This invention relates to the treatment of textile materials. More particularly, the invention relates to a method for preparing textile fabrics that have improved wrinkle and shrink resistance and other improved properties.

Specifically, the invention provides a novel process for preparing crease resistant and shrink resistant, resilient textile fabrics having improved washability and no chlorine retention which comprises applying to the textile fabric a solution containing a polyepoxide and subsequently curing the polyepoxide within the fibers of the fabric in the presence of a curing agent. The invention further provides improved fabrics prepared by the aforesaid process.

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

It is an object of the invention, therefore, to provide a new method for treating textile materials. It is a further object to provide a process for rendering textile fabrics crease and shrink resistant without giving a harsh feel and undue stiffness to the fabric. It is a further object to provide a method for making fabrics more resilient. It is also an object to provide a method for preparing crease- and shrink-proof, resilient fabrics that have no chlorine retention. It is a further object to provide a method where the non-creasing and non-shrinking properties will be resistant to washing. It is a further object to provide a method for treating textile fabrics which, while imparting wrinkle and shrink resistance to the fabric, has little if any detrimental effect on the other desired properties of the fabric. It is a further object to provide a method for crease-proofing of textile materials that in many cases brings about an increase in the tear strength of the fabric. It is still a further object to provide textile fabrics having many 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 applying to the textile fabric a solution containing a polyepoxide and subsequently curing the polyepoxide within the fibers of the fabric in the presence of a curing agent. Fabrics treated in this manner, even with relatively small quantities of the polyepoxide, have excellent resistance to creasing and rubbing and still have a soft feel. The fabrics also have improved resistance to shrinkage and are quite resilient. Surprisingly, these properties are all obtained by the aforesaid treatment with little if any loss of other desired properties, such as tear and tensile strength, which loss generally occurs with the addition of the conventional crease-proofing resins. In fact, with many of the polyepoxides it has been found that there is actually an increase in the tear strength of the treated fabric.

It has further been surprisingly found that the fabrics treated in the above-described manner have no ability to retain chlorine and the coated fabrics may be bleached or otherwise exposed to chlorine without danger of being discolored, charred or weakened during subsequent heat treatments. In addition, the fabrics have been found to have improved washability and can be washed numerous times without danger of losing any substantial amount of the polyepoxide resin.

The polyepoxides used in treating the fabrics include those organic compounds having at least two epoxy groups per molecule. The polyepoxides may be saturated or unsaturated, aliphatic, cyclic, halophatic, aromatic or heterocyclic and may be substituted if desired with non-interfering substituents, such as hydroxy 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 an epoxy equivalency. The term "epoxy equivalency" 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 pyridin chloride 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 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 the polymeric-type polyepoxides, many of the materials may contain some of the monomeric monooepoxides or have some of their epoxy groups hydrated or otherwise reacted and/or contain macro-molecules of somewhat different molecular weight so the epoxy equivalency may be quite low and containing fractional values. The polymeric material may, for example, have an epoxy equivalency of 1.5, 1.8, 2.5 and the like.

The polyepoxides may be exemplified by the following: 1,4-bis(2,3-epoxypropoxy)benzene, 1,3-bis(2,3-epoxypropoxy)benzene, 4,4'-bisp(2,3-epoxypropoxy)benzene, 4,4'-bisp(2,3-epoxypropoxy)biphenyl ether, 1,8-bisp(2,3-epoxypropoxy)biphenyl ether, 1,4-bisp(2,3-epoxypropoxy)cyclohexane, 4,4'-bisp(2-hydroxy-3,4-epoxybiphenyl) diphenylmethylene, 1,3-bisp(2,3-epoxypropoxy)-5-chlorobenzene, 1,4-bisp(3,4-epoxybutoxy)-2-chlorocyclohexane, diglycidyl thioether, diglycidyl ether, ethylene glycol diglycidyl ether, resorcinol diglycidyl ether, 1,2,5,6-disopropoxyxyn, 1,2,5,6-
2,752,269

diepoxyhexane, and 1,2,3,4-tetra(2 - hydroxy - 3,4 - epoxybutoxy)butane.

