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SHRINKPROOFING WOOL-CONTAINING TEXTILES WITH POLYEPOXIDES AND POLYAMIDES IN THE PRESENCE OF A REDUCING AGENT

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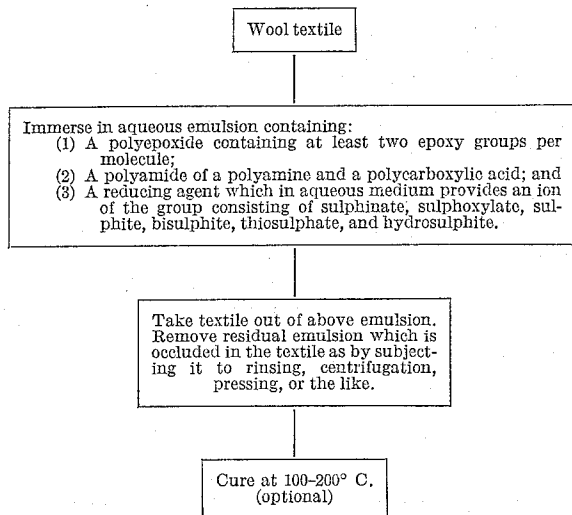
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This invention relates to and has among its objects the treatment of textiles in order to improve their dimensional stability. A particular object of the invention concerns the treatment of wool textiles to produce modified textiles which exhibit a marked resistance to shrinking and felting as compared with the original wool. Further objects and advantages of the invention will be evident from the following description wherein parts and percentages are by weight unless otherwise designated.

The simplified flow sheet set forth below is furnished to provide a graphic exemplification of the process of the invention.



It has been previously shown that the shrinkage properties of wool textiles can be substantially improved by depositing a polyepoxide-polyamide resin in situ on the fibers. In the copending application of Clay E. Pardo, Jr., and Robert E. Foster, Serial No. 836,830, filed August 28, 1959, there is disclosed a method for accomplishing such an end by a system which involves immersing the textile in a heated aqueous emulsion of a polyepoxide and a polyamide and holding the textile in the emulsion for a time long enough to permit the polyepoxide and polyamide to deposit onto the fibers of the textile. The textile is then withdrawn from the emulsion and treated as by rinsing and/or centrifugation to remove excess liquid. The product is then air-dried and is ready for use directly or it may be given an oven cure to ensure completion of the resin-forming reactions.

In accordance with the present invention, the system described above is modified by applying a reducing agent to the textile prior to or at the time the polyepoxide and

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polyamide are deposited on the fibers. Thereby, several significant advantages are attained as follows:

A particularly important advantage is that the present invention yields an increased efficiency of exhaustion; that is, more of the resin-forming ingredients (polyepoxide and polyamide) are deposited on the fibers from the emulsion in a given time. Thus, comparative tests under equal conditions of time, temperature, concentration, etc., have indicated that the present system yields efficiencies anywhere from 3 to 10 times those obtained with the former procedure.

Another item is that there is less yellowing of the fabric. In the prior process the deposition of the resin on the fibers is accompanied by development of a yellowish coloration whereas with the present process this yellowing effect is completely absent or markedly less evident.

In general, the procedure of the present invention provides a better degree of shrinkproofing per unit weight of resin deposited on the fibers.

In the prior technique it was necessary for best results to pretreat the fabric with a hydrogen peroxide solution. In the present process such pretreatment is eliminated whereby the process is simpler and more economical.

The process of the present invention not only yields the aforesaid advantages over the prior system but retains all the advantages inherent in the process as disclosed in the aforesaid Pardo and Foster application. Many of these retained advantages are based on the fact that the instant process involves an exhaustion technique in contrast to a padding technique. The importance of the distinction is explained below.

In padding techniques—for example, as disclosed in the copending application of Clay E. Pardo, Jr., and Richard A. O'Connell, Serial No. 750,274, filed July 22, 1958, now U.S. Patent No. 3,019,076—the desired proportion of resin on the textile is obtained by applying (padding) onto the fabric a definite weight of polyepoxide-polyamide dispersion in accordance with the weight of the fabric and then curing the fabric containing this amount of dispersion enmeshed within its fibrous structure. For example, if it were desired to have a resin content of 5%, using a dispersion containing 10% of polyamide and polyepoxide, then a unit weight of textile would be impregnated with one-half its weight of dispersion and subjected to curing. This padding technique has the disadvantage that some of the resinous components exist in inter-fiber areas as well as on the fibers. When the impregnated textile is cured, the resinous components in the inter-fiber spaces will cause bonding of adjacent fibrous elements with the end result that the product will not be as soft as the original textile. In accordance with the present invention, the polyamide-polyepoxide dispersion is applied under such conditions that the resinous components (the polyamide and polyepoxide) are absorbed onto the surface of the fibers and excess dispersion containing unabsorbed polyepoxide and polyamide is removed, for example, by rinsing the treated fiber with water. As a result, there is little or no resinous material in the textile except that on the fiber surfaces themselves. The net result is that inter-fiber bonding is greatly reduced and the final product is as soft as the original textile.

Another advantage which accrues from the present method of absorbing the resinous components from the dispersion is that resin coating on the fibers is uniform. Where padding techniques are used uniformity is difficult of obtainment because of variations in pressure exerted by the padding rolls, variations in textile thickness and density, etc.

The present method makes it practicable to cure the resinous components as they are absorbed on the fiber

surfaces. This makes it possible to eliminate the usual oven-curing step.

The process of the invention makes it possible to shrinkproof wool textiles in all physical forms. That is, it can be applied not only to woven or knitted textiles but even to tops, slivers, rovings, yarns, or bulk (loose) fibers.

By applying the process of this invention one is enabled to obtain textile products which are dimensionally stabilized yet which retain unimpaired the intrinsic properties which make them useful for textile purposes. Thus textiles treated in accordance with the invention can be washed in aqueous soap or detergent media since they are highly resistant to shrinking and felting. However, the treated textile is still useful for the usual textile applications since the hand, resiliency, porosity, textile strength and other valuable attributes of the material are retained. A particular advantage is that the improvement is essentially permanent; the treated textiles can be washed repeatedly without losing their dimensional stability. A further advantage is that a relatively minor proportion of resinous material deposited on the fibers imparts a very drastic improvement in dimensional stability. For example, wool treated with less than 10% total resin displays virtually no shrinkage on washing with aqueous media.

