' mercury method and a molecular weight of 483. The product had an epoxy value of 0.40 eq./100 g., and an epoxy equivalency of 1.9. For convenience, this product will be referred to as polyether E.

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.

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

Of particular value in the process of the invention are the polyepoxides containing only carbon, hydrogen, oxygen and halogen atoms.

The amine catalyst employed with the polyether polyepoxide may be any monomeric or polymeric compound having at least one



and preferably at least one



group, in an open chain or cyclic portion of the molecule. Examples of these amines include, among others, diethylene triamine, triethylene tetramine, dicyandiamide, melamine, pyridine, cyclohexylamine, benzyldimethylamine, 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, 2,7-diamino-2,6-dimethyloctane, dibutylamine, dioctylamine, dinonylamine, distearylamine, diallylamine, diolelylamine, dicyclohexylamine, methylethylamine, ethylcyclohexylamine, o-tolynaphthylamine, pyrrolidine, 2-methylpyrrolidine, tetrahydropyridine, 2-methylpiperidine, 2,6 - dimethylpiperidine, diaminopyridine, tetraethylene pentamine, meta-phenylene diamine, and the like.

Particularly preferred amines are the primary amines, and particularly the aliphatic hydrocarbon primary amines, aromatic hydrocarbon primary amines, and the heterocyclic primary amines, and especially those containing no more than 12 carbon atoms.

The amount of the amine catalyst employed in the process will vary depending upon the nature of the catalyst and the desired degree of cure. In general, amounts of catalyst varying from 3% to 30% by weight of polyether polyepoxide give satisfactory results. Particularly preferred amounts vary from 5% to 20% by weight of polyether polyepoxide.

The polyether polyepoxides and amine catalyst are applied to the wool-containing fabric in an aqueous medium. If the polyether polyepoxides are water-soluble they may be employed in a straight aqueous solution. Many of the polyepoxides, however, have limited solubility in water and it is usually preferred to employ aqueous mediums containing emulsifying agents and/or organic solvents. Emulsifying agents employed may be anionic, cationic or nonionic, and may be exemplified by monooleate or sorbitan polyoxyethylene, the trioleate of sorbitan polyoxyethylene, sorbitan tristearate, sorbitan monolaurate, polyoxyethylene esters of alkylphenols, carboxymethylcellulose starch, gum arabic, polyvinyl alcohol, aryl and alkylated aryl sulfonates, such as cetyl sulfonate, oleylate 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 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 aqueous medium employed to treat the textiles 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 tricesyl phosphates, sulphonamides, sulphonylides, 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 delta-decyl ether, pentadecyl phenol, octodecyl succinic acid, octodecyl 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 solution containing the polyepoxide to the wool-containing fabric may be effected in any suitable manner. It is generally preferred to impregnate the fabric by simply dipping it in the solution and running it through conventional-type padding rollers.

The amount of the polyepoxides to be deposited on the fabric will vary over a wide range depending upon the degree of 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.

If the desired amount of the polyepoxide 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 polyepoxide 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, alcohol, and the like. This accomplished by framing the fabric to original dimensions and exposing the framed fabric 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 polyepoxide. In most instances, drying periods of from 1 to 30 minutes should be sufficient.

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 min-

utes. 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 wool-containing fabric. Such materials include wool as well as fabrics containing wool and other materials such as cotton, linen, natural silk and artificial silk, such as the artificial silk obtained from cellulose acetate or other organic esters of ethers of cellulose and the regenerated cellulosic type of artificial silk obtained by the viscose, cuprammonium or nitrocellulose process, jute, hemp, rayon, animal fibers, hair, mohair, and the like, and mixtures thereof. Fabrics comprising blends of wool and new synthetic fabrics, as nylon and the like may also be used in the process. The above mixtures preferably contain at least 40% wool. While the invention has been particularly described with relation to the treatment of woven fabrics, it may also be applied to other materials, for example, fibers, knitted or netted fabrics. The fabrics may be white or colored.