Other examples include the glycidyl polyethers of polyhydricphenols obtained by reacting a polyhydric phenol with a great excess, e.g., 4 to 8 mol excess, of a halogen-containing epoxide in an alkaline medium. Thus, Polymer F described hereinafter, which is substantially 2,2-bis(3-epoxypropoxyphenyl)propane is obtained by reacting 2,2-bis(3-epoxypropoxyphenyl)propane with an excess of epichlorohydrin. Other polyhydric phenols that can be used for this purpose include resorcinol, catechol, hydroquinone, methyresorcinol, or polymeric phenols, such as 2,2-bis(4-hydroxyphenyl)butane, 4,4'-dihydroxybenzophenone, bis(4-hydroxyphenyl)propane, and 1,5-dihydroxynaphthalene. The halogen-containing epoxides may be further exemplified by 3-chloro-1,2-epoxybutane, 3-bromo-1,3-epoxyhexane, 3-chloro-1,2-epoxyoctane, and the like.

Still a further group of the polyepoxides comprises the polyepoxy polyethers obtained by reacting, preferably in an alkaline medium, a polyhydric alcohol or polyhydric phenol with a polyepoxide, such as glycerol trichloride, one of the aforesaid halogen-containing epoxides with a polyhydric alcohol, and subsequently treating the resulting product with an alkaline component. Polyhydric alcohols that may be used for this purpose include glycerol, propylene glycol, ethylene glycol, diethylene glycol, butylene glycol, hexanetriol, sorbitol, mannitol, pyranetritrol, pentaerithytritol, polyglycerol, dulcitol, inositol, carbohydrates, methyltrimethylolpropane, 2,6-octanediol, tetrahydroxy cyclohexane, 2-ethylhexanetriol-1,2,6, glycerol methyl ether, glycerol allyl ether, polyvinyl alcohol and polyyallyl alcohol, and mixtures thereof. Such polyepoxides may be exemplified by glycidyl trichloride ether, mannitol tetrakis glycidyl ether, pentaerythritol tetraglycidyl ether and sorbitol tetragecydyl ether. Other polyepoxides include the polyepoxy polyhydroxy polyethers obtained by reacting, preferably in an alkaline medium, a polyhydric alcohol or polyhydric phenol with a polyhydroxy polyepoxide, such as 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 polyepoxides comprises the hydroxy-substituted polyepoxy polyethers obtained by reacting, preferably in an alkaline medium, a slight excess, e.g., 5 to 3 mol excess, of a halogen-containing epoxide as described above, with any of the aforesaid polyhydric phenols, such as resorcinol, catechol, bis-phenol, bis(2,2'-dihydroxy-diphenyl)methane, and the like.

Other polymeric polyepoxides include the polymers and copolymers of the epoxy-containing monomers possessing at least one polyhydric aliphatic ethylenic linkage. When this type of monomer is polymerized in the substantial absence of alkaline or acidic catalysts, such as in the presence of heat, oxygen, peroxo compounds, acetic light, and the like, they undergo addition polymerization at the multiple bond leaving the epoxy group unaffected. These monomers 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, chloroallyl acetate, and vinyl methallyl pimelate. Illustrative examples of these polymers include poly(allyl 2,3-epoxypropyl ether), allyl 2,3-epoxypropyl styrene dimethacrylate, methacryl 3,4-epoxybutyl ether-allyl benzate copolymer, poly(vinyl 2,3-epoxypropyl)ether, allyl glycidyl ether-vinyl acetate copolymer and poly(4-glycidyl oxystyrene).

Preferred polyepoxides to be used in treating the textile fabrics according to the process of the present invention comprise the members of the group consisting of diglycidyl ether, diglycidyl thioether, monomeric aliphatic polyepoxides containing a plurality of glycidyl radicals joined through oxygen or sulfur ether linkages to aliphatic hydrocarbon radicals, monomeric aromatic polyepoxides containing a plurality of glycidyl radicals joined through oxygen or sulfur ether linkages to mononuclear or poly-nuclear aromatic radicals, the polyepoxy-containing reaction product of an aliphatic polyhydric alcohol and epichlorohydrin, the polyepoxy-containing polymeric reaction product of an aromatic polyhydric phenol and epichlorohydrin, the polyepoxy-containing reaction product of an aliphatic polyhydric alcohol and a polyepoxide compound, the polyepoxy-containing reaction product of a polyhydric phenol and a polyepoxide compound, the polymers of epoxy-containing monomers possessing at least one polymerizable ethylenic linkage prepared in the absence of alkaline or acid catalysts, and copolymers of the aforesaid epoxy-containing monomers and at least one monomer containing a CH₂-O= group prepared in the absence of alkaline or acid catalysts.

