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2,903,381

TREATMENT OF SYNTHETIC TEXTILES WITH A POLYEPOXIDE HAVING A PLURALITY OF 1,2 EPOXY GROUPS

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No Drawing. Application September 3, 1954
Serial No. 454,193

12 Claims. (Cl. 117—138.8)

This invention relates to the treatment of synthetic fibers and fabrics. More particularly, the invention relates to a process for treating synthetic fibers and fabrics to improve their ability to be colored, and to a method for coloring the resulting fibers and fabrics.

Specifically, the invention provides a new and highly efficient method for improving the colorability of synthetic fibers and fabrics, and particularly those prepared from acrylonitrile polymers, polyesters, polyamides, vinyl halide polymers, vinylidene halide polymers, vinylidene cyanide polymers, protein polymers, and cellulose esters, which comprises impregnating the said synthetic material with an aqueous medium containing a polyepoxide and an amine curing agent, and subjecting the resulting impregnated material to an elevated temperature to cure the polyepoxide. The invention further provides a method for coloring the synthetic fibers and fabrics treated in the above-described manner.

Many new fabrics are prepared from synthetic materials, such as acrylonitrile polymers, terephthalic acid-glycol polyesters, super polyamides, and the like. While these fabrics have many desired properties, they have certain characteristics which prevent their wide scale acceptance in the textile industry. Many of these synthetic materials are, for example, very difficult to dye properly. In many cases, the synthetic materials are chemically inert and lack affinity for dyes. In other cases, the synthetic materials can be dyed but the dye is absorbed in an uneven manner. In other cases, the synthetic fibers accept only certain types of dyes, such as acid dyes, and are not affected by the others. In addition, in many cases where the fibers accept the dye, the dye is not fast and the coloring rapidly fades on washing and/or exposure to the atmosphere.

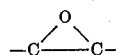
It is an object of the invention, therefore, to provide a method for treating synthetic fibers and fabrics to improve their ability to be colored. It is a further object to provide a method for rendering synthetic fibers and fabrics more receptive to all conventional dyes, and pigments. It is a further object to provide a method for preparing synthetic fibers and fabrics which can be dyed evenly without streaks and shade variations. It is a further object to provide a process for preparing synthetic fibers and fabrics which retain the dye over a longer period of time. It is a further object to provide a process for coloring synthetic fibers and fabrics, and particularly those prepared from protein polymers, polyesters, polyamides, acrylonitrile polymers, vinyl halide polymers, vinylidene halide polymers, vinylidene cyanide polymers, and cellulose esters. 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 are accomplished in part by impregnating the synthetic fibers and fabrics with an aqueous medium containing a polyepoxide and an amine curing agent and subjecting the impregnated material to an elevated temperature to cure the polyepoxide. Synthetic materials which have been

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treated in this manner have exceptionally fine affinity for all of the conventional dyes and pigments and the coloring material is absorbed in an even manner without formation of streaks and shade variations. In addition, the colored fibers and fabrics have excellent stability and do not fade or change color on washing and/or exposure to the atmosphere. Further advantage is found in the fact that the synthetic fabrics treated with the polyepoxide as indicated above do not fray when cut but maintain a fine even cutting line. In addition, fabrics, such as those prepared from polyester-type materials as Dacron, do not "pill" or mesh together as do the untreated polyester fabrics.

The polyepoxides to be used in the process of the invention comprise those compounds possessing a plurality of 1,2-epoxy groups (i.e.



groups). These 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 has the same meaning as described in U.S. 2,633,458.

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

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-epoxy-butoxy)diphenyldimethylmethane, 1,3-bis(4,5-epoxypentoxy)-5-chlorobenzene, 1,4-bis(3,4-epoxybutoxy)-2-chlorocyclohexane, diglycidyl ether, 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)] 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 polyepoxides comprises the polyepoxy polyethers obtained by reacting, preferably in the presence of an acid-acting compound, such as hydrofluoric acid, one of the aforescribed halogen-containing epoxides with a polyhydric alcohol, and subsequently treating the resulting product with an alkaline component,