For use in the process of the invention, a preferred reducing agent is thiourea dioxide which may be prepared by reacting thiourea, in known manner, with hydrogen peroxide in a neutral system. Thiourea dioxide, despite its name which suggests oxidizing activity, is actually a very powerful reducing agent. The formula of the compound has been depicted as $(\text{NH}_2)_2\text{CSO}_2$ but from more detailed studies it is believed to have an inner salt or betaine type of structure as shown below:



Different investigators refer to the compound under such names as formamidine sulphinic acid, formamidine sulphinic acid betaine, or iminoaminomethane sulphinic acid betaine. Homologous compounds which may also be used in the process of the present invention may be prepared by methods known in the art, for example, by reacting hydrogen peroxide in neutral solution with N-alkylated derivatives of thiourea such as methyl thiourea, ethyl thiourea, propyl thiourea, N,N-dimethyl thiourea, etc. Thus the invention encompasses not only thiourea dioxide itself but the lower alkyl homologues thereof as well.

Another class of reducing agents useful in the process of the invention are the formaldehyde sulphonylates. Generally, these compounds are used in the form of the alkali-metal, zinc, ammonium, or amine salts.

Other reducing agents which may be employed are the alkali-metal (or ammonium) sulphites, bisulphites, thiosulphates, and hydrosulphites. Typical among these are sodium sulphite, sodium bisulphite, sodium thiosulphate, and sodium hydrosulphite. Since there is some confusion in the literature about nomenclature, the name "sodium hydrosulphite" is used herein to refer to the compound of the formula $\text{Na}_2\text{S}_2\text{O}_4$, well known in the textile dyeing industry for its vat dye reducing properties. Although the alkali salts of these compounds are generally preferred, it is evident that one may employ their amine salts such as their salts with monoethanol amine, diethanol amine, triethanol amine, etc.

The effect of a sulphite or bisulphite may also be achieved by adding sulphur dioxide gas to the emulsions although this procedure is not preferred because of the need for special gas-handling equipment. The effect of a sulphite or bisulphite can also be attained by using as the reducing agent aldehyde- or ketone-addition products with sulphites or bisulphites, for example, sodium

formaldehyde bisulphite, sodium acetaldehyde bisulphite, sodium acetone bisulphite, sodium glucose bisulphite, etc.

Since the aim in operating in accordance with the present invention is to provide a compound which contains a moiety of reducing character of the above-described classes it is immaterial what other moieties are present in the compounds. Thus, generically we may use in our process any reducing agent which provides in water an ion selected from the group consisting of sulphinate, sulphonylate, sulphite, bisulphite, thiosulphate, and hydrosulphite.

The amount of reducing agent may be varied depending on individual circumstances such as the efficiency of exhaustion desired and the efficacy of the agent selected. Even small amounts of reducing agents will improve the exhaustion but for practical purposes it is preferred to apply at least 0.1% of reducing agent based on the weight of textile being treated. In general, an increased proportion of reducing agent will afford a greater efficiency of exhaustion but it is advised to employ not more than 5% of reducing agent (based on the weight of textile) whereby to avoid any possibility of damage to the fibers. In the preferred modification of the invention the reducing agent is incorporated into the emulsion containing the polyepoxide and polyamide. This method is preferred because of its simplicity in that only one treatment-liquid is applied to the fabric. In applying such technique, we generally add to the emulsion approximately 0.05 to 0.1% of reducing agent based on the weight of emulsion. Such emulsions used, for example, in a fabric/emulsion ratio of 1:30 will provide about 1.5 to 3% of reducing agent based on the weight of fabric. It is obvious that if a different fabric/emulsion ratio is selected, a suitable adjustment may be made of the concentration of reducing agent in the emulsion.

It is not maintained that all of the types of reducing agents disclosed above are equally effective and in any particular case one may readily determine the optimum amount of reducing agent by conducting pilot trials with different proportions of the selected reducing agent in the polyepoxide-polyamide emulsion and noting the degree of exhaustion and shrinkproofing attained when the emulsion is applied to the particular textile being processed. Selection of the appropriate amount of reducing agent can then be made by a comparison of the results obtained. In many cases we prefer to use thiourea dioxide or the alkali-metal hydrosulphites, bisulphites or sulphites as these compounds afford superior results from the standpoint of exhaustion efficiency and degree of shrinkproofing of the fabric.

In a less-preferred modification of the invention, the reducing agent is applied to the fabric prior to application of the polyepoxide-polyamide emulsion. For this purpose, the fabric is soaked in an aqueous bath containing a small concentration (usually about 0.5 to 3%) of the reducing agent. Generally it is preferred that the bath have a pH about from 9 to 10. To attain such a condition one may add a suitable proportion of a mild alkaline material such as sodium carbonate, borax trisodium phosphate, tetrasodium pyrophosphate sodium metaphosphate, ammonium acetate, or the like. A minor proportion of a conventional wetting agent may be added to enable foster penetration of the solution into the textile. Also, conventional sequestering agents such as alkali-metal salts of ethylenediamine tetraacetic acid may be added to the solution to chelate any heavy metal ions which may be present in the fabric or in the water. The wool is soaked in the aforesaid bath long enough to ensure thorough impregnation. If desired, the bath may be heated, for example, up to about 60° C. A preferred treatment is to soak the wool in an aqueous solution containing about 0.3% reducing agent, 0.8% tetrasodium pyrophosphate and 0.25% ethylenediamine tetraacetic acid tetrasodium salt. The soak is continued for about

45 minutes at 50° C. Following treatment of the wool with the reducing agent solution, the fabric is rinsed in water and then is ready for application of the polyepoxide-polyamide emulsion.