Coming under special consideration, particularly because of the excellent non-chlorine retention and wash-ability characteristics of the resulting crease-proof fabrics, are the polymers of the polyglycidyl ether-containing monomers, and more particularly the glycidyl ethers of unsaturated aliphatic alcohols, such as allyl 1,3-glycidyl ether, vinyl 2,3-glycidyl ether, allyl 2,3-glycidyl ether, crotyl 2,3-epoxybutyl ether, 2-methyl-2-hexeny 2,3-glycidyl ether, and the like. These polymers are preferably prepared by heating the monomer or monomers in bulk or in the presence of an inert solvent such as benzene in the presence of air or a peroxo catalyst, such as diteriarybutyl peroxide, at temperatures ranging generally from 75° C. to 200° C.

The preparation of polymers of this type may be illustrated by the following example showing the preparation of poly(allyl glycidyl ether).

**PREPARATION OF POLYMERS OF GLYCIDYL ETHERS**

**POLYMER A**

About 100 parts of allyl glycidyl ether was combined with an equal amount of benzene and the resulting mixture heated at 135° C. in the presence of 3% tertiary butyl peroxide. The solvent and unreacted monomer were then removed by distillation. The poly(allyl glycidyl ether) obtained as the resulting product had a molecular weight of about 481－542 and an epoxide value of 0.50 eq./100 g. For convenience, this product will be referred to hereinafter as Polymer A.

Particularly preferred members of the above-described group comprise the polymers of the 2-alkenyl glycidyl ethers having a molecular weight between 300 and 1000 and an epoxy equivalency greater than 1.0, and preferably between 1.2 and 6.0.

Also demanding special interest, particularly because of the superior properties, such as the excellent non-chlorine retention properties, of the textile fabrics treated therewith, are the polyglycidyl polyethylene alcohols obtained by reacting the polyethylene alcohol with epichlorohydrin, preferably in the presence of 0.1% to 5% by weight of an acid-chelating 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 polyethylene alcohol. The resulting chlorohydrin dehydrated 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 preparation 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 B

About 276 parts (3 mols) of glycerol was mixed with 832 parts (9 mols) 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 maintained at 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 pressure, the insoluble material was filtered from the reaction mixture and the 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 epoxide equivalency of this product was 2.13. For convenience, this product will be referred to hereinafter as Polyether B.

Particularly preferred members of this group comprise the glycidyl polyethers of aliphatic polyhydric alcohols containing 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 epoxide 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 alkaline medium. The monomeric products of this type may be represented by the general formula

\[
\begin{align*}
\text{CH}_2\text{CCH}_2\text{O} & \quad \text{CH}_2\text{CCH}_2\text{O} \\
\text{R-O-CH}_2\text{CH}- & \quad \text{R-O-CH}_2\text{CH}-
\end{align*}
\]

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

\[
\begin{align*}
\text{CH}_2\text{CCH}_2\text{O} & \quad \text{CH}_2\text{CCH}_2\text{O} \\
\text{R-O-CH}_2\text{CH(O-CH}_2\text{CH}_2\text{O}_\text{n} & \quad \text{R-O-CH}_2\text{CH(O-CH}_2\text{CH}_2\text{O}_\text{n}}
\end{align*}
\]

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 polynor n is an integer, the fact that the obtained polynor 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 end groups in hydrated form.

The aforesaid 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 C

About 2 mols of bis-phenol was dissolved in 10 mol of epichlorohydrin and 1 to 2% water added to the resulting mixture. The temperature was then brought to 80° C. and 4 mols of solid sodium hydroxide added in small portions over a period of about 1 hour. During the addition, the temperature of the mixture was maintained 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 epoxide equivalency of 1.75. For convenience, this product will be referred to hereinafter as Polyether C.

POLYETHER D

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 epoxide equivalency of 1.9. For convenience, this product will be referred to as Polyether D.

POLYETHER E

About 228 parts of bis-phenol and 84 parts sodium hydroxide as a 10% aqueous solution were combined and heated to about 45° C. whereupon 176 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 was drawn off. The residual layer remained when washed with hot water and then drained and dried at 130° C. The Durrans' 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. and an epoxide equivalency of 1.9.

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 epoxide equivalency between 1.1 and 2.0 and a molecular weight between 300 and 900. Particularly preferred are those having Durrans' mercury method softening point below about 60° C.