As used herein and in the claims, the expression "polyhydric alcohol" is meant to include those compounds having at least two free alcoholic OH groups and includes the polyhydric alcohols and their ethers and esters, hydroxy-aldehydes, hydroxyketones, halogenated polyhydric alcohols, and the like. Polyhydric alcohols that may be used for this purpose may be exemplified by glycerol, propylene glycol, ethylene glycol, diethylene glycol, butylene glycol, hexanetriol, sorbitol, mannitol, pentaerythritol, polyallyl alcohol, polyvinyl alcohol, 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, dimethylolanisoles, beta hydroxyethyl ethers of polyhydric alcohols, such as diethylene glycol, polyethylene glycols, bis(beta hydroxyethyl ether) of hydroquinone, bis(beta hydroxyethyl ether) of bisphenol, beta hydroxyethyl ethers of glycerol, pentaerythritol, sorbitol, mannitol, etc., condensates of alkylene oxides, such as ethylene oxide, propylene oxide, butylene oxide, isobutylene oxide, glycidyl, epichlorohydrin, glycidyl ethers, etc., with polyhydric alcohols, such as the foregoing and with polyhydric thioethers, such as 2,2'-dihydroxydiethyl sulfide, 2,2'-3,3'-tetrahydroxy dipropyl sulfide, etc. The hydroxyaldehydes and ketones may be exemplified by dextrose, fructose, maltose, glyceraldehyde. The mercapto (thiol) alcohols may be exemplified by alpha-monothioglycerol, alpha,alpha'-dithioglycerol, etc. The polyhydric alcohol esters may be exemplified by mono-glycerides, such as monostearin, monoesters of pentaerythritol and acetic acid, butyric acid, pentanoic acid, and the like. The halogenated polyhydric alcohols may be exemplified by the monochloride of pentaerythritol, monochloride of sorbitol, monochloride of mannitol, monochloride of glycerol, and the like.

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

Other polyepoxides include the polyepoxypolyhydroxy 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.

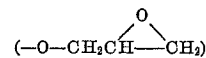
A group of polymeric-type polyepoxides comprises the hydroxy-substituted polyepoxide polyethers obtained by reacting, preferably in an alkaline medium, a slight excess, e.g., 5 to 3 mole excess, of a halogen-containing epoxide, such as epichlorohydrin, with any of the afore-described polyhydric phenols, such as resorcinol, catechol, 2,2 - bis(4' - hydroxyphenyl)propane, bis[4-(2'-hydroxynaphth-1-yl)-2-2-hydroxynaphth-1-yl] methane, and the like.

Other polymeric 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 mono-

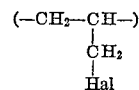
mers, such as styrene, vinyl acetate, methacrylonitrile, acrylonitrile, vinyl chloride, vinylidene chloride, methyl acrylate, methyl methacrylate, diallyl phthalate, vinyl allyl phthalate, divinyl adipate, 2-chloroallyl acetate, and vinyl methyllyl pimelate. Illustrative examples of these polymers include poly(allyl 2,3-epoxypropyl ether), allyl 2,3-epoxypropyl ether-styrene copolymer, methyllyl 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 dyeing properties of the materials treated 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

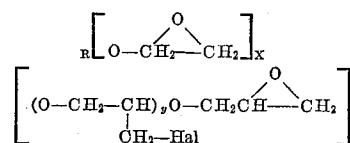


groups and halogen attached to a carbon of an intermediate



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 POLYESTERS 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-epi-

chlorohydrin condensate was dissolved in 900 parts of dioxane containing about 300 parts of sodium aluminate. While agitating, the reaction mixture was heated and refluxed at 93° C. for 9 hours. After cooling to atmospheric temperature, the insoluble material was filtered from the reaction mixture and low boiling substances removed by distillation to a temperature of about 150° C. at 20 mm. pressure. The polyglycidyl ether, in amount of 261 parts, was a pale yellow viscous liquid. It had an epoxide value of 9.671 equivalent per 100 grams and the molecular weight was 324 as measured ebullioscopically in dioxane solution. The epoxy equivalency of this product was 2.13. For convenience, this product will be referred to hereinafter as Polyether A.

