

2,826,592

EPOXY ESTERS OF PHOSPHORUS-CONTAINING ACIDS AND THEIR USE IN TREATING TEXTILES

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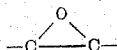
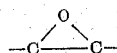
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This invention relates to a new class of phosphorus-containing organic compounds. More particularly, the invention relates to novel esters of certain phosphorus-containing acids and epoxy alcohols, and to their utilization, particularly as crease- and shrink-proofing agents for textile fabrics.

Specifically, the invention provides new and particularly useful esters of a phosphorus-containing acid component of the group consisting of phosphoric acids, acid esters of phosphoric acid wherein the said acid esters possess at least two free acidic groups, and derivatives of the foregoing members obtained by replacing the oxygen atom attached to the phosphorus atom with a dissimilar chalcogen, wherein all of the acid groups of the said acid components are esterified and at least two of the acid groups are esterified with an alcohol containing at least one

group, said



remaining intact in the ester molecule. The invention also provides polymers obtained by treating the above-described phosphorus-containing esters with epoxy-curing agents, such as amines, polycarboxylic acids, polymercaptans, metal salts, and the like.

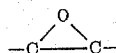
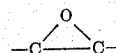
As a special embodiment, the invention provides a method for utilizing the above-described epoxy esters as crease- and shrink-proofing agents for textile fabrics wherein the fabric is impregnated with an aqueous solution or dispersion containing the said epoxy ester and an epoxy curing agent and the treated fabric is then heated to effect the cure of the epoxy groups within the fibers of the fabric.

Many 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 resins, such as urea- or melamine-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 chlorine and when the fabric is subsequently exposed to heat as in ironing or hot-air drying, the cloth is charred or discolored and the strength of the material seriously degraded. In addition, many of the fabrics treated with these resins have poor washability, i. e., the resin is easily lost from the fabric after a few washings with soap and water.

It is an object of the invention to provide a new class of organic compounds containing phosphorus. It is a further object to provide novel epoxy-substituted esters of certain phosphorus-containing acids and a method for their preparation. It is a further object to provide a new class of phosphorus-containing polyepoxides which are particularly useful as crease- and shrink-proofing agents for textile fabrics. It is a further object to provide novel phosphorus-containing polyepoxides that are particularly useful as crease- and shrink-proofing agents for white goods. It is a further object to provide novel phosphorus-containing esters that may be used to impart crease- and shrink-resistance to textile fabrics without imparting a harsh feel and undue stiffness to the fabrics. It is a further object to provide new crease- and shrink-proofing agents that impart no chlorine retentive properties to the treated fabrics. It is a further object to provide new crease- and shrink-proofing agents that impart flame-resistance to the textile fabrics and, in some cases, improved water repellency. It is a further object to provide new crease- and shrink-proofing agents that have improved resistance to washing. It is still a further object to provide a new method for imparting crease- and shrink-resistance to textile fabrics. 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 in part by the novel compounds of the invention comprising esters of a phosphorus-containing acid component of the group consisting of phosphoric acids, acid esters of phosphoric acid wherein the said acid esters possess at least two acidic groups, and derivatives of the foregoing members obtained by replacing at least one of the oxygen atoms attached to the phosphorus atom with a dissimilar chalcogen, i. e., sulfur, selenium or tellurium, wherein all of the acid groups of the said acid components are esterified and at least two of the acid groups are esterified with an alcohol possessing at least one

group, said



group remaining as such in the ester molecule. These particular neutral phosphorus-containing esters have been found to be surprisingly good crease- and shrink-proofing agents for textile fabrics as they have good solubility in water and may be easily applied to the fabrics in the form of aqueous solution or dispersions, can be rapidly cured within the fibers of the fabrics and gives as a final product fabrics having excellent resistance to creasing and shrinking. Surprisingly, the novel compounds impart these properties to the fabrics without giving the fabrics a harsh feel and without seriously impairing the tear strength and tensile strength of the fabric. The fabrics treated in this manner also have no ability to retain chlorine and may be bleached or otherwise exposed to chlorine without danger of being discolored or charred during subsequent heat treatments. In addition, it has been found that the fabrics treated with these particular epoxy esters have improved washability and can be washed numerous times without danger of losing any substantial amount of cured resin. Furthermore, these special crease- and shrink-proof agents act also as fire retardants and impart improved flame resistance to the treated fabric.

The phosphorus-containing esters of the higher epoxy alcohols, i. e., those containing at least 12 carbon atoms, as well as those epoxy esters derived from acid esters of

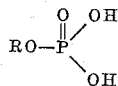
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phosphoric acid and higher alcohols, i. e., those containing at least 12 carbon atoms, also act as water repellent agents for the aforementioned textile fabrics.

The phosphorus-containing acids, the epoxy esters of which are provided by the present invention, comprise phosphoric acids, acid esters of phosphoric acid which esters possess at least two free acid groups, i. e., free acidic OH groups attached directly to phosphorus, and derivatives of the aforescribed phosphoric acid and acid esters wherein at least one of the oxygen atoms attached to phosphorus is replaced by a dissimilar chalcogen such as sulfur, selenium and tellurium.