In the practice of the invention the resin is formed on the textile fibers by impregnating the textile with an aqueous emulsion of a polyamide and a polyepoxide. This emulsion, in the preferred modification of the invention also contains the reducing agent. The emulsion should be dilute; that is, the total concentration of polyamide and polyepoxide should not exceed 1%. Generally, emulsions containing 0.05 to 0.8% of total polyamide and polyepoxide are preferred. The emulsion should be substantially neutral; that is, its pH should be in the range of about 6.5 to 7.5. It has been observed that when the pH is too low (below 6.5) ineffective shrinkproofing is obtained and when the pH is too high (above 7.5) the resins are precipitated and gum up the textile and treating vessel. In general, when the emulsion is prepared it is necessary to add acidic reagents to attain the desired pH of approximate neutrality. For this purpose one may use any of the usual acidifying agents such as hydrochloric acid, sulphuric acid, phosphoric acid, formic acid, acetic acid, or the like. To maintain the desired pH during treatment it is often desirable to add a buffer such as sodium sulphate, ammonium sulphate, or mixtures of acids and bases proportioned to provide a neutral product. To assist in forming and maintaining the emulsion one may add a conventional emulsifying agent in a small proportion; i.e., about 1 to 5% based on the amount of resinous materials (polyamide and polyepoxide). For such purpose one may employ agents such as soaps, long chain alkyl sodium sulphates or sulphonates, long chain alkyl benzene sodium sulphonates, esters of sulphonosuccinic acid, etc., typical examples being sodium oleate, sodium lauryl sulphate, sodium dodecane sulphonate, sodium alkyl (C₁₀-C₂₀) benzene sulphonate, sodium dioctylsulphosuccinate, etc. Preferably, agents of the non-ionic type are used, for example, the reaction products of ethylene oxide with fatty acids, polyhydric alcohols, alkyl phenols, and so forth. Typical examples of such agents are a polyoxyethylene stearate containing 20 oxyethylene groups per mol, a polyoxyethylene ether of sorbitan monolaurate containing 16 oxyethylene groups per mol, a distearate of polyoxyethylene ether of sorbitol containing 40 oxyethylene groups per mol, iso-octyl ether of polyethylene glycol, and so forth. Cationic agents may also be used, for example, long-chain alkyl trimethyl ammonium chlorides, bromides, and methosulphates. Other suspending agents such as gums, gelatin, pectin, soluble starch, dextrans, etc., can of course be employed to keep the active agents in suspension. Although water is the primary vehicle in the emulsions, the emulsions may contain, in lesser amount, organic water-miscible solvents such as methanol, ethanol, propanol, isopropyl alcohol, acetone, and the like, or emulsifiable solvents such as benzene, toluene, xylene, ethyl acetate, butanols, monoethyl ether of ethylene glycol, etc. The aqueous emulsions can be prepared by any of the known emulsification techniques. A preferred procedure is to dissolve the polyepoxide and polyamide in separate batches of an organic solvent such as toluene and add these solutions to the water with vigorous agitation. In this manner the contact of the solutions with the water will precipitate the polyepoxide and polyamide in minute particles which are relatively easy to emulsify. The ingredients may be agitated in a blender or subjected to the action of a colloid mill or homogenizer to obtain a uniform dispersion. In the preferred modification of the invention wherein the reducing agent is incorporated into the emulsion, this agent may be added at any point as the emulsion is prepared, but in general we prefer to add the reducing agent after the emulsion is prepared just prior to the entry of the fabric.

Having prepared the emulsion as described above, the

next step involves immersing the textile in the emulsion to permit it to absorb the polyamide and polyepoxide onto its fibrous elements. During the immersion, the textile is agitated to attain uniform absorption. The process may be suitably carried out in apparatus conventionally used for dyeing wherein means is provided for continuously threading the textile through the emulsion or otherwise moving it about in the system. During the treatment the emulsion is kept hot; that is, at a temperature about from 60 to 100° C., preferably 80 to 100° C. Such heating is desirable as it accelerates absorption of the resinous components by the textile. Another advantage of heating is that it causes curing of the resinous components as they are absorbed on the fibers. That is, the polyamide and polyepoxide are enabled to react to produce a water-insoluble resin coating on the fibers. Thus, where the emulsion is kept at about 80-100° C. during the impregnation it is not essential to employ a post-cure; that is, curing of the impregnated textile in a hot oven. However, oftentimes such post-cure is used to ensure complete cure of the resin. The time of immersion depends on various factors, for example, the temperature of the emulsion, the characteristics of the reducing agent selected and the concentration thereof, and the amount of resin desired to be deposited on the textile. As the immersion continues the absorption of the resin-forming components onto the fibers can be observed by a clearing of the emulsion. Generally, the immersion is continued until the textile absorbs about from 0.1 to 10% of its weight of the resin components. This, depending on the circumstances mentioned above, may take anywhere from 5 minutes to several hours.

After the immersion period it is necessary to treat the textile to remove the emulsion which is mechanically occluded between fibrous elements since if this is allowed to remain in place it will cause the textile to be stiff. To this end the textile, after removal from the emulsion bath, is rinsed with water and then passed through wringer rolls or centrifuged. Instead of rinsing with water, the textile may be rinsed or washed with conventional aqueous soap or detergent washing formulations. It is evident that the residual emulsion occluded in the textile can be removed by any conventional manner as would be used in removing any liquid from a textile material.

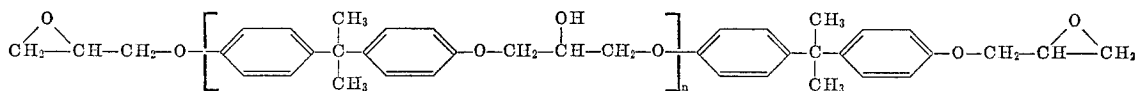
After the removal of residual emulsion from the textile, the textile is subjected to curing, particularly if lower temperatures have been used in the immersion step. This curing or post-curing as it is preferably termed simply involves heating the textile at a temperature of about 100-200° C. The time of cure will vary depending on such factors as the reactivity of the polyepoxide and polyamide selected, on the degree of cure which has taken place during the immersion step, and on the temperature at which the cure is carried out. For example the cure may require more than 30 minutes at 100° C., about 10-30 minutes at 125° C., about 3-15 minutes at 150° C., and 5 minutes or less at 175° C. A preferred type of treatment involves first drying the treated textile in a current of air at about 20 to 50° C. then curing in an oven at 125-150° C. for 20 to 10 minutes.