Polyether B

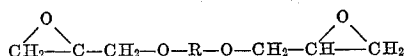
10.5 moles of ethylene oxide was bubbled through 3.5 moles glycerine containing an acid catalyst at 40–50° C. The resulting product had a molecular weight of 224 and a hydroxyl value of 1.417 eq./100 g. 101 parts of this ethylene oxide glycerine condensate was placed in a reaction kettle and heated to 65–70° C. Sufficient BF₃-ethyl ether complex was added to bring the pH to about 1.0 and then 132 parts of epichlorohydrin added dropwise. After all the epi had been added, the reaction was continued for about 15 minutes to assure complete reaction. This product was then dissolved in benzene and 57 parts of sodium hydroxide were added in 7 equal portions at about 87–89° C. over a period of ¾ hours 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

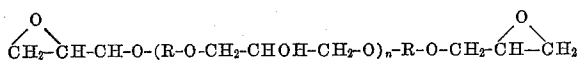
One equivalent of 1,2,6-hexanetriol was placed in a reaction kettle and heated to 65–70° C. Sufficient BF₃-ethyl ether complex was added to bring the pH to about 1.0 and then 1 equivalent of epichlorohydrin added dropwise. After all the epi had been added, the reaction was continued for about 15 minutes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

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

Also of importance are the monomeric 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



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

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

PREPARATION OF GLYCIDYL POLYETHERS OF DIHYDRIC PHENOLS

Polyether D

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

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

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 curing agent employed with the 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, ethylene diamine, diethylene triamine, triethylene tetramine, dicyandiamide, melamine, pyridine, cyclohexylamine, benzyl dimethylamine, 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, distearyl-

ylamine, diallylamine, dioleamine, dicyclohexylamine, methylethylamine, ethylcyclohexylamine, o-tolynaphthylamine, pyrrolidine, 2-methylpyrrolidine, tetrahydropyridine, 2-methylpiperidine, 2,6-dimethylpiperidine, diamino-pyridine, 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 curing agent employed in the process will vary depending upon the nature of the curing agent and the desired degree of cure. In general, amounts of curing agent varying from 3% to 30% by weight of polyepoxide give satisfactory results. Particularly preferred amounts vary from 5% to 20% by weight of polyepoxide.

The polyepoxide and amine curing agent are applied to the synthetic fibers or fabrics in an aqueous medium. If the polyepoxide is water-soluble it 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 of 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 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 fibers or fabrics may also contain plasticizers to improve their flexibility, although these should not be present in such proportions as to render the finished materials soft or sticky at temperatures and humidities to which they would be so exposed. It is found, however, that the substances employed in the present invention yield products which are sufficiently flexible for most purposes without the use of plasticizers. Among plasticizers that may be used according to the present invention may be mentioned organic and inorganic derivatives of phenols, for example, diphenylol propane and triphenyl and tricresyl phosphates, sulphonamides, sulphonarylides, 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 fibers or fabrics. Examples of these agents include, among others, epoxidized glycerides, such as epoxidized soybean oil, glycidyl delta-decyl ether, pentadecyl phenol, octodecyl

succinic acid, octodecenyl 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 synthetic fibers or fabrics may be effected in any suitable manner as by spraying, dipping, or brushing. It is generally preferred, however, to impregnate the fibers or fabrics by simply dipping them in the solution and running them through conventional-type padding rollers.

The amount of the polyepoxides to be deposited on the fibers or fabric will vary over a wide range. 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.

If the desired amount of the polyepoxide deposited on the fibers or 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 fiber or fabric the treated material may be dried for a short period to remove some or all of the dispersing liquid, such as water, alcohol, and the like. 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.

In some cases, the drying may be omitted and the fibers or fabric exposed directly to relatively high temperatures to accelerate the cure of the polyepoxides. Temperatures used for this cure generally range from 100° C. to 200° C., and more preferably, from 130° C. to 190° C. At these preferred temperature ranges the cure can generally be accomplished in from 1 to 10 minutes. Exposures of less than 3 minutes, e.g., 1 minute, may probably be used in continuous, commercial processing.