The polyepoxides are preferably applied to the fabric in the form of a solution or dispersion in order to insure a proper distribution of the materials throughout the fibers of the fabric. Any liquid medium, such as water, aqueous emulsions, volatile or relatively volatile solvents, may be used in the preparation of these solutions. The liquid medium employed with the polyepoxides should have no pronounced solvent action on the fibers of the fabric being treated, though the use of a medium having a slight solvent action or latent solvent or swelling action upon the fibers is not excluded and may, in fact, be advantageous. Suitable solvents include ethyl alcohol, butyl
alcohol, isopropyl alcohol, acetone, dioxane, diacetone alcohol, esters, ethers and other esters of glycol and glyce- 
rol, ethylene dichloride, benzene, toluene, and the like, 
and mixtures thereof.
The more soluble polyepoxides, such as those of the 
aliphatic-type, are preferably employed in a water solu- 
tion or a solution made up of water and other miscible 
components, such as the lower aliphatic alcohols, such 
as ethyl alcohol, isopropyl alcohol, methanol, and the like. 
Particularly preferred mediums of this type comprise 
water-alcohol mixtures having a weight ratio varying 
from 3:1 to 1:5.

The less soluble polyepoxides, such as the viscous liquid 
to solid gelc of polyethylenes of the dihydric phenols de- 
scribed above, are preferably employed in a volatile sol- 
vent or in an aqueous emulsion. Emulsifying agents em- 
ployed for this purpose are preferably those that are free 
of nitrogen and strong acidic groups, such as the mono- 
oclate of sorbitan polyoxyethylene, the triololeate of sorbit- 
an polyoxyethylene, sorbitan tristearate, sorbitan mono- 
nolaurate, polyoxyethylene ethers of alkylphenols, carboxy- 
methylcellulose, starch, gum arabic, and alkylated 
aryl sulfonates, such as cetyl sulfonate, cetyl sulfate, 
sulfonated mineral oils, and the like, and mixtures thereof. 

The emulsifying agents are generally employed in amounts 
varying from 0.1% to 5% by weight and more preferably 
from 1% to 2% by weight.
The amount of the 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 90% to 100% 
pick-up by weight of the fabric in the dry state, a 
concentration ranging from 3% to 25% by weight will ordi-
narily suffice. If less than 80% pick-up is permitted, the 
concentration may in some cases go as high as 30% to 
50%.
The hardening or curing agents may be added to the polyepoxide solution before it is applied to the fabric 
or it may be applied by spraying or other suitable methods 
to the fabric after it has been impregnated with the poly- 
epoxide. The curing agents are preferably added to the 
solution before it is applied to the fabric. Preferred 
curing agents to be used include the acid and acid-acting 
curing agents, such as the organic and inorganic acids and 
their derivatives as citric acid, acetic acid, adipic acid, 
hydantoin, butyric acid, caproic acid, phthalic acid, 
phthalic acid anhydride, tartaric acid, acetic acid, oxalic 
acid, succinic acid, succinic acid anhydride, lactic acid, 
malic acid, maleic acid anhydride, fumaric acid, gluca-
conic acid, 1,2,4-butanetricarboxylic acid, isophthalic acid, 
terephthalic acid, malonic acid, 1,1,5-pentanetricarboxylic 
acid, acetoacetic acid, naphthalic acid, trimellitic acid, 
phosphoric acid, boric acid, sulfuric acid, phosphinic acid, 
perchloric acid, persulfuric acid, p-toluensulfonic acid, 
ethanesulfonic acid, and the like compounds having at 
least one sulfonic group linked to a hydrocarbon radical.
The boron-trifluoride complex, such as the p-creosol and 
urea complex, may also be used as hardening agents. The 
amino compounds, such as triethylamine, ethylene dia- 
mine, and diethylene triamine may also be used but are 
less preferred. Particularly preferred curing agents com- 
prise the organic carboxylic acids and inorganic acids and 
their corresponding anhydrides, and more preferably the 
organic monocarboxylic acids and polycarboxylic acids 
containing from 2 to 12 carbon atoms, and their respec-
tive anhydrides, and the inorganic acids containing sulfur, 
phosphorous or boron, such as boric acid, phosphoric 
acid and sulfuric acid.
The amount of the curing agent to be utilized will 
only to 2 times the stoichiometric amount, the stoicho- 
metric quantity in this case being that amount sufficient 
to furnish one carbonyl group for every epoxide group. 
Particularly amounts of organic acids and acid anhydrides 
vary from 0.2 to 1.5 times the stoichiometric amount. 
The inorganic acids are preferably employed in amounts 
varying from 0.5% to 20% by weight of the polyepoxide, 
and more preferably from 2% to 10% by weight. 
The boron-trifluoride complexes are generally employed in 
amounts varying from 0.25% to 5% and more preferably 
from 1% to 3% by weight.
The solutions employed to treat the textiles may also 
contain plasticizers to improve their flexibility, though 
these should not be present in such proportions as to 
render the finished materials soft or sticky at temperature 
and humidities to which they would be exposed. It is 
found, however, that the substances employed in the pres-
cent invention yield products which are sufficiently flexi-
ble 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, diphenyl propane 
and triphenyl and tricresyl phosphates, sulphonamides, 
sulphonarylides, alkyl phthalates, for example, diethyl 
phthalate and glycolip phthalates, diethyl tarslate, deriva-
tives of polyhydric alcohols, for example, mono-, di- 
and triacetin, and products obtained by condensing polyhy-
dric alcohols with themselves or with aldehydes or ketones. 
The compositions may also contain natural resins, e.g., 
shellac, rosin, and other natural resins and synthetic 
or semi-synthetic resins, e.g., ester gum, polyoxypoly-
alkyl resins, phenolaldehyde and urea-aldehyde resins.