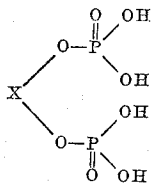
The phosphoric acids, epoxy esters of which are provided by the present invention, include orthophosphoric acid, pyrophosphoric acid, triphosphoric acid, tetraphosphoric acid, pentaphosphoric acid and higher polyphosphoric acids as described in U. S. 2,486,658.

The acid esters of phosphoric acid used in the preparation of the epoxy esters are those derived by the partial esterification of phosphoric acid with monohydric or polyhydric compounds. In the case of monohydric compounds, only one of the acid groups may be esterified to form acid esters of the formula



wherein R is derived from the monohydric compound by removing the OH group. Monohydric compounds used for this purpose may be aliphatic, cycloaliphatic, aromatic or heterocyclic and may be saturated or unsaturated. Examples of such alcohols include, among others the following alcohols having at least 3 carbon atoms per molecule, allyl alcohol, butyl alcohol, octyl alcohol, decyl alcohol, cyclohexanol, cyclopentanol, benzyl alcohol, phenol, 3-thiaoctanol, 4-thiadodecanol, chloroallyl alcohol, cyclohexanol, tetrahydropyran-3-methanol, tetrahydrofuran-3-ethanol, furfuryl alcohol, and the like. Preferred monohydric alcohols are the alkanols, alkenols and phenols containing up to 20 carbon atoms and preferably up to 12 carbon atoms. Coming under special consideration, particularly because of the ability of the resulting esters to produce improved resinous products are the ethylenically unsaturated monohydric alcohols, such as allyl alcohol, methallyl alcohol, and the like.

If the acid esters are derived from polyhydric compounds, two molecules of the phosphoric acid should be reacted with a mole of the polyhydric compound to form esters of the formula

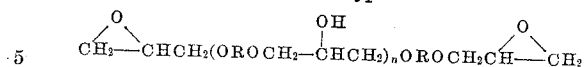


wherein X is derived from the polyhydric compound by removing two of the OH groups. The polyhydric compounds used in the preparation of these acid esters may have two, three or more hydroxyl groups and may be aliphatic, cycloaliphatic, aromatic or heterocyclic, such as, for example, the following having at least 2 carbon atoms: ethylene glycol, diethylene glycol, glycerol, pentaerythritol, mannitol, sorbitol, cellulose, methyltrimethylolmethane, 1,4,6-octanetriol, butanediol, 1,5-pentanediol, glycerol allyl ether, sucrose, fructose, maltose, 3,3'-thiodipropanol, 4,4'-sulfonyldipropanol, 1,3,6-hexanetriol, 3,6-dithiaoctanediol-1,8, cyclohexanediol-1,4, tetrahydrofuran-2,5-dipentanol, tetrahydropyrrole-2,5-dipropanol, 2,5-dihydroxy-3,4-dihydro-1,2-pyran, 4,4'-sulfonyldipropanol, bisphenol (2,2-bis(4-hydroxyphenyl)propane), 2,2-bis(4-hydroxyphenyl)butane, and the like.

Other examples of polyhydric compounds include those

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obtained by reacting polyhydric phenols with epichlorohydrin to form products of the type

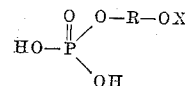


wherein R is a bivalent radical derived from the polyhydric phenol and n is an integer greater than one. Suitable polyhydric compounds may also be derived from polyepoxides, such as above, and others by opening the epoxide group by hydrolysis, reaction with amines, etc.

Preferred polyhydric compounds comprise the aliphatic and cycloaliphatic alcohols containing from 2 to 5 hydroxyl groups and no more than 20 carbon atoms, and more preferably no more than 12 carbon atoms. Of special interest are the alkanediols, cycloalkanediols, alkanetriols, cycloalkanetriols and the bis(hydroxyaryl)-alkanes.

As indicated above, the novel epoxy esters derived from acid esters of phosphoric acid and the higher monohydric alcohols and polyhydric alcohols which contain at least 12 carbon atoms, and preferably from 18 to 26 carbon atoms, such as octadecanol, nonadecanol, docosanol, pentacosanol, 1,18-octadecandiol, 1,18-ococandiol, and the like, are good water repellent agents as well as crease- and shrink-proofing agents, so these higher alcohols also represent preferred groups.

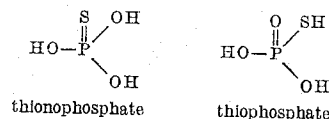
Less preferred acid esters used in preparing the novel epoxy esters may also be obtained by reacting one mole of the above-described polyhydric compounds or their ethers with a mole of phosphoric acid. Such compounds may be exemplified by the formula



wherein R is residue of the polyhydric compound and X is hydrogen or a hydrocarbon radical.

Examples of the acid esters used in preparing the epoxy esters of the invention include, among others, allyl dihydrogen phosphate, octadecyl dihydrogen phosphate, cresyl dihydrogen phosphate, cyclohexyl dihydrogen phosphate, nonadecyl dihydrogen phosphate, methallyl dihydrogen phosphate, dodecyl dihydrogen phosphate, 1,5-pentanediol bis(dihydrogen phosphate), 1,6-hexanediol bis(dihydrogen phosphate), bis-phenol bis(dihydrogen phosphate), glycerol tri(dihydrogen phosphate), 4,4'-sulfonyldipropanol bis(dihydrogen phosphate), bis-phenol bis(dihydrogen phosphate), and tetrahydropyran-2,4-dipropanol bis(dihydrogen phosphate).