The process of the invention may be applied to the treatment of any synthetic fiber or fabric. As used herein "synthetic" refers to those materials that do not occur in nature and is meant to exclude materials, such as cotton, wool and the like. Synthetic fibers and fabrics include, among others, those prepared from acrylonitrile polymers, vinyl chloride polymers, vinylidene chloride polymers, vinylidene cyanide polymers, polyesters, polyamides, polyester-polyamides, cellulose ethers and esters, and polymers prepared from corn protein and formaldehyde (Zein). The polymers of acrylonitrile, vinyl chloride, vinylidene chloride and vinylidene cyanide referred to above includes the homopolymers of these monomers as well as copolymers of the monomers with dissimilar monomers, particularly those containing at least one $\text{CH}_2=\text{C}=\text{}$ group, such as, for example, vinyl acetate, methacrylonitrile, allyl glycidyl ether, allyl alcohol, allyl mercaptan, methyl methacrylate, methyl acrylate, styrene, butadiene, methylpentadiene, methacrylamide, chlorostyrene, butyl chloroacrylate, diallyl phthalate, vinyl methyl ether, allyl butyl ketone, ethylene glycol dimethacrylate, and the like, as well as the above monomers themselves when dissimilar to the basic monomer, such as vinyl chloride, acrylonitrile and vinylidene chloride. These copolymers preferably contain at least 15%, and more preferably from 20% to 95% of at least one of the basic monomers vinyl chloride, acrylonitrile, vinylidene chloride and vinylidene cyanide. Examples of these copolymers include Acrylan (85% acrylonitrile and 15% vinyl acetate), Dynel (60% vinyl chloride and 40% acrylonitrile) and Saran (85% vinylidene chloride and 15% vinyl chloride).

The polyesters used in preparation of the synthetic

fibers are preferably those high molecular weight products obtained by reacting glycols, such as ethylene glycol, propylene glycol and the like, with polycarboxylic acids, such as, for example, terephthalic acid, isophthalic acid, adipic acid, succinic acid, stilbenedicarboxylic acids and the like. The polyamides are preferably those high molecular weight products obtained by reacting polyamines, and particularly the alpha, omega-diamines as 1,6-hexamethylenediamine, 1,5-pentamethylenediamine and 1,8-octamethylenediamine, with polycarboxylic acids, such as adipic acid, succinic acid, phthalic acid, chlorophthalic acid and the like. The polyamides may also be prepared by polymerization of aminocarboxylic acids, such as aminocaproic acid. The polyesterpolyamides are preferably those high molecular weight products obtained by reacting polycarboxylic acids as described above with amino alcohols, such as 4-aminobutanol, 5-aminohexanol, 6-aminooctanol and the like. The cellulose derivatives are preferably the alkanolic acid esters of cellulose, such as cellulose acetate and cellulose butyrate.

Other synthetic fibers that can be used include those prepared from polyethylenes, polyurethanes (Perluran), mineral fibers (Fiberglas) and alginic materials as Alginate rayon.

As indicated above, the synthetic fabrics or fibers treated with the polyepoxides and amine catalyst have excellent color-reception and can be easily colored by dipping or otherwise applying the desired coloring thereto.

Printed material may also be obtained by first printing the polyepoxide on the material in the desired design and then applying the dyeing solution thereto. In those cases where the untreated fabric is completely inert to coloring material, such as Orlon and Dacron when printed with dyes such as acid and direct dyes, a color print on a white background can be obtained by this technique. In those cases where the untreated fabric absorbs some dye, the above-described technique may be utilized to print with different shades.

Any of the conventional organic and inorganic coloring materials may be used. This includes the known water-soluble or insoluble dyes and pigments. Particularly preferred material to be used are the direct, acid and acetate dyes for this purpose.