Textile softening agents, and particularly those of the 
cationic type as stearamidized diethyl methyl quaternary 
ammonium methyl sulphate, trimethyl ammonium methyl 
sulphate of monostearlymetaphenylendiamine, sd-i 
(1-
(2-palmmitamidoethyl)) urea monosuccate, palmityl amine 
hydrochloride, and the like, and mixtures thereof, may 
also be added in varying amounts to improve the feel of 
the treated fabrics.
The application of the solution containing the poly- 
epoxide to the textile fabric may be effected in any suit-
able manner, the method selected depending upon the 
results desired. If it is desired to apply the solution only 
to one surface of the material, as, for example, when it is 
desired to impart crease-resistance to natural silk and a 
smooth texture in the face of artificial or natural silk and a 
cotton back, the application may be effected by spraying or by means of 
rollers, or the composition may be spread upon the sur-
face by means of a doctor blade. When, however, it 
is desired to coat both surfaces of the material, or if the 
material is to be thoroughly impregnated with it, the fab-
rics may be simply dipped in the solution or run through 
convventional-type padding rollers. The solutions may 
also be applied locally to the material, for example, by 
means of printing rollers or by stencilling.
The amount of the polyepoxides to be deposited on the 
fabric will vary over a wide range depending upon the 
degree of wrinkle-resistance and shine-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 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. In determin-
ing the amount of resin deposited, it should be 
remembered that the presence of the polyepoxides in a 
few instances causes a slight decrease in tear strength of 
the fabric and the amount deposited should be balanced 
between the desired wrinkle resistance and the desired 
tear strength. 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 is generally accomplished by exposing the wet sheets to hot gas at temperatures ranging from 50° C. to 80° C. The period of drying will depend largely on the amount of pick-up permitted during the application of the solution, and the concentration of the polyepoxide. In most instances, drying periods of from 5 to 30 minutes should be sufficient.

The dried 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 100° C. to 150° C. At these preferred temperature ranges the cure can generally be accomplished in from 5 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 cellulosic fabrics as cotton fabric and fabric made up of regenerated cellulose (rayon) such as obtained by the viscose, cuprammonium or nitrocellulose process. 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, knitted or netted fabrics.

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

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

The wrinkle recovery values reported in 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 50% relative humidity and 78° F.

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

### Example I

(a) About 100 parts of a glycidyl polyether of glycerol having an epoxy equivalency of 2.13 and a molecular weight of about 324 (Polyether B described above) was dissolved in a solution made up of 140 parts of isopropyl alcohol and 420 parts of water, and then 20 parts of citric acid was added to the resulting solution.

5.6 yd./lb. cotton gingham (about 80 x 70 count) cloth was then impregnated with the above-described solution by means of a Butterworth 3-roll laboratory paddler. The cloth after padding showed a 65% wet pick-up. The impregnated cloth was then dried at 60° C. for 15 minutes and cured at 160° C. for 5 minutes. The finished product was washed in a 0.15% solution of Ivory flakes and 0.065% NaSCN solution at 70° C. for 12 minutes and then rinsed three times in warm water to remove any soluble materials.