The curing may be effectuated through the medium of hot gas or liquid. It has been observed that a more rapid cure is attained when the treated textile is contacted with steam or boiling water as compared to heating in an oven wherein heating is accomplished by contact with hot air at the same temperature.

To ensure uniform deposition of the polyepoxide and polyamide on the textile, it is preferred that the textile prior to application of these agents be in a clean state and free from spinning oils, lubricants, and other extraneous materials. To this end the textile, before application of the polyepoxide and polyamide, may be scoured with conventional aqueous washing media containing soap or synthetic detergents. In the alternative,

the textile may be extracted with fat-solvents such as benzene, Stoddard solvent, naphtha, carbon tetrachloride, ethanol, or the like. It is also preferred that the textile material be in a neutral to slightly alkaline state (pH about 7 to 9) prior to application of the polyepoxide and polyamide since acid conditions (as may be encountered with wool dyed in acid baths) will hinder the desired reaction between epoxy groups of the polyepoxide and the amino groups of the polyamide. Generally, where the textile is washed in conventional soap or detergent-containing media it will be at a proper pH for the treatment. If the textile is in an acid condition it may be properly conditioned by soaking in a dilute solution (about 0.1 to 5%) of a mild alkaline agent such as sodium carbonate, sodium bicarbonate, borax, trisodium phosphate, tetrasodium pyrophosphate, sodium metaphosphate, ammonia, ammonium acetate, or the like. A minor proportion of a wetting agent is preferably added to the solution to enable faster penetration of the liquid into the textile. After such soaking the textile is rinsed with water to remove the alkaline agents and is then ready for treatment with the emulsion, or it may be air-dried prior to treatment with the emulsion. In the less preferred form of the invention wherein the reducing agent is applied to the fabric prior to impregnating it with the emulsion, the reducing agent may be added to this alkaline soaking solution.

The polyepoxides used in accordance with the invention are organic compounds having at least two epoxy groups per molecule and may be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic and may be substituted with non-interfering substituents such as hydroxyl groups, ether radicals, and the like. Polyepoxides containing ether groups, generally designated as polyepoxide polyethers, may be prepared as well known in the art by reacting a polyol with a halogen-containing epoxide employing at least 2 moles of the halogen-containing epoxide per mole of polyol. Thus, for example, epichlorohydrin may be reacted with a polyhydric phenol in an alkaline medium. In another technique the halogen-containing epoxide is reacted with a polyhydric alcohol in the presence of an acid-acting catalyst such as hydrofluoric acid or boron trifluoride and the product is then reacted with an alkaline compound to effect a dehydrohalogenation. A preferred example of the halogen-containing epoxide is epichlorohydrin; others are epibromohydrin, epiodohydrin, 3-chloro-1,2-epoxybutane, 3-bromo-1,2-epoxyhexane, and 3-chloro-1,2-epoxyoctane. Examples of polyols which may be reacted with the halogen-containing epoxide are glycerol, diglycerol, propylene glycol, ethylene glycol, diethylene glycol, butylene glycol, hexanetriol,

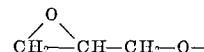


sorbitol, mannitol, pentanetriol, pentaerythritol, dipentaerythritol, polyglycerol, dulcitol, inositol, carbohydrates, methyltrimethylol propane, 2,6-octanediol, tetrahydroxycyclohexane, 2-ethyl hexanetriol-1,2,6, glycerol methyl ether, glycerol allyl ether, polyvinyl alcohol, polyallyl alcohol, resorcinol catechol, hydroquinone, 4,4-dihydroxydiphenyl ether, methyl resorcinol, 2,2-bis (parahydroxyphenyl) propane, 2,2-bis (parahydroxyphenyl) butane, 4,4'-dihydroxybenzophenone, bis (parahydroxyphenyl) ethane, 1,5-dihydroxynaphthalene, 1,4-dihydroxycyclohexane, bis (2,2'-dihydroxydinaphthyl) methane, etc. Illustrative examples of polyepoxide polyethers are as follows: 1,4-bis (2,3-epoxypropoxy) benzene; 1,3-bis (2,3-epoxypropoxy) benzene; 4,4'-bis (2,3-epoxypropoxy) diphenyl ether; 1,8-bis (2,3-epoxypropoxy) octane; 1,4-bis (2,3-epoxypropoxy) cyclohexane; 4,4'-bis (2-hydroxy-2,4-epoxybutoxy) diphenyl dimethylmethane; 1,3-bis (4,5-epoxypentoxy) - 5 - chlorobenzene; 1,4-bis (3,4-epoxybutoxy) - 2 - chlorohexane; diglycidyl thioether; diglycidyl ether; ethylene glycol diglycidyl ether; propylene glycol

diglycidyl ether; diethylene glycol diglycidyl ether; resorcinol diglycidyl ether; 1,2,3,4-tetrakis (2-hydroxy-3,4-epoxybutoxy) butane; 2,2-bis (2,3-epoxypropoxyphenyl) propane; glycerol triglycidyl ether; mannitol tetraglycidyl ether; pentaerythritol tetraglycidyl ether; sorbitol tetraglycidyl ether; glycerol di-glycidyl ether; etc. It is evident that the polyepoxide polyethers may or may not contain hydroxy groups, depending primarily on the proportions of halogen-containing epoxide and polyol employed. Polyepoxide polyethers containing polyhydroxyl groups may also be prepared by reacting, in known manner, a polyhydric alcohol or polyhydric phenol with a polyepoxide in an alkaline medium. Illustrative examples are the reaction product of glycerol and diglycidyl ether, the reaction product of sorbitol and bis (2,3-epoxy-2-methylpropyl) ether, the reaction product of pentaerythritol and 1,2,3,5-diepoxy pentane, the reaction product of 2,2-bis (parahydroxyphenyl) propane and bis (2,3-epoxy-2-methylpropyl) ether, the reaction product of resorcinol and diglycidyl ether, the reaction product of catechol and diglycidyl ether, and the reaction product of 1,4-dihydroxycyclohexane and diglycidyl ether.