The materials treated according to the process of the invention will have excellent shrink resistance as well as good water repellancy. The woven 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 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. Unless otherwise indicated, parts disclosed in the examples are parts by weight.

#### Example I

(A) This part of the example illustrates the superior results obtained by using polyether A as the shrink proofing agent with amine catalysts.

100 parts of polyether A described above (epoxy equivalency of 2.13 and molecular weight of about 324) was combined with 5 parts of a polyglycol fatty acid ester emulsifier and 100 parts of water. The mixture was stirred and then 50 parts of a 5% solution of polyvinyl alcohol, 15 parts of diethylene triamine in 100 parts of water was then added and additional water added to bring the solution up to 666 parts (15% polyether A solution).

Light wool flannel cloth was then impregnated with the above-described solution by means of a Butterworth 3-roll laboratory padder. The cloth after padding showed a 100% wet pick-up. The impregnated cloth was then framed to original dimensions and dried for 7 minutes at 100° C., and then cured on the frame for 5.5 minutes at 160° C. The treated cloth had a soft feel, good hand, outstanding shrink resistance and improved water repellancy.

The excellent shrink resistance is demonstrated by the following. The treated cloth was washed in an automatic washer using 10 parts of concentrated ammonia and 10 parts of Triton X-100<sup>1</sup> for 6 minutes at 160° F. After washing, the cloth was rinsed and tumbled dried for 3 minutes in a drier. The cloth was then ironed with a flat bed press without tension. The treated cloth after one laundering showed a 1.3% shrinkage, and after five launderings showed a 1.8% shrinkage. An untreated cloth showed an 8.0% shrinkage after the first laundering and a 28.9% shrinkage after 5 launderings.

(B) This part of the example illustrates the inferior results obtained by using polyether A as the shrink proofing agent with an acid-type catalyst.

An aqueous solution containing 100 parts of polyether A, 511 parts of water, 5 parts of the glycol fatty acid ester, and the polyvinyl alcohol was prepared as in (A) above and 7.5 parts of zinc fluoborate added thereto. Light wool flannel cloth was impregnated with this solution by means of the Butterworth 3-roll laboratory padder. The treated cloth was then framed to dimensions, dried for 7 minutes at 100° C. and then cured for 5.5 minutes at 160° C.

The treated cloth was then washed in an automatic washer using 10 parts of concentrated ammonia and 10 parts of Triton X-100 for 6 minutes at 160° F. After washing, the cloth was rinsed and tumbled dry for 3 minutes in a drier and then ironed with a flat bed press without tension. The treated cloth after one laundering showed a 9.4% shrinkage and after five launderings showed a 29.5% shrinkage. Wool treated in the same manner with a solution containing 15 parts of the zinc fluoborate showed a 7% shrinkage after the first wash.

#### Example II

This example illustrates various proportions of the polyether A and the amine catalysts that may be used and still obtain the desired superior improvement in shrink resistance.

A series of padding solutions were prepared as in Example I(A) wherein the amount of polyether A in the solution varied from 10 to 15 parts and the amount of diethylenetriamine catalyst varied from 1.5 to 1.1 parts. Wool flannel cloth was treated with the solutions and the treated cloth dried and cured as in Example I(A). In each case, the treated fabric had a soft feel, good hand, excellent shrink resistance and improved water repellancy.

#### Example III

This example illustrates the use of polyether A as a shrink proofing agent using triaminotoluene as the catalyst.

About 100 parts of polyether A described above was combined with 5 parts of glycol fatty acid ester and 100 parts of water. This mixture was stirred and then 50 parts of a 5% solution of polyvinyl alcohol, 15 parts of triaminotoluene in 100 parts of water was added and additional water added to bring the solution to 666 parts.