The cloth treated in the above-described manner was quite soft and had excellent wrinkle resistance, good tear and tensile strength, good washability and no chlorine retention. Some of the properties of the cloth are shown in the table below in comparison to an unplated sheet and similar sheets treated with an urea-formaldehyde resin.

### TABLE NO. I

<table>
<thead>
<tr>
<th>Resin</th>
<th>Monsanto Wrinkle Recovery, %</th>
<th>Trapezoid Tear Strength, lb.</th>
<th>Percent degree in Wrinkle Recovery</th>
<th>Percent degree in Tear Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyether B</td>
<td>107</td>
<td>109</td>
<td>2.94</td>
<td>2.23</td>
</tr>
<tr>
<td>Do...</td>
<td>101</td>
<td>101</td>
<td>2.24</td>
<td>2.66</td>
</tr>
<tr>
<td>Urea-Formaldehyde</td>
<td>107</td>
<td>102</td>
<td>1.84</td>
<td>1.31</td>
</tr>
<tr>
<td>Resin</td>
<td>84</td>
<td>84</td>
<td>1.26</td>
<td>1.63</td>
</tr>
<tr>
<td>Blank</td>
<td>70</td>
<td>70</td>
<td>0.80</td>
<td>2.61</td>
</tr>
</tbody>
</table>

(b) The chlorine retention of the fabrics shown in (a) above was demonstrated in the following manner. The treated fabrics were first dipped for 10 minutes in a hypochlorite bleaching solution containing 0.4% available chlorine using a bath to cloth ratio of 30:1 and maintained at 140° F. They were then rinsed 6 times for 5 minutes at 100° F. and dried as smooth as possible. A hot iron at 400° F. was placed on the cloth for 30 seconds. The cloth was then examined to determine the discoloration of the spot under the iron and tested to determine amount of degradation. A dark color indicated charring due to chlorine retention. The results obtained in these tests are shown in the table below.

### TABLE NO. II

<table>
<thead>
<tr>
<th>Resin</th>
<th>Ironed</th>
<th>Unironed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Br. Tear Strength</td>
<td>Color</td>
</tr>
<tr>
<td>Polyether B</td>
<td>.96</td>
<td>86.4</td>
</tr>
<tr>
<td>Urea-Formaldehyde Resin</td>
<td>.86</td>
<td>88.4</td>
</tr>
<tr>
<td>Melamine-Formaldehyde Resin</td>
<td>.97</td>
<td>86.1</td>
</tr>
<tr>
<td>Commercially treated Cloth</td>
<td>.95</td>
<td>83.2</td>
</tr>
<tr>
<td>Blank (no resin treatment)</td>
<td>1.27</td>
<td>69.5</td>
</tr>
</tbody>
</table>

1 Readings taken from Luminotron using tri-green filter—700 Standard white reflector plate.

It can be seen from an examination of the data in Table II that the cloth treated with the Polyether B had a negligible if any chlorine retention and could be subjected to extensive bleach without fear of discoloration or strength loss during subsequent exposures to heat.

**Example II**

(c) About 100 parts of poly(allyl glycidyl ether) (Polymer A described above) was dissolved in a solution
made up of 140 parts of isopropyl alcohol and 420 parts of water, and then 40 parts of citric acid was added to the resulting solution.

Cotton print cloth (80 x 80 count) was then impregnated with this solution as shown in Example I. The impregnated cloth was dried at 60° C. for 15 minutes and cured at 160° C. for 5 minutes. It was then washed as in Example I to remove any soluble material.

The cloth treated in the above-described manner had a 61% increase in wrinkle recovery.

(b) The treated fabric prepared in (a) above was washed at 70° C. for 12 minutes using a 0.13% solution of Ivory flakes and .063% NaClO. The loss in weight due to the washing is shown in the following table in comparison to similar results obtained by washing cotton print fabrics treated with urea-formaldehyde and melamine-formaldehyde resins.

TABLE NO. III

<table>
<thead>
<tr>
<th>Resin</th>
<th>Percent loss in weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer A</td>
<td>1.6</td>
</tr>
<tr>
<td>Urea-Formaldehyde Resin</td>
<td>21.2</td>
</tr>
<tr>
<td>Melamine-Formaldehyde Resin</td>
<td>29.1</td>
</tr>
</tbody>
</table>

Example III

A series of impregnating solutions containing Polyether B and a variety of different curing agents was prepared in the following manner: 100 parts of the polyether was dissolved in a solution made up of 140 parts of isopropyl alcohol and 420 parts of water and then the curing agent was added thereto.