Polyepoxides which do not contain ether groups may be employed as for example, 1,2,5,6-diepoxyhexane; butadiene dioxide (that is, 1,2,3,4-diepoxybutane); isoprene dioxide; limonene dioxide.

For use in accordance with the invention, we prefer the polyepoxides which contain ether groups; that is, polyepoxide polyethers. More particularly, we prefer to use the polyepoxide polyethers of the class of glycidyl polyethers of polyhydric alcohols or glycidyl polyethers of polyhydric phenols. These compounds may be considered as being derived from a polyhydric alcohol or polyhydric phenol by etherification with at least two glycidyl groups—



The alcohol or phenol moiety may be completely etherified or may contain residual hydroxy groups. Typical examples of compounds in this category are the glycidyl polyethers of glycerol, glycol, diethylene glycol, 2,2-bis (parahydroxyphenyl) propane, or any of the other polyols listed hereinabove as useful for reaction with halogen-containing epoxides. Many of the specific glycidyl polyethers derived from such polyols are set forth hereinabove. Particularly preferred among the glycidyl polyethers are those derived from 2,2-bis (parahydroxyphenyl) propane and those derived from glycerol. The compounds derived from the first-named of these polyols have the structure—

wherein n varies between zero and about 10, corresponding to a molecular weight about from 350 to 8,000. Of this class of polyepoxides it is preferred to employ those compounds wherein n has a low value; i.e., less than 5, most preferably where n is zero.

In commerce, the polyepoxide polyethers are conventionally termed as epoxy resins even though the compounds are not technically resins in the state in which they are sold and employed because they are of relatively low molecular weight and thus do not have resinous properties as such. It is only when the compounds are cured that true resins are formed. Thus it will be found that manufacturers' catalogs conventionally list as epoxy resins such relatively low-molecular weight products as the diglycidyl ether of 2,2-bis (parahydroxyphenyl) propane, the diglycidyl ether of glycerol, and similar polyepoxide polyethers having molecular weights substantially less than 1,000.

It is within the purview of the invention to employ mixtures of different polyepoxides. For example, good

results are attained by employing mixtures of two commercially-available polyepoxides, one being essentially a diglycidyl ether of glycerol, the other being essentially a diglycidyl ether of 2,2-bis (parahydroxyphenyl) propane. Particularly preferred are mixtures containing more than 1 and less than 10 parts by weight of the glycerol diglycidyl ether per part by weight of the diglycidyl ether of 2,2-bis (parahydroxyphenyl) propane.

The polyamides used in accordance with the invention are those derived from polyamines and polybasic acids. Methods of preparing these polyamides by condensation of polyamines and polycarboxylic acids are well known in the art and need not be described here. One may prepare polyamides containing free amino groups or free carboxylic acid groups or both free amino and free carboxylic acid groups. Generally, it is preferred to employ polyamides which contain free amino groups since the active hydrogens on these groups are especially reactive with the epoxy groups of the polyepoxide to form insoluble polyepoxide-polyamide reaction products. The polyamides may be derived from such polyamines as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, 1,4-diamino butane, 1,3-diaminobutane, hexamethylene diamine, 3-(N-isopropylamino) propylamine, 3,3'-iminobispropylamine, and the like. Typical polycarboxylic acids which may be condensed with the polyamines to form polyamides are glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, isophthalic acid, terephthalic acid, betamethyl adipic acid, 1,2-cyclohexane dicarboxylic acid, malonic acid, polymerized fat acids, and the like. Depending on the amine and acid constituents and conditions of condensation, the polyamides may have molecular weights varying about from 1,000 to 10,000 and melting points about from 20-200° C. Particularly preferred for the purpose of the invention are the polyamides derived from aliphatic polyamines and polymeric fat acids. Such products are disclosed for example by Cowan et al., Patent No. 2,450,940. Typical of these polyamides are those made by condensing ethylene diamine or diethylene triamine with polymeric fat acids produced from the polymerization of drying or semi-drying oils, or the free acids, or simple aliphatic alcohol esters of such acids. The polymeric fat acids may typically be derived from such oils as soybean, linseed, tung, perilla, oiticica, cottonseed, corn, tall, sunflower, safflower, and the like. As well known in the art, in the polymerization the unsaturated fat acids combine to produce a mixture of dibasic and higher polymeric acids. Usually the mixture contains a preponderant proportion of dimeric acids with lesser amounts of trimeric and higher polymeric acids, and some residual monomeric acid. Particularly preferred are the polyamides of low melting point (about 20-90° C.) containing free amino groups which may be produced by heating together an aliphatic polyamine, such as diethylene triamine, triethylene tetramine, 1,4-diaminobutane, tetraethylene pentamine, 1,3-diaminobutane, and the like with the polymerized fat acids. Typical among these is a polyamide derived from diethylene triamine and dimerized soybean fatty acids. The polyamides derived from aliphatic polyamines and polymerized fat acids, like the polyepoxides, are often referred to in the trade as resins even though not actually resins in the state in which they are sold and applied.

As noted above, the total concentration of polyamide and polyepoxide in the emulsion should be low; that is, not to exceed 1%. The relative proportions of polyamide and polyepoxide may be varied widely, for example, from 0.1 to 10 parts by weight of polyamide per part by weight of polyepoxide. In many cases mixtures containing 30 to 70% by weight of polyamide and 70 to 30% by weight of polyepoxide give superior results. Since the number of reactive groups in the polyepoxide and polyamide may vary, the proportions for optimum results may be more accurately described by stoichiometric relations. Thus,

it is preferred that the polyamide be employed in such proportion as to provide about from 0.2 to 1.6 amino groups per epoxy group provided by the polyepoxide.