Light wool flannel cloth was then padded with the above-described solution. The impregnated cloth was framed to dimensions and dried for 7 minutes at 100° C. and cured on the frame for 5.5 minutes at 160° C. The textile treated in this manner had a soft feel, good hand, excellent resistance to shrinkage and improved water repellancy. The cloth after 1 laundering showed a 1.4% shrinkage and a 2.9% shrinkage after 5 launderings while the untreated cloth showed 9.4% shrinkage after the first laundering and a 35.5% shrinkage after the fifth laundering.

#### Example IV

This example illustrates the use of polyether A as a shrink proofing agent using ethylene diamine as the catalyst.

About 100 parts of polyether A described above was combined with 5 parts of a polyglycol fatty acid ester and 100 parts of water. This mixture was stirred and then 50 parts of a 5% solution of polyvinyl alcohol, 15 parts of ethylene diamine in 100 parts of water was added and additional water added to bring the solution to 666 parts.

Light wool flannel cloth was then padded with the above-described solution. The impregnated cloth was framed to dimensions and dried for 7 minutes at 100° C. and cured on the frame for 5.5 minutes at 160° C. The textile treated in this manner had a soft feel, good hand, excellent resistance to shrinkage and improved water repellancy. The cloth after 1 laundering showed a 2.0% loss and after the fifth laundering showed a 2.5% loss,

<sup>1</sup> An alkylaryl polyether alcohol.

while the untreated cloth showed a 9.4% loss after the first laundering and 35.5% loss after the fifth laundering.

#### Example V

This example illustrates the use of polyether B as a shrink proofing agent using diethylene triamine as the catalyst.

About 100 parts of polyether B described above is combined with 5 parts of a polyglycol fatty acid ester and 100 parts of water. This mixture is stirred and then 50 parts of a 5% solution of polyvinyl alcohol, 15 parts of diethylene triamine in 100 parts of water was added and additional water added to bring the solution to 666 parts.

Wool flannel cloth was then padded with the above-described solution. The impregnated cloth was framed to dimensions and dried for 7 minutes at 100° C. and cured on the frame for 5.5 minutes at 160° C. The textile treated in this manner had a soft feel, good hand, excellent resistance to shrinkage and improved water repellancy. The cloth after 1 laundering showed a 3.1% loss and after the fifth laundering showed a 4.0% loss, while the untreated cloth showed a 9.4% loss after the first laundering and a 35.5% loss after the fifth laundering.

Wool flannel fabrics having related properties are obtained by replacing polyether B in the above-described process with equivalent amounts of each of the following: polyether C, polyether D, polyglycidyl ether of sorbitol.

#### Example VI

This example illustrates the use of polyether B as a shrink proofing agent using triaminotoluene as the catalyst.

About 100 parts of polyether B is combined with 5 parts of a polyglycol fatty acid ester and 100 parts of water. This mixture is stirred and then 50 parts of a 5% solution of polyvinyl alcohol, 15 parts of triaminotoluene in 100 parts of water are added and additional water added to bring the solution to 666 parts.

Wool flannel cloth is then padded with the above-described solution. The impregnated cloth is framed to dimensions and dried for 7 minutes at 100° C. and cured on the frame for 5.5 minutes at 160° C. The textile treated in this manner has a soft feel, good hand, excellent resistance to shrinkage and improved water repellancy.

#### Example VII

The same procedure was used as in Example VI with the exception that the amine catalyst employed was diamino pyridine. Cloth treated in this manner has good shrink resistance and improved water repellancy.

#### Example VIII

This example illustrates the use of polyether C as a shrink proofing agent using phenylene diamine as the catalyst.

About 100 parts of polyether C described above is combined with 5 parts of a glycol fatty acid ester, polyvinyl alcohol and 15 parts of phenylene diamine as in Example III and then sufficient water added to bring the solution to 666 parts.

Light wool flannel cloth is then padded with the above solution. The impregnated cloth is framed to dimensions and dried for 7 minutes at 100° C. and cured on the frame for 5.5 minutes at 160° C. The resulting textile has a soft feel, good hand, excellent resistance to shrinkage and improved water repellancy.