Sheets of cotton print cloth were then impregnated with the individual solutions as indicated in Example I to give a 5-6% resin pick-up. The sheets were dried at 60° C. for 5 to 15 minutes and then cured at 160° C. for 5 minutes.

The increase in wrinkle recovery of each of the sheets is shown in the following table.

TABLE NO. IV

<table>
<thead>
<tr>
<th>Curing Agent</th>
<th>Amount of Agent (FBR)</th>
<th>Increase in Percent Wrinkle Recovery Warp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citric Acid</td>
<td>35.9</td>
<td>33.3</td>
</tr>
<tr>
<td>Tannic Acid</td>
<td>38.6</td>
<td>28.2</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>38.6</td>
<td>26.2</td>
</tr>
<tr>
<td>Maleic Acid</td>
<td>38.6</td>
<td>24.0</td>
</tr>
<tr>
<td>Oxalic Acid</td>
<td>27.0</td>
<td>21.0</td>
</tr>
<tr>
<td>Boric Acid</td>
<td>35.9</td>
<td>14.3</td>
</tr>
<tr>
<td>Phosphoric Acid</td>
<td>35.9</td>
<td>34.4</td>
</tr>
</tbody>
</table>

1 Parts per hundred parts of resin.

Example IV

In this experiment, the Polyether B-citric acid impregnating solution prepared in Example I and the Polymer A-citric acid solution shown in Example II were used to treat rayon gabardine cloth. This was accomplished by impregnating the cloth with the aforesaid solutions by means of the Butterworth 3-roll laboratory paddle (about 80% pick-up), drying the impregnated cloth at 60° C. for about 15 minutes and curing the cloth at 140° C.

The rayon cloth treated in the above-described manner was quite soft and had increased wrinkle resistance, good washability and excellent shrink resistance. The wrinkle recovery is shown in the following table in comparison to an unpadded sheet and a similar sheet padded with an urea-formaldehyde resin.

TABLE NO. V

<table>
<thead>
<tr>
<th>Wrinkle Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin</td>
</tr>
<tr>
<td>Polyether B</td>
</tr>
<tr>
<td>Polyurethane A</td>
</tr>
<tr>
<td>Urea-Formaldehyde Resin</td>
</tr>
<tr>
<td>Blank</td>
</tr>
</tbody>
</table>

Example V

This example illustrates the increase in tear strength that is obtained by using many of the polyepoxides described in the foregoing specification.

About 100 parts of a diglycidyl ether of resorcinol having an epoxy value of 0.941 eq./100 g. was dissolved in a solution made up of 140 parts of water and 420 parts of isopropyl alcohol, and then about 3% by weight of a boron-trifluoride p-cresol complex was added to the resulting solution.

Cotton print cloth was then treated with the above-described solution as shown in Example I, dried at 60° C. and then cured at 160° C. for 5 minutes. The finished sheets had a 14% increase in wrinkle resistance and a 14.3% increase in tear strength. The sheets also had improved washability and no chlorine retention.

Example VI

About 100 parts of diglycidyl ether of ethylene glycol having an epoxy value of 1.039 eq./100 g. was dissolved in a solution made up of 140 parts of isopropyl alcohol and 420 parts of water, and then about 40 parts of citric acid was added.

Cotton print cloth treated with the above-described solution as indicated in Example V was soft and had increased wrinkle resistance, improved washability and no chlorine retention.

Example VII

About 100 parts of a glycicyl polyether of bis-phenoxy having an epoxy equivalency of 1.75 and a molecular weight of about 350 (Polyether C produced above) was combined with 30 parts of citric acid and 10 parts of an emulsifying agent comprising a copolymer of ethylene oxide and propylene oxide (Pluronic F-68). This mixture was warmed to form a solution of the components and then cooled. Water was then added dropwise with gentle padding until the emulsion inverted. A further quantity of water was then added rapidly to form a solution having a 10% resin concentration.

Cotton print cloth described above was impregnated with the above-described emulsion by means of the Butterworth 3-roll laboratory paddle. The cloth after padding showed a 80% wet pick-up. The impregnated cloth was dried at 60° C. for 15 minutes and cured at 160° C. for 5 minutes. The resulting fabric had an increase in wrinkle resistance of 23.5% and a 35% decrease in tear strength.