The process of the invention may be applied to all-wool textiles or textiles containing wool blended with other fibers, for example, animal hair; mohair; silk; synthetic fibers made from proteins such as zein, casein, peanut protein, soybean protein, keratins, etc.; cellulosic fibers such as cotton, linen, rayon, viscose, cellulose, acetate, jute, hemp, etc.; nylon; Dynel; Orlon; Dacron; or other organic textile fibers. The expression "wool-containing textile" as used herein is intended to encompass all-wool textiles and blended textiles containing a significant proportion; that is, at least 25% by weight of wool. The process of the invention may be applied to wool-containing textile materials in the form of fibers, threads, yarns, slivers, woven or knitted fabrics, or even garments made of woven or knitted fabrics. The textiles may be white or dyed goods, although preferably white as the reducing agent tends to strip most dyes.

The process of the invention is well adapted for effectively accomplishing both shrinkproofing and dyeing. Thus, following the impregnation with the above-described emulsion and subsequent rinsing, the textile may be dyed directly. For this purpose one may use any of the dyes conventionally applied to wool textiles, such as acid milling dyes. Moreover, the dyeing is conducted in the customary manner. It has been observed that the presence of the resin deposit on the fibers does not significantly impede the dyeing processes and brilliant, level dyeings are readily obtainable. The customary boiling of the textile in the dye bath does not impair the shrinkproofing effect attained and indeed tends to enhance the effect by effecting a further curing and insolubilization of the resin deposit on the fibers. In commercial practice of the invention, both impregnation with the emulsion and dyeing may be accomplished in a single piece of apparatus such as a dye beck. Thus the textile is first subjected to impregnation with the emulsion containing polyepoxide, polyamide, and reducing agent as described, then the emulsion is dropped. Clear water is entered into the system to rinse the textile and remove occluded emulsion. After the rinsing is complete, the dye bath is introduced and the dyeing operation conducted in the customary manner. Following this the dye bath is dropped, rinse water is introduced and after rinsing the textile is removed, centrifuged and dried in air.

The invention is further demonstrated by the following illustrative examples.

The tests for shrinkage referred to below were conducted in the following way: The wool samples were milled at 1700 r.p.m. for 2 minutes at 40-42° C. in an Accelerotor with 0.5% sodium oleate solution using a liquor/wool ratio of 30:1. After this washing operation the samples were measured to determine their area and the shrinkage was calculated from the original area.

The textile used in Examples I to VII was an all-wool 1/1 shirting, 6 oz. per sq. yd., woven of yarn spun by the woolen system. This material (as received) washed by the manner described immediately above exhibited an area shrinkage of 37%.

Example I

An emulsion was prepared containing the ingredients listed below.

Ingredient:	Amount
Polyepoxide	grams-- 4.8
Polyamide	do-- 3.2
Hydrocarbon solvent.....	ml-- 8
Emulsifying agent.....	gram-- 0.4
Sulphuric acid (1 Normal).....	ml-- 6
Water, sufficient to make 2,000 grams (total).	

The polyepoxide was a commercial product (Epon 828), essentially the diglycidyl ether of 2,2-bis (parahydroxyphenyl) propane.

The polyamide was a commercial product (Versamid 125), a condensation product of a lower aliphatic polyamine and heat-dimerized, unsaturated fat acids. This polyamide, containing free amino groups, has these characteristics: Amine value, 290–320; liquid at room temperature; viscosity at 40° C.; 80–120 poises; specific gravity, 0.97.

The hydrocarbon solvent was a petroleum solvent containing 96% aromatics, 1% paraffins, and 3% naphthenes, specific gravity 0.87, boiling range 314–362° F.

The emulsifying agent was a commercial product (Igepal DM-710), a higher alkylphenoxy polyoxyethylene ethanol.

In preparing the emulsion the polyepoxide and polyamide were dissolved in separate portions of the hydrocarbon solvent, then blended with the water, acid, and emulsifying agent. To obtain a uniform dispersion the materials were subjected to the action of a blender or colloid mill. As a final step, sulphuric acid (1 Normal) was added as necessary to adjust the pH of the emulsion to 7.2. The emulsion prepared as above described contained 0.4% of polyepoxide and polyamide. Other emulsions were made in the same manner but increasing the amount of water to provide 0.1, 0.2, or 0.3% of the resin-forming components (polyepoxide and polyamide).

Example II

A batch of the polyepoxide-polyamide emulsion (0.4%) prepared as described in Example I was divided into three portions. Thiourea dioxide was added to two of the portions to provide a concentration of this compound of 0.05 and 0.1% respectively. Nothing was added to the third portion, thus to provide a control.

Samples of wool cloth were treated with each of the three portions of emulsion in the following manner.

The cloth was entered into the emulsion maintained at 80° C., using a wool/emulsion ratio of 1:30. The cloth was held in the emulsion for one hour with occasional stirring. At the end of this time the cloth was removed from the emulsion, rinsed in running water for 5 or 10 minutes, centrifuged to remove excess liquid, dried in air, and cured in an oven at 275° F. for 10 minutes.

The three samples of cloth were weighed, under standard temperature and humidity conditions (70° F. and 65% relative humidity) before and after treatment, to determine the uptake of resin by the cloth, examined for color, and tested for shrinkage. Also, the efficiency of exhaustion was calculated from the original amount of resin-forming ingredients in the emulsion and the amount of resin taken up by the cloth. The results are tabulated below:

Run	Added Agent	Resin Uptake on Cloth, Percent	Efficiency of Exhaustion, Percent	Color	Area Shrinkage, Percent
1	None (control)	1.9	15.8	Yellowish	17.1
2	Thiourea dioxide (0.05%)	9.4	78.3	White	1.0
3	Thiourea dioxide (0.1%)	10.9	90.8	do	2.5

Example III

Into a batch of the polyepoxide-polyamide emulsion (0.4%) prepared as described in Example I was incorporated sodium hydrosulphite in an amount to furnish a concentration of 0.1% of this compound.