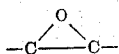
Derivatives of the above-described phosphoric acid and acid esters obtained by replacing the oxygen atom attached to phosphorus with sulfur, selenium or tellurium may also be used in preparing the novel epoxy esters. When the oxygen atom attached to the phosphorus atom through the double bond is replaced by the sulfur atom, the compounds will be named herein by placing the term "thiono" before "phosphate," and when the oxygen atom joined to the phosphorus atom through the single bond is replaced by the sulfur atom, the compounds will be named by replacing the term "thio" before "phosphate." Thus, the sulfur-substituted phosphate may be illustrated by the following formula



When the oxygen atom is replaced by selenium, the compounds will be referred to herein by placing the term "selenono" before the acid name, and when the oxygen joined to the phosphorus atom through the single bond is replaced by selenium, the term "seleno" will be placed before the acid name. The corresponding terms "tellurnono" and "tellurno" will be used when tellurium is

used to replace the oxygen atom joined to the phosphorus atom through the double bond and through the single bond, respectively. Illustrative examples of these substituted phosphoric acids and their acid esters include, among others, thiophosphoric acid, thionophosphoric acid, dithiophosphoric acid, selenophosphoric acid, selenonophosphoric acid, allyl dihydrogen thionophosphate, cresyl dihydrogen thiophosphate, cyclohexyl dihydrogen selenophosphate, S-allyl dihydrogen thiophosphate, S-phenyl dihydrogen thiophosphate, cyclohexyl dihydrogen telluronophosphate, and methallyl dihydrogen telluronophosphate.

The epoxy-substituted alcohols, the phosphorus-containing esters of which are provided by the present invention, comprise those alcohols possessing at least one epoxy group, i. e., a



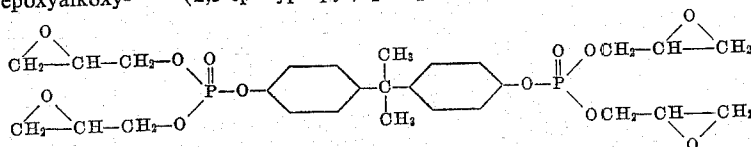
group. The alcohols may be monohydric or polyhydric, primary, secondary or tertiary and may be saturated, unsaturated, branched or unbranched and open-chain or cyclic. Examples of these alcohols include: 2,3-epoxypropanol (glycidol), 3,4-epoxybutanol, 2,3-epoxybutanol, 2,3-epoxyhexanol, 3,4-epoxydodecanol, 8,9-epoxyoctadecanol, epoxidized tetradecadienol, 3,4-epoxydihydropyran-5-propanol, 2,3-dimethyl-4,5-epoxyoctanol, 2-methoxy-4,5-epoxyoctanol, 3,4-epoxy-5-chlorocyclohexanol, 2,3-epoxypropoxypropanol, 2,3-epoxypropoxyhexanol, 2,3-epoxypropoxy-2,3-dihydroxyheptanol, 2,3-epoxydodecanol and 4-chloro-5,6-epoxydodecanol.

Preferred epoxy-substituted alcohols are the epoxy-substituted aliphatic and cycloaliphatic monohydric alcohols containing from 3 to 20 carbon atoms, such as 2,3-epoxypropanol, 3,4-epoxybutanol, 3,4-epoxydodecanol, 2-methyl-2,3-epoxypropanol, 2,3-cyclohexanol, 2,3-epoxypropoxyethanol, 2,3-epoxypropoxyoctanol, and the like.

Particularly preferred epoxy-substituted alcohols are the epoxyalkanols, epoxyalkoxyalkanols, epoxyalkoxy-

groups have been esterified with appropriate alcohols. Examples of the claimed epoxy esters include, among others, tri(2,3-epoxypropyl) phosphate, phenyl bis(2,3-epoxypropoxyphenyl) phosphate, tri(2,3-epoxypropyl) thionophosphate, cresyl di(2,3-epoxyhexyl) phosphate, allyl di(2,3-epoxypropyl) phosphate, octadecyl di(2,3-epoxypropyl) phosphate, benzyl di(2,3-epoxyoctyl) phosphate, chlorophenyl di(2,3-epoxyhexyl) phosphate, tri(2,3-epoxyhexyl) phosphate, S-(2,3-epoxypropyl) O,O-di(2,3-epoxypropyl) thiophosphate, tri(3,4-epoxyhexyl) selenonophosphate, tri(3,4-epoxyhexyl) telluronophosphate, Se(2,3-epoxypropyl) O,O-di(3,4-epoxyhexyl) selenonophosphate, tri(epoxypropoxypropyl) phosphate, tri(epoxybutoxyethyl) thionophosphate, 1,5-pentanediol bis[di(2,3-epoxypropyl) phosphate], 1,10-decanediol bis[di(3,4-epoxyhexyl) phosphate], glycerol tri[di(epoxypropoxyethyl) phosphate], pentaerythritol bis[di(2,3-epoxyoctyl) thiononophosphate], diethylene glycol bis[S-(2,3-epoxypropyl) O-(2,3-epoxyhexyl) thiophosphate], 1,6-hexanediol bis[Se-(2,3-epoxyhexyl) O-(4,5-epoxy octyl) selenophosphate], and the like.