Example VIII

About 200 parts of a glycicyl polyether of bis-phenoxy having an epoxy equivalency of 1.9 and a molecular weight of 483 (Polyether D produced above) is stirred with 2 parts of sorbitan monoleate (Span 20) and this mixture is then added to 200 parts of a 1% solution of a monooleate of sorbitan polyoxyethylene (Tweens 80) and the resulting mixture stirred at full speed with the Brookfield 12,000 R. M. stirrer. 20 parts of citric acid is then added to the resulting emulsion.

Cotton print cloth treated with the above-described emulsion as in the preceding example is soft and has increased wrinkle resistance, improved washability and low non-chlorine retention.
Crease resistant fabrics which were unusually soft and had a pleasant feed were obtained by the following procedure.

About 100 parts of Polyether B described above was dissolved in a solution made up of 140 parts of isopropyl alcohol and 420 parts of water, and then 40 parts of citric acid added to the solution. Aerotex Softener H (a mixed cationic and anionic long chain derivative) was then added to separate portions of the above-described solution in proportions indicated in the table below.

80 square cotton print cloth (80 x 80) was then impregnated with the above-described solutions by means of a Butterworth 3-roll laboratory padder. The cloth sheets were then dried at 60° C. for 15 minutes, cured at 160° C. for 5 minutes, and then washed as shown in Example I.

The treated sheets were very soft and had a pleasant feel but still had very good crease and shrink resistance. The wrinkle recovery values are shown in the following table.

### Table NO. VI

<table>
<thead>
<tr>
<th>Percent Softener Added</th>
<th>Wrinkle Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Warp</td>
</tr>
<tr>
<td>0</td>
<td>116</td>
</tr>
<tr>
<td>1</td>
<td>118</td>
</tr>
<tr>
<td>1.5</td>
<td>116</td>
</tr>
<tr>
<td>2</td>
<td>118</td>
</tr>
<tr>
<td>3</td>
<td>110</td>
</tr>
</tbody>
</table>

1. The soften in this case was added after the cloth had been treated with the polyoxyde and subsequently cured.

We claim as our invention:

1. A process for producing crease resistant and wrinkle resistant textile fabrics containing substantially all cellulosic material of the group consisting of cotton and rayon having a soft feel and improved resistance to washing and low chlorine retention which comprises impregnating the textile fabric with a water-alcohol solution containing a saturated polyglycidyl ether of a polyhydric alcohol having an epoxy equivalency of about 1 to 1.5 and a molecular weight between 300 and 900.

2. The process as defined in claim 1 wherein the acid curing agent is citric acid.

3. The process as defined in claim 1 wherein the acid curing agent is phosphoric acid.

4. The process as defined in claim 1 wherein the acid curing agent is a member of the group consisting of acid or acid-acting curing agents.

5. A process for producing crease resistant and shrink resistant textile fabrics containing substantially all cellulosic material of the group consisting of cotton and rayon having a soft feel and improved washability and low chlorine retention which comprises impregnating the textile fabrics with an aqueous emulsion containing a saturated polyglycidyl ether of a polyhydric alcohol having an epoxy equivalency greater than 1.0, and an acid curing agent, and then heating the composition at a temperature between 50° C. and 200° C. to cure the polyoxyde within the fabric fibers.

6. A process for producing crease-resistant and shrink-resistant cellulosic textile fabrics containing substantially all cotton which comprises impregnating the textile fabric with an aqueous dispersion containing a glycidyl polyether of glycerol, having an epoxy equivalency of about 2 to 3 and a molecular weight between 300 and 900, and a curing agent, and then heating the treated fabric to cure the glycidyl polyether of glycerol within the treated fabric.

7. A process for producing crease-resistant and shrink-resistant textile fabrics containing substantially all cellulosic material of the group consisting of cotton and rayon to make them crease-resistant and shrink resistant without affecting feel and chlorine-retentive properties which comprises impregnating the textile material with an aqueous medium containing a saturated polyglycidyl ether of a polyhydric alcohol having an epoxy equivalency greater than 1.0, and a curing agent, and then heating the treated textile material to cure the polyglycidyl ether within the treated textile material.

8. A process as in claim 9 wherein the polyhydric alcohol is glycerol.

9. A process as in claim 9 wherein the polyhydric alcohol is diethylene glycol.

10. A process as in claim 9 wherein the curing agent is an acid-acting curing agent.

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