Various examples of dyes and pigments that may be used in coloring the above-described fabrics and examples of the preferred direct, acid and acetate dyes in particular, may be found in Technical Manual and Year Book of the American Association of Textile Chemists and Colorists, vol. XXVII, pages 164 to 223 (1952 ed.). The dyes which are chemically identical with one of the 1316 types described in the "Color Index" (published by the Society of Dyers and Colourists) has its corresponding "Colour Index Number" recorded after the name of the dye. Those dyes which have no Colour Index Number are usually given a Pr. or prototype number which refers to a recognized foreign prototype listed on pages 245 and 258 of the Technical Manual referred to above. Examples of direct dyes include, among others, Calcodur Blue S1-Pr-71, Calcodur Blue 4G1 533 (Col. Index), Calcodur Gray L-Pr. 24, Calcodur Orange G1 Conc. 653, Calcodur Violet 4 BL 325, Calcodur Yellow NN 814, Calcomine Black G 200% 581, Calcomine Brilliant Green Y, Calcomine Fast Red 8 B-Pr. 246, Cloramine Blue BX 472, Chloratine Fast Brown G1 Pr. 48, Chloratine Fast Orange 4G1-Pr 333, Congo Red 4BX conc. 370, Diamine Brown 3GPA 596, Erie Scarlet 3B-382, Interchem Direct Blue 2B-406 and Nyanza Fast Orange S-419. Examples of acid dyes include, among others, Aceko Brilliant Scarlet-185, Aceko Dark Brown RD-235, Acko Milling Blue B-Pr 136, Acid Black BX-246, Acid Violet 4 BNS 698, Alizarine Blue SAE, 1053, Alizarine Cyanine Green CG-1078, Alizarine Violet R Pdr-1080, Amacid Red 2G-Pr. 194, Anthra Milling Red 3B-487, Bixacid Fuschsine 6B-57, Brilliant Cyanine 6B-Pr. 222, Calcocid Orange AD-151, Chinoline Yellow D conc.-

801, Durol Black B-307, Fast Light Orange PO-Pr. 513, Kiton Fast Green A, Kiton Fast Violet-696, Kiton Fast Red R, Metamine Fast Light Yellow 3GA-636, Neotolyl Black and Pontacyl Brilliant Blue-672. Examples of acetate dyes include, among others, Acetamine Diazo Black 3B Pr. 58, Acetamine Yellow RR-Pr. 243, Acetate Yellow GC conc.-Pr. 242, Amacel Brilliant Blue B Ex.-Pr. 228, Bixacyl Rubine 3B-Pr. 239, Celanthrene Pure Blue BRS 400%-Pr. 62, Celliton Scarlet BA-Pr. 244, Nacelan Violet 4R-Pr. 237, Tetracele Black G and Tetracele Yellow R. Other types of dyes, such as vat, mordant acid, lakes, ink, pigments and the like as listed in the above-noted tech. manual are less preferred but may be utilized in the process.

After application of the dye solution, the fibers or fabrics may then be dried by conventional techniques and utilized directly in commercial applications, such as in the preparation of dresses, blouses, suits, draperies, 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. Unless otherwise indicated, parts disclosed in the examples are parts by weight.

EXAMPLE I

Examples I to IV illustrate the superior properties imparted to Orlon (100% acrolonitrile polymer) fabric by treatment with Polyether A and an amine curing agent. 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, 20 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).

White Orlon fabric was then treated 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 treated cloth was then cured at 160° C., for 5.5 minutes. The treated cloth had a soft feel, good hand and was free of "pilling." The treated cloth did not fray at the cut edges.

The treated cloth also had excellent dye-receptive properties as shown by the following. A dye solution was prepared by adding .225 part of Calcodur Blue SL-Pr-71 (direct cotton dye-Pr-71) and 1.22 parts of sodium chloride to 1000 parts of water. This mixture was heated to boiling and the treated Orlon cloth was placed therein and the mixture boiled for 20 minutes. The cloth which was then dyed a good blue color was removed, rinsed, and dried. Repeated washings with soap and water failed to affect the color. The color also appeared to be resistant to solvents, such as acetone.

A similar untreated white Orlon fabric was placed in the same dye solution and boiled for 20 minutes but was still white on removal.

EXAMPLE II

The white Orlon fabric treated with Polyether A, as shown in Example I, was also dyed with Kiton fast Red R. dye (acid dye). 5 parts of the dye was placed in 1000 parts of water and the mixture heated to boiling. The treated Orlon fabric was then placed in the dye and the mixture boiled for 20 minutes. The cloth was then removed, rinsed and dried. The dried cloth was dyed an even deep red color. The color underwent little change even after repeated washings with soap and water. The color was also resistant to solvents, such as acetone.