The preferred epoxy esters of the invention are those derived from (1) phosphoric acid, acid esters of phosphoric acid and monohydric alcohols containing no more than 12 carbon atoms and aliphatic and cycloaliphatic polyhydric alcohols containing from 2 to 5 hydroxyl groups and not more than 12 carbon atoms, and (2) the preferred epoxy-substituted aliphatic and cycloaliphatic monohydric alcohols containing from 3 to 20 carbon atoms, such as, for example, octadecyl di(2,3-epoxypropyl) phosphate, tri(2,3-epoxyhexyl) phosphate, di(2,3-epoxypropyl) 4,5-epoxyhexyl phosphate, tri(3,4-epoxycyclohexyl) phosphate, tri(3,4-epoxyhexyl) phosphate, tri(epoxypropoxyhexyl) phosphate, 1,5-pentanediol bis[di(2,3-epoxypropyl) phosphate], 1,6-hexanediol bis[di(3,4-epoxyhexyl) phosphate], diethyleneglycol bis[di(3,4-epoxyamyl) phosphate], 4,4'-sulfonyldipropyl bis[di(2,3-epoxyamyl) phosphate], and bis-phenol bis[di(2,3-epoxypropyl) phosphate].



phenols, epoxyalkanols, epoxyalkoxyalkanols, epoxycycloalkanols and epoxyalkoxyalkanols, epoxycycloalkanols and epoxyalkoxyalkanols, and particularly those containing not more than 12 carbon atoms, such as 2,3-epoxypropanol, 2,3-epoxypropoxyphenol, 3,4-epoxyhexanol, 2,3-epoxypropoxyoctanol, 2,3-epoxy-5-octanol, 2,3-epoxy-6-dodecanol, 2,3-epoxypropoxy-5-octanol, 3,4-epoxycyclohexanol, 2,3-epoxypropoxy-4-cyclohexanol, and the like.

Of special interest are the monoepoxy-substituted alkanols containing from 3 to 8 carbon atoms and having the epoxy group in the terminal position. 2,3-alkanols, such as 2,3-epoxypropanol, are of particular interest, particularly because of the ease of preparation of their esters as well as the superior properties possessed by such esters.

As indicated above, the novel epoxy esters derived from epoxy alcohols containing at least 12 carbon atoms, and preferably from 18 to 26 carbon atoms, such as 8,9-epoxyoctadecanol, 10,11-epoxynonadecanol, 8,9,12,13-diepoxyoctadecanol, and 8,9-epoxyoctadecanediol, are good water repellent agents as well as crease- and shrink-proofing agents, so these higher epoxy alcohols also represent a preferred group.

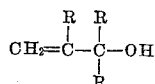
The novel epoxy esters of the present invention are the neutral esters of the above-described phosphoric acids and acid esters and the above-described epoxy alcohols. The expression "neutral ester" as used in reference to the claimed compounds indicates that all of the acidic

The novel esters of the invention may be prepared by a variety of different methods. Many of them may be prepared, for example, by epoxidizing the corresponding unsaturated ester of a phosphoric acid, or acid ester, or they may be prepared by reacting the epoxy-substituted alcohol with a phosphorus halide corresponding to the desired acid or acid ester.

The epoxidation of the unsaturated esters of the phosphorus-containing acids or acid ester is advantageously carried out by reacting the unsaturated ester with an epoxidizing agent at a temperature between about -20°C . to about 60°C . Organic peracids, such as peracetic, perbenzoic, monoperphthalic and the like acids, are usually effective epoxidizing agents for this type of reaction. It is preferred to carry out the reaction in a suitable mutual solvent for the reactants and product. Chloroform is an especially useful solvent for this purpose, but other materials such as ethyl ether, dichloromethane, benzene, ethyl acetate, etc., are also suitable. It is not necessary to operate under anhydrous conditions but the amount of water present should be limited so as to avoid excessive hydrolysis of the epoxy groups. Up to 25% water in the reaction mixture can be tolerated. The epoxy-substituted esters may be recovered from the reaction mixture by any suitable means, such as distillation, extraction, and the like.

The unsaturated esters of the phosphorus-containing acids or acid esters used in the above-described epoxidation reaction are preferably the esters of the above-

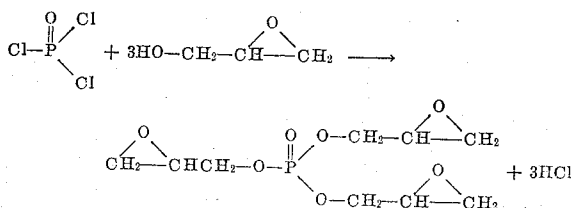
described phosphorus-containing acids or acid esters and ethylenically unsaturated alcohols, such as, for example, allyl alcohol, methallyl alcohol, crotyl alcohol, 4-hexenol, 5-decenol, 2,3-hexadienol, 3-pentenol, 4,6-octadecenol, 2-butyl-2-propenol, 2-phenyl-2-propenol, 2-methyl-3-butenol, and the like. Preferred esters are those of the aliphatic monohydric alcohols having an ethylenic group in the terminal position, such as, for example, allyl alcohol, methallyl alcohol, 4-butenol, 5-pentenol, 4,6-hexadienol, and the like. Of special interest are the esters of the allylic alcohols, i. e., the beta-gamma-monoethylenically unsaturated alcohols, and particularly those of the formula



wherein R is a hydrocarbon radical, and preferably an alkyl radical containing from 1 to 6 carbon atoms.