Wool flannel fabrics having related properties are obtained by replacing polyether C in the above process with equivalent amounts of each of the following: polyether A, polyether B and the polyglycidyl ether of pentaerythritol.

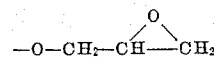
This application is a continuation-in-part of application Serial No. 259,504, filed December 1, 1951.

I claim as my invention:

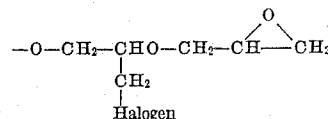
1. A process for treating fabrics containing at least 40% wool to reduce their tendency to shrink and to improve their water repellancy which comprises impregnating the wool-containing fabric with an aqueous medium containing a polyether polyepoxide of the group consisting of glycidyl polyether of polyhydric alcohols and glycidyl polyether of polyhydric phenols, said glycidyl ethers having an epoxide equivalency greater than 1.1 and an amine catalyst and subjecting the impregnated fabric to an elevated temperature to cure the polyether polyepoxide in the fibers of the fabric.

2. A process as in claim 1 wherein the polyether polyepoxide is a glycidyl polyether of an aliphatic polyhydric alcohol wherein the polyepoxide has an epoxide equivalency between 1.1 and 3 and a molecular weight between 170 and 800.

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



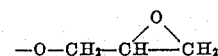
and any hydroxyl groups which are not so replaced being unchanged hydroxyl groups.

4. A process as in claim 1 wherein the polyether polyepoxide is a glycidyl polyether of an alkanetriol-ethylene oxide condensate.

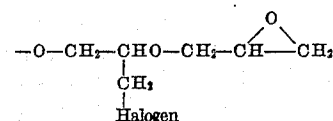
5. A process as in claim 1 wherein the amine catalyst is employed in amounts varying from 3 to 20 parts of polyether polyepoxide and the catalyst is an aliphatic hydrocarbon primary amine.

6. A process for treating woolen fabrics to reduce their tendency to shrink and to improve their water repellancy which comprises impregnating the fabric with an aqueous solution containing a polyether polyepoxide of the group consisting of glycidyl polyether of polyhydric alcohols and glycidyl polyether of polyhydric phenols, said glycidyl ethers having an epoxide equivalency greater than 1.1, a minor amount of an amine catalyst, and an emulsifying agent, drying the treated fabric at a temperature between 100° C. and 200° C. for a few minutes so as to cure the polyether polyepoxide in the fibers of the fabric.

7. A process for treating woolen fabrics as in claim 6 wherein the polyether polyepoxide is a chlorine-containing polyether polyepoxide consisting of a mixture of ethers of glycerol with at least two of the hydroxyl groups of the glycerol replaced in part by the group



and in part by the group



and any remaining hydroxyl groups which are so replaced being unchanged hydroxyl groups.

8. A process as in claim 6 wherein the polyether polyepoxide is a polyglycidyl ether of a glycerol-ethylene oxide condensate.

9. A process as in claim 6 wherein the polyether polyepoxide is a glycidyl polyether of a hexanetriol.

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10. A process as in claim 6 wherein the amine catalyst is used in amounts varying from 3 parts to 20 parts per 100 parts of polyether polyepoxide and is an aliphatic hydrocarbon primary amine.

11. A process as in claim 6 wherein the amine catalyst is an aliphatic hydrocarbon primary amine.

12. A process as in claim 6 wherein the amine catalyst is an aromatic hydrocarbon amine.

13. A process as in claim 6 wherein the amine catalyst is a heterocyclic amine.

14. A process as in claim 7 wherein the amine is diethylene triamine.

15. A process as in claim 8 wherein the amine is ethylene diamine.

16. A process as in claim 9 wherein the amine catalyst is triaminotoluene.

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