A similar untreated white Orlon fabric was placed in the same red dye solution and boiled for 20 minutes. On removal, the cloth was only a very light red color.

EXAMPLE III

The white Orlon fabric treated with Polyether A, as shown in Example I, was also dyed with Celanthrene Pure Blue BRS 400% (acetate dye-Pr-62). 5 parts of the dye was placed in 1000 parts of water and the mixture heated to boiling. The treated Orlon fabric was then placed in the dye and the mixture boiled for 20 minutes. The cloth was removed, rinsed and dried. The resulting fabric was dyed a deep blue color which underwent little change on repeated washing. The cloth after five washes had a much better color than a similar piece of Orlon fabric which had been treated with benzoic acid as a dye carrier before being dyed with the Celanthrene Pure Blue and washed five times.

A similar untreated white Orlon fabric containing no carrier was only a very light blue color after being treated as described above with Celanthrene Pure Blue BRS dye.

EXAMPLE IV

The white Orlon fabric treated with Polyether A, as shown in Example I, was also dyed with Anthraquinone Blue SWF 150% (acid dye-Pr-12). 5 parts of the dye was placed in 1000 parts of water and the mixture heated to boiling. The treated Orlon fabric was then placed in the dye and boiled for 20 minutes. The cloth was then removed and dried. The fabric, after drying, had a good blue color which underwent little change on repeated washing. A similar untreated white Orlon fabric was still white after being placed in the dye solution and boiled for 20 minutes.

EXAMPLE V

Examples V to VII illustrate the superior properties imparted to Dacron (a glycol-terephthalic acid polyester) fabric by treatment with Polyether A and an amine curing agent.

100 parts of Polyether A described above were 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, 20 parts of diethylene triamine in 100 parts of water was then added and additional water added to bring the solution up to 666 parts.

White Dacron fabric was then treated 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 treated cloth was then cured at 160° C., for 5.5 minutes. The treated cloth had a soft feel, good hand, and was free of "pilling." The treated cloth did not fray at the cut edges.

The treated cloth also had excellent dye-receptive properties. A dye solution was prepared by adding .22 part of Calcodur Blue S1 and 1.22 parts of sodium chloride to 1000 parts of water. This mixture was heated to boiling and the treated Dacron fabric was placed therein and the mixture boiled for 20 minutes. The cloth was then rinsed and dried. The resulting cloth had a deep blue color which showed little change on repeated washing. The color also appeared to be resistant to solvents, such as acetone.

A similar untreated white Dacron fabric was placed in the same dye solution and boiled for 20 minutes but was still white on removal.

EXAMPLE VI

The white Dacron fabric treated with Polyether A, as shown in Example V, was also dyed with Anthraquinone Blue SWF 150%. 5 parts of the dye was placed in 1000 parts of water and the mixture heated to boiling. The treated Dacron cloth was then placed in the dye and the mixture boiled for 20 minutes. The cloth was removed, rinsed and dried. The resulting fabric was dyed a deep blue color which underwent little change on repeated washing. The dye was also resistant to solvents, such as acetone.

A similar untreated white Dacron fabric was placed in the same dye solution and boiled for 20 minutes but was still white on removal.

EXAMPLE VII

The white Dacron fabric treated with Polyether A, as shown in Example V, was also dyed with Celanthrene Pure Blue BRS 400% by the method shown in Example III. The fabric, after drying, had a very good deep blue color which underwent little change on repeated washing. The dyed cloth after five washes had a better color than a similar piece of Dacron fabric which had been treated with benzoic acid as a dye carrier before being dyed with the Celanthrene Pure Blue BRS 400% dye, and washed five times.

A similar untreated white Dacron fabric containing no carrier was only a very slight blue after being treated as described above with Celanthrene Pure Blue BRS 400%.

EXAMPLE VIII

Examples VIII to X illustrate the superior properties imparted to cellulose acetate fabric by treatment with Polyether A and an amine curing agent.

100 parts of Polyether A described above 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, 20 parts of diethylene triamine in 100 parts of water was then added and additional water added to bring the solution up to 666 parts.

White cellulose acetate fabric was then treated 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 cured at 160° C., for 5.5 minutes. The treated cloth had a soft feel, good hand, and did not fray at the cut edges.