Examples of the unsaturated esters that can be used in the above-described epoxidation reaction include: triallyl phosphate, triallyl thionophosphate, pentanediol-1,5-bis(diallyl phosphate), diethylene glycol bis(diallyl phosphate), cresyl diallyl phosphate, bis-phenol bis(diallyl phosphate), phenyl dimethallyl phosphate, trimethallyl selenophosphate.

The novel esters of the invention may also be prepared by treating the desired epoxy alcohol with a phosphorus halide corresponding to the desired acid or acid ester in the presence of a halide absorbing material. This method of preparation may be illustrated by the following equation showing the preparation of tri(2,3-epoxypropyl) phosphate from glycidol and phosphorus oxychloride:



This type of reaction may be carried out by simply mixing the desired phosphorus halide with the alcohol in an inert solvent, such as toluene or benzene, in the presence of a hydrogen halide absorbing material at relatively low temperatures. The reactants may be employed conveniently in substantially stoichiometrically required amounts, although in the event one reactant is more precious than the other, a moderate excess of the less precious may be employed to insure high conversion of the other reactant to desired product. The reaction is preferably carried out at temperatures within the range of -10°C . to 20°C ., and more preferably, between the range of 0°C . to 15°C .. In the event excessive heat is liberated in the reaction mixture, the reaction mixture may be cooled or the reaction may be maintained under control by dilution of the mixture with an inert solvent. The reaction may also be regulated by the controlled addition of one reactant, e. g., the phosphorus halide may be added dropwise to the other reactant. The material used to absorb the hydrogen halide should be one that would not react with the acid halide or epoxy group or cause polymerization of the epoxide. Preferred materials are the inorganic bases and tertiary amines, such as triethylamine, triamylamine, pyridine, and the like. Upon completion of the reaction, any salt formed by the reaction of the added hydrogen-halide absorbing material and the liberated hydrogen halide may be removed from the reaction mixture by filtration or equivalent means and the filtrate suitably treated to recover the desired ester. In most cases, fractional distillation is the most convenient method for recovering the desired prod-

uct although it will be appreciated that other applicable methods may be used in the appropriate cases.

The esters of the polyphosphoric acids may be obtained by reacting a chloro diester of phosphoric acid, such as diglycidyl chlorophosphate, with a triester of phosphoric acid under the conditions disclosed in U. S. 2,486,658.

The epoxy esters of the present invention are viscous liquids to resinous solids. They are all neutral esters possessing at least two 1,2 epoxy groups. They are soluble in aqueous solutions or dispersions and in a great many oils and solvents and are compatible with synthetic resins and polymers, such as the vinyl chloride polymers. In combination with these various materials, they may act as a heat and light stabilizing agent as well as a flame resistant additive.

The epoxy esters are also of considerable value in the formation of improved resinous products as they may be cured alone or in combination with other epoxide containing materials to produce valuable infusible insoluble products. Polyepoxides that may be copolymerized with these polyepoxides of the present invention include, among others, glycidyl polyethers of polyhydric phenols obtained by reacting polyhydric phenols, such as bis-phenol, resorcinol, and the like, with an excess of a chlorohydrin, such as epichlorohydrin, polyepoxide polyethers obtained by reacting an alkane polyol, such as glycerol and sorbitol, with epichlorohydrin and dehydrochlorinating the resulting product, polymers prepared from ethylenically unsaturated epoxides, such as allyl glycidyl ether, alone or with other ethylenically unsaturated monomers, and polyepoxide polyethers obtained by reacting a polyhydric alcohol or polyhydric phenol with any of the abovedescribed polyepoxides. The glycidyl polyethers of polyhydric phenols obtained by condensing the polyhydric phenols with epichlorohydrin as described above are also referred to as "ethoxylene" resins. See Chemical Week, vol. 69, page 27, for September 8, 1951.

Curing of the epoxy esters of the present invention alone or in combination with the above-noted dissimilar polyepoxides is preferably accomplished by heating the product or products in the presence of a catalyst such as an amine catalyst as ethylene diamine, amine-aldehyde or amide-aldehyde type resins, such as those prepared from formaldehyde and amides or amines as urea, thiourea, hydroxy urea, phenyl thiourea, and the like, diisocyanates, dialdehydes, polycarboxylic acids, polymercaptans, and the like. The amount of catalyst utilized will vary depending upon the type of catalyst and reactants selected, but in most cases will vary from about .1% to 5% by weight. The temperatures employed in the polymerization may also vary over a wide range. In most instances, the polymerization may be accomplished at a temperature varying from about 25°C . to about 100°C ., and more preferably from 30°C . to 70°C .

The polymers and copolymers prepared from the polyepoxide of the present invention as described above are useful for the formation of pottings, castings, coatings and rigid plastic articles.

The epoxy esters of the present invention, however, are particularly valuable as crease- and shrink-proofing agents for textile fabrics. When these materials are applied in solution to the fabric and cured within the fabric fibers, they impart excellent crease- and shrink-resistance without giving undue stiffness to the fabric. As indicated above, these products are superior to known crease- and shrink-proofing agents in that they do not retain chlorine and have improved washability and, in addition, impart flame resistance to the treated fabric.