Wool cloth was entered into the emulsion at 30° C. The bath was then heated to 70° C. in 20 minutes and held at this temperature for an hour. At the end of this time the cloth was removed from the emulsion, rinsed in running water, and dried in air. A piece of the cloth was removed and tested for shrinkage with the result that the shrinkage was 3%.

The remainder of the resin-treated cloth was subjected to dyeing in the following manner.

A dye bath was prepared containing 3% Cibalan Scarlet GL (Colour Index Acid Red 209) and 3% ammonium sulphate. The cloth was entered into the dye bath (wool/solution ratio 1:50) at 40° C. and the bath was then raised to the boil and held at the boil one hour. The cloth was then removed, rinsed in running water, and dried in air. Tests on the dyed cloth showed a shrinkage of 0.5% and the dyeing was level.

Example IV

A bath of the polyepoxide-polyamide emulsion (0.4%) prepared as described in Example I was divided into several portions. Different reducing agents were added to the emulsions, as described in the table below.

Samples of wool cloth were treated with these emulsions in the following manner:

Time in emulsion	-----hr-----	1
Temperature of emulsion	-----°C-----	80
Wool/emulsion ratio	-----	1:30

After treatment with the emulsions, the cloths were rinsed in running water, centrifuged and dried in air.

The results are tabulated below:

Run	Added reducing agent and concentration thereof in emulsion	Resin uptake on cloth, percent	Area shrinkage, percent
1	None (control)	1.4	27
2	Sodium hydrosulphite (0.05%)	3.5	2
3	Sodium hydrosulphite (0.1%)	6.1	1
4	Sodium bisulphite (0.05%)	4.1	3
5	Sodium bisulphite (0.1%)	10.3	4
6	Sodium sulphite (0.05%)	8.7	6
7	Sodium sulphite (0.1%)	11.3	11
8	Sodium formaldehyde sulphonylate (0.05%)	2.3	18
9	Sodium formaldehyde sulphonylate (0.1%)	10.8	16
10	Sodium thiosulphate (0.1%)	8.2	12

Example V

The procedure described in Example IV was prepared with the following variation: After treatment with the emulsions, the cloths were rinsed in running water, centrifuged, dried in air and then cured in an oven at 300° F. for 10 minutes. The results are tabulated below:

Run	Added reducing agent and concentration thereof in emulsion	Resin uptake on cloth, percent	Area shrinkage, percent
1	None (control)	1.4	23
2	Sodium hydrosulphite (0.05%)	3.5	0
3	Sodium hydrosulphite (0.1%)	6.1	1
4	Sodium bisulphite (0.05%)	4.1	0
5	Sodium bisulphite (0.1%)	10.3	0
6	Sodium sulphite (0.05%)	8.7	2
7	Sodium sulphite (0.1%)	11.3	5
8	Sodium formaldehyde sulphonylate (0.05%)	2.3	8
9	Sodium formaldehyde sulphonylate (0.1%)	10.8	10
10	Sodium thiosulphate (0.1%)	8.2	9

Example VI

Three batches of polyepoxide-polyamide emulsion were prepared containing 0.1%, 0.2%, and 0.3% of the resin-forming ingredients (polyepoxide and polyamide) as described in Example I. To all the emulsions was added sodium hydrosulphite in an amount to provide a concentration of 0.05% of this compound.

A. Samples of wool cloth were treated with these emulsions in the following manner: Time in emulsion—1 hr.; temperature of emulsion—80° C.; wool/emulsion ratio—1:30. The emulsion-treated cloth samples were then given various post-treatments as follows:

B. One set of the cloths treated as in part A, above, were rinsed in running water, centrifuged and dried in air.

C. A second set of the cloths treated as in part A, above, were rinsed in running water, centrifuged, dried in air and cured in an oven at 275° F. for 10 minutes.

D. A third set of the cloths treated as in part A, above, were rinsed in running water, then dyed as follows:

Dye bath: 3% Cibalan Scarlet GL and 3% ammonium sulphate in water.

Dyeing conditions: Wool/dye solution ratio 1:50, cloths entered in bath at 40° C., bath raised to boil and held at boil one hour. The dyed cloths were then removed from the dye bath, rinsed and dried in air.

The results obtained are tabulated below:

Concentration of polyepoxide and polyamide in emulsion, percent	Post-treatment	Resin uptake on cloth, percent	Area shrinkage, percent
0.1-----	B. Air-drying-----	3.1	6
0.2-----	do-----	7.0	0
0.3-----	do-----	9.0	2
0.1-----	C. Oven cure-----	3.1	1
0.2-----	do-----	7.0	0
0.3-----	do-----	9.0	1
0.1-----	D. Dyeing-----	3.1	4
0.2-----	do-----	7.0	2
0.3-----	do-----	9.0	0

Example VII

A series of aqueous solutions were prepared containing 3% reducing agent (as given below), 0.8% tetrasodium pyrophosphate, and 0.25% ethylenediamine tetraacetic acid tetrasodium salt.

Samples of wool cloth were treated with these solutions as follows:

The cloth was entered into the solution at a wool/solution ratio of 1:20 and at a temperature of 50° C. The cloth was held in the solution for 45 minutes, then removed, rinsed thoroughly and dried in air.

The treated cloths were then provided with a resin coating, using the emulsion containing 0.2% polyepoxide and polyamide described in Example I. Conditions of the treatment were: Temperature of emulsion—80° C.; time of immersion—1 hr.; wool/emulsion ratio—1:30.

After the resin treatment the cloths were rinsed in water, centrifuged and dried in air. Half the samples were given no further treatment, the other half were cured in an oven at 375° F. for 10 minutes. The results are tabulated below:

Run	Reducing agent in pre-treating bath	Post-treatment	Resin uptake on cloth, percent	Area shrinkage, percent
1-----	Thiourea dioxide-----	Air-dried-----	4.5	3
2-----	do-----	Oven cured-----	4.5	2
3-----	Sodium hydrosulphite-----	Air-dried-----	4.1	7.8
4-----	do-----	Oven cured-----	4.1	8.8
5-----	No pre-treatment ¹ -----	Air-dried-----	2.2	31.0
6-----	do ¹ -----	Oven cured-----	2.2	25.2

¹ In runs 5 and 6 the cloths were not pre-treated but were impregnated with the emulsion as received.