The treated cellulose acetate fabric also had excellent dye-receptive properties. A solution of Calcodur Blue SL was prepared as shown in Example I and the treated cellulose acetate fabric placed therein. The mixture was boiled for 20 minutes and then the cloth was removed, rinsed, and dried. The resulting fabric was dyed an even deep blue color which was not affected by repeated washings with soap and water.

A similar untreated white cellulose acetate fabric was placed in the same solution and boiled for 20 minutes but was still white on removal.

EXAMPLE IX

The white cellulose acetate fabric treated with Polyether A as shown in Example VIII was also dyed with Kiton fast Red R dye. The dye solution was prepared as shown in Example II and the treated cellulose acetate fabric placed therein. The mixture was boiled for 20 minutes. The cloth was removed, rinsed and dried. The dried cloth was dyed a deep red color which was not affected by repeated washings. A similar untreated cellulose acetate fabric was only a slight red color after being treated with the Kiton fast Red dye as described above.

EXAMPLE X

The white cellulose acetate fabric treated with Polyether A as shown in Example VIII was also dyed with Anthraquinone Blue SWF 150% dye by the method shown in Example IV. The fabric, after drying, had a deep blue color which underwent little change on repeated washing. A similar untreated cellulose acetate fabric had only a slight blue color after being treated with the Anthraquinone Blue dye.

EXAMPLE XI

This example illustrates the superior properties imparted to nylon fabric (super polyamide fiber) by treatment with Polyether A and amine curing agent.

100 parts of polyether A described above were com-

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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, 20 parts of diethylene triamine in 100 parts of water was then added and additional water added to bring the solution up to 666 parts.

White nylon fabric was then treated 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 treated cloth was then cured at 160° C., for 5.5 minutes. The treated cloth had a soft feel, good hand and did not fray at the cut edges.

The treated nylon fabric also had excellent dye-receptive properties as shown by the following. A dye solution was prepared by adding .22 part of Calcodur Blue SL and 1.22 parts of sodium chloride to 1000 parts of water. This mixture was heated to boiling and treated nylon fabric was placed therein and the mixture boiled for 20 minutes. The cloth which was then dyed an even deep blue color, was removed, rinsed, and dried. Repeated washings with soap and water failed to affect the color.

A similar untreated nylon fabric had only a slight blue color when treated with the Calcodur Blue SL dye as described above.

EXAMPLE XII

This example illustrates the preparation of dye-receptive Orlon fabric using Polyether B and ethylene diamine as the curing agent.

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 ethylene diamine in 100 parts of water is added and additional water added to bring the solution to 666 parts.

Orlon fabric is then padded with above-described solution. The treated fabric is dried for 5 minutes at 160° C. The resulting fabric had a soft feel, good hand, and is easily dyed with Calcodur blue SL and Kiton fast red R dye as shown in the preceding examples.

EXAMPLE XIII

This example illustrates the preparation of dye-receptive Vinyon fabric (prepared from vinyl chloride-vinyl acetate copolymer) using Polyether B and triaminotoluene as the curing agent.

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, 25 parts of triaminotoluene in 100 parts of water are added and additional water added to bring the solution to 666 parts.

The Vinyon fabric is then padded with the above-described solution. The impregnated fabric is dried for 5 minutes at 160° C. The resulting fabric has a soft feel, good hand, and is easily dyed with Calcodur Gray L and Kiton fast Red R dye.

Similar results are obtained by replacing the Vinyon fabric in the above-described process with a Saran fabric (85% vinylidene chloride and 15% vinyl chloride copolymer).

EXAMPLE XIV

The same procedure is used as in the preceding example with the exception that the amine curing agent employed is diamino pyridine. Nylon fabric treated in this manner is easily dyed with the Calcodur Brown 4 GL, Kiton fast-Violet 10B and Kiton Fast Yellow 3G.

EXAMPLE XV

This example illustrates the preparation of a dye-receptive Orlon fabric using Polyether C and phenylene diamine as the curing agent.

About 100 parts of Polyether C described above is combined with 5 parts of a glycol fatty acid ester, poly-

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vinyl alcohol and 15 parts of phenylene diamine as in Example VIII and then sufficient water added to bring the solution to 666 parts.