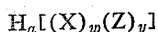
The epoxy esters of the present invention are preferably applied to the fabric in the form of a solution or dispersion. For most applications, they are preferably applied as an aqueous solution or emulsion. Emulsifying agents employed for this purpose are preferably those

that are free of nitrogen and strong acidic groups, such as the monooleate of sorbitan polyoxyethylene, the trioleate of sorbitan polyoxyethylene, sorbitan tristearate, sorbitan monolaurate, polyoxyethylene ethers of alkylphenols, carboxymethylcellulose, starch, gum arabic, aryl and alkylated aryl sulfonates, such as cetyl sulfonate, oleyl sulfonate, sulfonated mineral oils, 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 epoxy ester 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 an 80% 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 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 epoxy ester 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 epoxy ester. 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 anhydrides as citric acid, acetic acid, acetic acid anhydride, butyric acid, caproic acid, phthalic acid, phthalic acid anhydride, tartaric acid, aconitic acid, oxalic acid, phosphoric acid, boric acid, sulfonic acids as benzenesulfonic acid, phosphinic acids as benzenephosphinic acid, perchloric acid, persulfuric acid, and the like; the boron trifluoride complexes such as p-cresol and urea complex, diethylaniline-boron trifluoride complex; and the salts of inorganic acids, such as zinc fluoborate, potassium persulfate, nickel fluoborate, copper fluoborate, selenium fluoborate, magnesium fluoborate, tin fluoborate, potassium perchlorate, cupric sulfate, cupric phosphate, cupric phosphite, magnesium arsenate, magnesium sulfate, cadmium arsenate, cadmium silicate, aluminum fluoborate, ferrous sulfate, ferrous silicate, manganese hypophosphite, nickel phosphate and nickel chlorate.

Particularly preferred curing catalysts to be used are the organic monocarboxylic and polycarboxylic acids and their anhydrides containing not more than 16 carbon atoms, inorganic acids of the formula



wherein X is a non-metal having an atomic weight above 2, Z is an element which tends to gain from 1 to 2 electrons in its outer orbit, w is an integer, y is an integer greater than 1, and a equals the valency of the radical $(X)_w(Z)_y$ and the salts of these acids and metals having an atomic weight between 24 and 210 and being selected from groups I to IV and VII of the periodic table of elements.

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

The amount of the epoxy ester to be deposited on the fabric will vary over a wide range depending upon the degree of wrinkle-resistance and shrink-resistance desired in the finished material. If the fabric is to have a soft feel, such as that intended for use for dresses, shirts, etc., the amount of epoxy ester 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 determining the amount of resin deposited, it should, of course, 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 epoxy ester 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 epoxy ester 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 either slack or framed to dimension at temperatures ranging up to 120° C. The period of drying will depend largely on the amount of the pick-up permitted during the application of the solution, and the concentration of the polyepoxides. In most instances, drying periods of from 1 to 30 minutes should be sufficient.

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

The epoxy ester of the invention may be applied to any textile fabric. Such materials include the natural or artificial textile materials, such as cotton, linen, natural silk and artificial silk, such as the artificial silk obtained from cellulose acetate or other organic esters of ethers of cellulose and regenerated cellulose type of artificial silk obtained by the viscose, cuprammonium or nitrocellulose process, jute, hemp, rayon, animal fibers, such as wool, hair, mohair, and the like, and mixtures thereof. 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 requiring more crispness and fullness such as the preparation of rugs, carpets, plushes, draperies, upholsteries, shoe fabrics, and the like.

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

The wrinkle recovery values reported in the examples were determined by the Monsanto wrinkle recovery

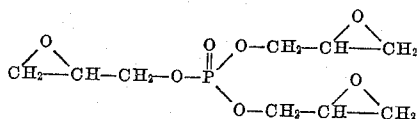
method. All tests were carried out at 50% relative humidity and 78° F.

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

Example I

This example illustrates the preparation and some of the properties of tri(2,3-epoxypropyl) phosphate.

About 54 parts of glycidol was combined with 200 parts of toluene and 61 parts of triethylamine and the mixture placed in a reaction kettle equipped with a stirrer, thermometer well, condenser and dropping funnel. The temperature of the mixture was reduced to 0° C. to 5° C. in an ice-salt bath. 31 parts of phosphorus oxychloride was then slowly added through the dropping funnel over a period of 1.5 hours and the temperature held at 10° C. The mixture was stirred continuously for several hours and the amine chloride filtered off. The filtrate was allowed to stand overnight and the white crystals that settled out were again filtered off. The filtrate was then stripped under a vacuum (45° C. at 1-2 mm.) to give a fluid amber colored material identified as tri(2,3-epoxypropyl) phosphate:



Epoxy value=1.03 eq./100 g.

P% theory=11.65%

Ester value=0.67 eq./100 g.

Found=11.4%

The tri(2,3-epoxypropyl) phosphate produced above was added in varying amounts to separate padding baths containing 250 parts of water, 1.25 parts of Pluronic F-68 as wetting agent and 3.6 parts of zinc fluoborate as catalyst. 5.6 yd./lb. cotton gingham (about 80 x 70 count) cloth was then impregnated with each solution by means of a Butterworth 3-roll laboratory padder. The impregnated sheets were dried 5 minutes at 100° C. and cured 5 minutes at 160° C. The finished sheets were then washed with Ivory Flakes and rinsed three times to remove any soluble material.