Having thus described our invention, we claim:

1. The process of shrinkproofing a wool-containing textile without significant impairment of its hand which comprises impregnating the textile with a dispersion of a polyepoxide containing at least two epoxy groups per molecule and a polyamide of a polyamine and a polycarboxylic acid, said impregnation being conducted in the presence of a reducing agent which in an aqueous medium provides an ion selected from the group consisting of sulphinate, sulphonylate, sulphite, bisulphite, thiosulphate and hydrosulphite, said reducing agent being supplied in an amount sufficient to enhance absorption of the polyepoxide and polyamide on the fibers of the textile but insufficient to damage the said fibers.

2. In the process of dimensionally stabilizing a wool-containing textile without substantial impairment of its hand wherein a wool-containing textile is impregnated

with an aqueous emulsion of a polyepoxide containing at least two epoxy groups per molecule and a polyamide of a polyamine and a polycarboxylic acid, the improvement which comprises conducting the said impregnation in the presence of a reducing agent which in an aqueous system provides an ion selected from the group consisting of sulphinate, sulphonylate, sulphite, bisulphite, thiosulphate, and hydrosulphite, the reducing agent being supplied in an amount sufficient to enhance the absorption of the polyepoxide and polyamide onto the fibers of the textile but insufficient to damage the said fibers.

3. The process of claim 2 wherein the reducing agent is thiourea dioxide.

4. The process of claim 2 wherein the reducing agent is sodium formaldehyde sulphonylate.

5. The process of claim 2 wherein the reducing agent is sodium hydrosulphite.

6. The process of claim 2 wherein the reducing agent is sodium thiosulphate.

7. The process of claim 2 wherein the reducing agent is sodium sulphite.

8. The process of claim 2 wherein the reducing agent is sodium bisulphite.

9. In the process of dimensionally stabilizing a wool-containing textile without significant impairment of its hand by immersing the textile in a heated, essentially-neutral, dilute aqueous emulsion of a polyepoxide containing at least two epoxy groups per molecule and a polyamide of polyamine and polycarboxylic acid, maintaining the textile in the emulsion until polyamide and polyepoxide from the emulsion are deposited on the surfaces of the fibrous elements of the textile, separating the textile from the emulsion, and removing residual emulsion occluded in the textile, the improvement which comprises carrying out the said immersion of the textile in the emulsion in the presence of a reducing agent which in an aqueous system provides an ion selected from the group consisting of sulphinate, sulphonylate, sulphite, bisulphite, thiosulphate, and hydrosulphite, said reducing agent being supplied in an amount sufficient to enhance the absorption of the polyepoxide and the polyamide onto the fibers of the textile but insufficient to damage the said fibers.

10. In the process of dimensionally stabilizing a wool-containing textile without significant impairment of its hand by immersing the textile in a heated, essentially-neutral, dilute aqueous emulsion of (1) a polyepoxide containing at least two epoxy groups per molecule and (2) a polyamide of an aliphatic polyamine and an aliphatic polycarboxylic acid, said polyamide containing free amino groups, maintaining the textile in the emulsion until polyamide and polyepoxide from the emulsion are deposited on the surfaces of the fibrous elements of the textile, separating the textile from the emulsion, and removing residual emulsion occluded in the textile, the improvement which comprises carrying out the said immersion of the textile in the emulsion in the presence of a reducing agent which in an aqueous system provides an ion selected from the group consisting of sulphinate, sulphonylate, sulphite, bisulphite, thiosulphate, and hydrosulphite, said reducing agent being supplied in an amount sufficient to enhance the absorption of the polyepoxide and the polyamide onto the fibers of the textile but insufficient to damage the said fibers.

11. In the process of dimensionally stabilizing a wool-containing textile without significant impairment of its hand by immersing the textile in a heated, essentially-neutral, dilute aqueous emulsion of (1) a polyepoxide containing at least two epoxy groups per molecule and (2) a polyamide of a lower aliphatic polyamide and a polymeric fat acid containing at least two carboxyl groups, said polyamide containing free amino groups, maintaining the textile in the emulsion until polyamide and polyepoxide from the emulsion are deposited on the surfaces of the fibrous elements of the textile, separating the textile from the emulsion, and removing residual emulsion occluded in the

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textile, the improvement which comprises carrying out the said immersion of the textile in the emulsion in the presence of a reducing agent which in an aqueous system provides an ion selected from the group consisting of sulphinate, sulphonylate, sulphite, bisulphite, thiosulphate, and hydrosulphite, said reducing agent being supplied in an amount sufficient to enhance the absorption of the polyepoxide and the polyamide onto the fibers of the textile but insufficient to damage the said fibers.

12. In the process of dimensionally stabilizing a wool-containing textile without significant impairment of its hand by immersing the textile in a heated, essentially-neutral, dilute aqueous emulsion of (1) a polyepoxide being a glycidyl polyether of 2,2-bis (parahydroxyphenyl) propane and (2) a polyamide of a lower aliphatic poly-amine and a polymeric fat acid containing at least two

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carboxyl groups, said polyamide having free amino groups, maintaining the textile in the emulsion until polyamide and polyepoxide from the emulsion are deposited on the surfaces of the fibrous elements of the textile, separating the textile from the emulsion, and removing residual emulsion occluded in the textile, the improvement which comprises carrying out the said immersion of the textile in the emulsion in the presence of a reducing agent which in an aqueous system provides an ion selected from the group consisting of sulphinate, sulphonylate, sulphite, bisulphite, thiosulphate and hydrosulphite, said reducing agent being supplied in an amount sufficient to enhance the absorption of the polyepoxide and the polyamide onto the fibers of the textile but insufficient to damage the said fibers.

No references cited.