Orlon fabric is then padded with the above-described solution. The treated fabric is dried for 5 minutes at 160° C. The resulting fabric has a soft feel, good hand, and is easily dyed with Calcodur blue S1 and Kiton Fast Orange GR.

Orlon fabric having related dyeing properties are obtained by replacing Polyether C in the above-described process with equivalent amounts of each of the following Polyether A, Polyether B and the polyglycidyl ether of pentaerythritol.

Similar results are obtained by replacing the Orlon fabric with a Dynel fabric (60% vinyl chloride and 40% acrylonitrile).

EXAMPLE XVI

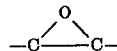
About 100 parts of Polyether A is combined with 5 parts of polyglycol fatty acid ester emulsifier and 100 parts of water. The mixture was stirred and then 50 parts of a 5% solution of polyvinyl alcohol, 20 parts of diethylene triamine in 100 parts of water was then added and additional water added to bring the solution up to 666 parts.

White Zein fabric (corn protein+formaldehyde) is treated with Calcodur Blue S1 as described in Example I. The cloth treated in this manner has a good blue color.

Similar results are obtained by replacing the Zein fabric with Zetek fabric (polymer of vinylidene cyanide).

I claim as my invention:

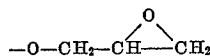
1. A process for treating synthetic textile materials prepared from polymers selected from the group consisting of acrylonitrile polymers, vinyl chloride polymers, vinylidene chloride polymers, vinylidene cyanide polymers, polyester reaction products of glycols and polycarboxylic acids and polyamide reaction products of polycarboxylic acids and polyamines to impart resistance to fraying at edge where cut and prevent "pilling," which consists of dipping the said synthetic textile material into an aqueous medium containing a polyepoxide having a plurality of



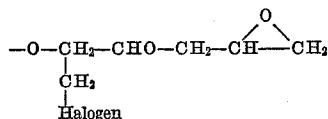
groups and containing elements selected from the group consisting of carbon, hydrogen, oxygen and halogen atoms and a minor amount of a curing agent of the group consisting of primary and secondary amines, removing any excess aqueous medium and then subjecting the treated material to a temperature above 100° C. to cure the polyepoxide.

2. A process as in claim 1 wherein the polyepoxide is a glycidyl polyether of an aliphatic polyhydric alcohol wherein the polyepoxide had 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 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 OH groups.

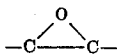
4. A process as in claim 1 wherein the polyepoxide

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is a glycidyl polyether of an alkanetriol-ethylene oxide condensate.

5. A process as in claim 1 wherein the amine curing agent is employed in amounts varying from 3 to 25 parts per 100 parts of polyepoxide and the catalyst is a primary amine.

6. A process for treating synthetic textile materials prepared from polymers selected from the group consisting of acrylonitrile polymers, vinyl chloride polymers, vinylidene chloride polymers, vinylidene cyanide polymers, polyester reaction products of glycols and polycarboxylic acids and polyamide reaction products of polycarboxylic acids and polyamines to impart resistance to fraying at the edge where cut and prevent "pilling," which consists of padding the textile material with an aqueous emulsion containing a polyether polyepoxide having a plurality of



groups and containing elements selected from the group consisting of carbon, hydrogen, oxygen and halogen atoms, a minor amount of an amine curing agent of the group consisting of primary and secondary amines, drying the treated material and subjecting the dried material to a temperature between 100° C. and 200° C. to cure the polyether polyepoxide.

7. A process as in claim 6 wherein the polyepoxide is a glycidyl polyether of glycerol.

8. A process as in claim 6 wherein the polyepoxide

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is a polyglycidyl ether of a glycerol-ethylene oxide condensate.

9. A process as in claim 6 wherein the amine is diethylene triamine.

10. A process as in claim 6 wherein the amine curing agent is ethylene diamine.

11. A process as in claim 6 wherein synthetic material is a fabric prepared from a polymer of acrylonitrile containing at least 20% acrylonitrile.

12. A process as in claim 6 wherein the synthetic material is a fabric prepared from a glycol-terephthalic acid polyester.

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