The sheets treated in the above-described manner were quite soft and had good wrinkle resistance, good washability, no chlorine retention, and improved fire resistance. The wrinkle recovery values of the sheets treated with the varying amounts of tri(2,3-epoxypropyl) phosphate are shown below in comparison to an untreated sheet:

Percent Tri(2,3-Epoxypropyl) Phosphate on Cloth	Monsanto Crease Recovery Angle Average Warp and Fill	Percent Shrinkage
15.....	117	1.0
10.....	109	1.2
5.....	92	2.0
0.....	79	2.3

Esters having related properties as crease- and shrink-proof agents are obtained by replacing the glycidol in the above-described method of preparing the ester with equivalent amounts of each of the following: 2,3-epoxyhexanol, 3,4-epoxycyclohexanol, and 4,5-epoxyoctanol.

Example II

This example illustrates the preparation and some of the properties of pentanediol - 1,5 - bis[di(2,3 - epoxypropyl) phosphate].

About 104 parts (1 mole) of pentanediol-1,5 is combined with 200 parts of diethyl ether and 160 parts of pyridine and the mixture placed in a reaction kettle equipped as shown in Example I. 302 parts of phosphorus oxychloride is then slowly added and the mixture kept at about 10° C. The mixture was stirred continuously for several hours and the pyridine salt filtered off. Distilla-

tion under reduced pressure yields the pentanediol-1,5 bis-(dichlorophosphate).

90 parts of glycidol is combined with 200 parts of toluene and 131 parts of triethylamine and the mixture placed in a reaction kettle shown in Example I. 100 parts of pentanediol - 1,5 bis(dichlorophosphate) produced above is then slowly added to the reaction mixture and the temperature kept at 10° C. The mixture is stirred for several hours and the amine chloride filtered off. The filtrate was then distilled under reduced pressure to yield the desired pentanediol-1,5 bis[di(2,3-epoxypropyl) phosphate].

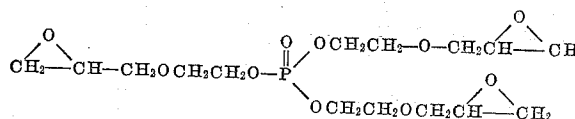
About 50 parts of the pentanediol-1,5 bis[di(2,3-epoxypropyl) phosphate] produced above is dissolved in 500 parts of an isopropyl alcohol-water solution, and then 20 parts of citric acid added to the resulting solution. Cotton gingham cloth is then impregnated with the above-described solution by means of the Butterworth 3-roll laboratory padder. The impregnated cloth is then dried at 60° C. and cured at 160° C. for 5 minutes. The finished cloth is then washed with Ivory Flakes and rinsed three times in warm water to remove any soluble material. The cloth treated in this manner is quite soft and has good wrinkle resistance and no chlorine retention.

Esters having related properties are obtained by replacing the pentanediol-1,5 in the above-described method of preparation with equivalent amounts of each of the following: 1,6-hexanediol, diethylene glycol and 4,4'-di-propanol.

Example III

This example illustrates the preparation and some of the properties of tri(epoxypropoxyethyl) phosphate.

About 90 parts of epoxypropoxyethanol (glycidyl ether of ethylene glycol) is combined with 200 parts of toluene and 61 parts of triethylamine and the mixture placed in a reaction kettle equipped with stirrer, thermometer well, condenser and dropping funnel. The temperature of the mixture is reduced to 0° C. to 5° C. in an ice-salt bath. 31 parts of phosphorus oxychloride is then slowly added through the dropping funnel over a period of several hours and the temperature held at 10° C. The mixture is stirred continuously for several hours and the amine chloride filtered off. The filtrate is then distilled under vacuum to yield a fluid light-colored liquid identified as tri(epoxypropoxyethyl) phosphate:



About 50 parts of the tri(epoxypropoxyethyl) phosphate produced above is dissolved in 500 parts of an isopropyl alcohol-water solution, and 10 parts of zinc fluoborate added. Cotton gingham cloth is then impregnated with the above solution by means of the Butterworth 3-roll laboratory padder. The impregnated cloth is dried at 60° C. and cured at 160° C. for 5 minutes. The finished cloth is soft and has good wrinkle resistance, no chlorine retention and improved fire resistance.

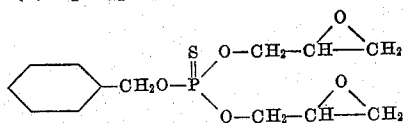
Example IV

This example illustrates the preparation and some of the properties of benzyl di(2,3-epoxypropyl) thionophosphate.

About 40 parts of glycidol is combined with 200 parts of toluene and 61 parts of triethylamine and the mixture placed in the reaction kettle described in Example I. The temperature of the mixture is reduced to about 5° C. 45 parts of liquid benzyl dichlorothionophosphate is slowly added to the reaction mixture and the temperature held at 10° C. The mixture is stirred continuously for several hours and the amine chloride filtered off. The filtrate is

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then stripped under vacuum to yield a liquid identified as benzyl di(2,3-epoxypropyl) thionophosphate:



Cloth treated with an aqueous solution of the above epoxy ester and zinc fluoborate as the catalyst and dried and cured as shown in Example III is soft and has good resistance to creasing and shrinking.

When 25 parts of the benzyl di(2,3-epoxypropyl) thionophosphate is mixed with 25 parts of the diglycidyl ether of bisphenol and 5 parts of 2,4,6-tri(dimethylamino-methyl)phenol, and the mixture heated to 65° C., the mixture sets up into a hard solid resin.

Esters having related properties are obtained by replacing the benzyl dichlorothionophosphate in the above-described method of preparation with equivalent amounts of each of the following: benzyl dichloroselenophosphate, cyclohexyl dichlorothionophosphate an cresyl dichlorotellurphosphate.

Example V

This example illustrates the preparation and some of the properties of allyl di(2,3-epoxypropyl) phosphate.

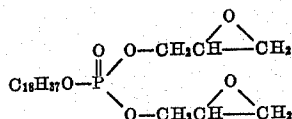
About 40 parts of glycidol is combined with 200 parts of toluene and 61 parts of triethylamine and the mixture placed in the reaction kettle described in Example I. The temperature of the mixture is then reduced to about 5° C. 35 parts of allyl dichlorophosphate is slowly added to the mixture and the temperature held at 5° C. The mixture is stirred continuously for several hours and the amine chloride filtered off. The filtrate is then stripped under vacuum to yield a fluid liquid identified as allyl di(2,3-epoxypropyl) phosphate.

Cloth treated with an aqueous solution of the above epoxy ester and zinc fluoborate as the catalyst and dried and cured as shown in Example III is soft and has good resistance to creasing and shrinking.

Example VI

This example illustrates the preparation and some of the properties of octadecyl di(2,3-epoxypropyl) phosphate.

About 40 parts of glycidol is combined with 200 parts of toluene and 50 parts of triethylamine and the mixture placed in the reaction kettle described in Example I. The temperature of the mixture is reduced to about 5° C. 75 parts of octadecyl dichlorophosphate is slowly added to the reaction mixture and the temperature held at 10° C. The mixture is stirred continuously for several hours and the amine chloride filtered off. The filtrate is then distilled to yield octadecyl di(2,3-epoxypropyl) phosphate:



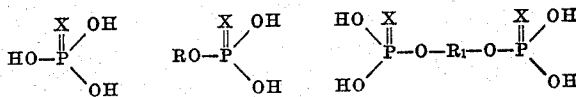
Cloth treated with an aqueous dispersion of the above epoxy ester and zinc fluoborate and dried and cured as shown in Example III is water repellent and has resistance to creasing.

Esters having related properties are obtained by replacing the octadecyl dichlorophosphate in the above-described method of preparation with equivalent amounts of each of the following: nonadecyl dichlorophosphate and pentacosyl dichlorothionophosphate.

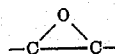
We claim as our invention:

1. A neutral ester of (1) a phosphorus-containing acid component of the group consisting of

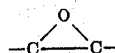
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- 5 wherein X represents a member of the class consisting of the oxygen and sulfur atoms, R represents a monovalent hydrocarbon radical containing from 3 to 20 carbon atoms, R₁ represents a bivalent radical containing from 3 to 20 carbon atoms selected from the class consisting of alkylene groups and alkylene-oxy-alkylene groups and (2) an alcohol, containing from 3 to 20 carbon atoms selected from the class consisting of alkanols containing at least one

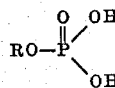


group and alkoxy alkanols containing at least one



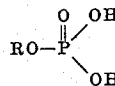
group.

2. An ester of (1) a dihydrogen phosphate of the formula



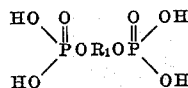
wherein R is an alkyl radical containing from 3 to 20 carbon atoms, and (2) an epoxyalkanol containing from 3 to 20 carbon atoms.

3. A neutral ester of (1) a dihydrogen phosphate of the formula



wherein R is an aliphatic hydrocarbon radical containing from 3 to 20 carbon atoms, and (2) an epoxyalkanol containing from 3 to 20 carbon atoms.

4. An ester of (1) a phosphorus-containing acid component of the formula



wherein R₁ is an alkylene radical containing from 2 to 20 carbon atoms, and (2) an epoxyalkanol containing from 3 to 20 carbon atoms.

5. A neutral epoxyalkyl ester of an alkane polyol bis(dihydrogen phosphate) wherein the epoxyalkyl portion of the molecule contains from 3 to 20 carbon atoms and the alkane polyol portion of the molecule contains from 2 to 20 carbon atoms.

6. A tri(epoxyalkyl) phosphate wherein each epoxyalkyl group contains from 3 to 20 carbon atoms.

7. A tri(epoxyalkoxyalkyl) phosphate wherein each epoxyalkoxyalkyl group contains from 3 to 20 carbon atoms.

8. Tri(epoxypropoxyethyl) phosphate.

9. Tri(2,3-epoxypropyl) phosphate.

10. Allyl di(2,3-epoxypropyl) phosphate.

11. Pentanediol - 1,5 bis(di(2,3 - epoxypropyl) phosphate).

12. A polymer of the ester defined in claim 1.

13. A polymer of the ester defined in claim 10.

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