

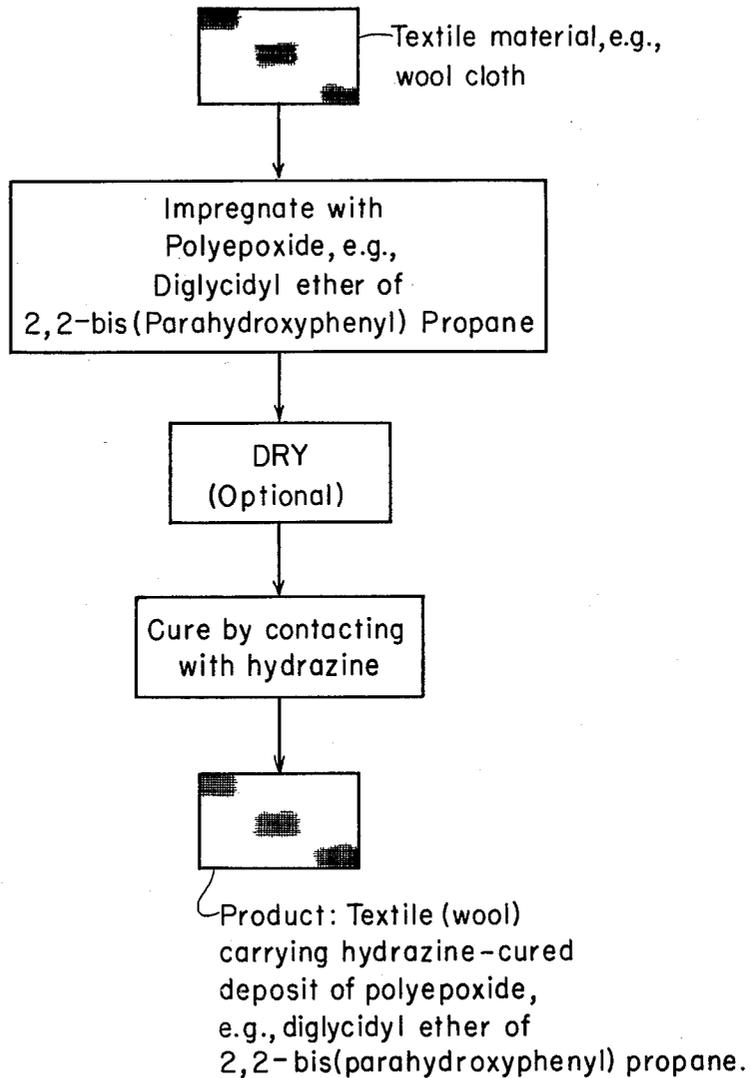
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T. J. COE

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SHRINKPROOFING TEXTILES WITH POLYEPOXIDES AND HYDRAZINE

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THOMPSON J. COE

INVENTOR

BY

*R. Hoffman*

*W. Bier*

ATTORNEYS

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**SHRINKPROOFING TEXTILES WITH POLY-  
EPOXIDES AND HYDRAZINE**

Thompson J. Coe, Albany, Calif., assignor to the United States of America as represented by the Secretary of Agriculture

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A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to and has among its objects the provision of novel processes for shrinkproofing and feltproofing textiles. The invention also includes the provision of improved textiles having superior qualities as to resistance to shrinking and felting. Further objects and advantages of the invention will be evident from the following description wherein parts and percentages are by weight unless otherwise specified.

It is well known in the art that many textile fibers exhibit poor dimensional stability. For example, laundering causes severe shrinkage of woolen textiles. This technical disadvantage seriously restricts the applications of wool in the textile industry and much research has been undertaken in order to modify the natural fibers in order to improve its shrinkage properties. In general, known methods of treating wool to improve its shrinkage characteristics have the disadvantage that the hand of the fabric is impaired, or, if the amount of agent applied is limited to avoid impairment of hand, the degree of shrinkage protection is relatively poor.

In accordance with the invention, wool, or other textile material, is impregnated with a polyepoxide then cured by subjection to hydrazine. This procedure yields a product which is virtually shrinkproof under normal procedures while the hand, resiliency, porosity, tensile strength, color, and other valuable properties of the textile are essentially unaltered. Additionally, the treated textile exhibits a great improvement in resistance to creasing and wrinkling as compared to the original textile.

The accompanying drawing is a schematic diagram illustrating the process and product of the invention.

The prior art discloses methods for shrinkproofing textiles by applying polyepoxides and curing the polyepoxides with such agents as triethylamine, ethylene diamine, diethylene triamine and other amino compounds. The curing method of the invention—involving subjection to hydrazine—offers many advantages over the known curing techniques, as follows:

(a) In curing with hydrazine the original color of the textile is retained. For example white wool remains white after the curing with hydrazine. On the other hand curing with polyamines generally causes the treated wool to turn yellow. Dyed textiles treated in accordance with the invention retain their original color in undiminished brightness whereas curing with amines causes a graying or dulling of the fabric.

(b) Curing with hydrazine has the advantage that this low-molecular weight curing agent can penetrate readily into the textile and ensure complete and uniform cure of the polyepoxide.

(c) The curing with hydrazine yields products of especially soft and resilient hand and more shrinkproofing

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effect per unit weight of resinous material deposited on the fibers is obtained.

(d) By the process of the invention the curing may be attained even with very dilute solutions of hydrazine whereby there is an economic advantage in the use of this curing agent.

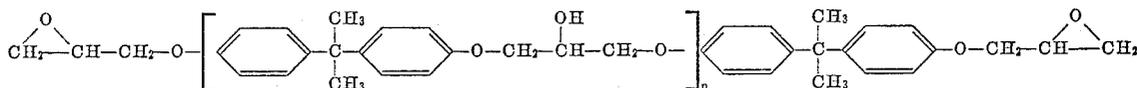
In applying the process of the invention in practice, the textile is first impregnated with a liquid preparation of the polyepoxide. The impregnation is performed in any of the usual ways. For example, the polyepoxide composition is applied by spraying, brushing, dipping, etc. To assist in wetting the textile, it may be run through padding rolls or the like. Excess liquid may be removed by passing the textile through wringer rolls. The proportion of active material in the liquid preparation is usually so selected that there is deposited on the textile about 1/2 to 10% of its weight of polyepoxide. In general, the greater the proportion of polyepoxide, the greater will be the shrinkage protection afforded. After the textile has been treated with the polyepoxide preparation it may be cured directly or dried in air prior to curing, the latter procedure being generally preferred.

Curing of the polyepoxide-impregnated textile involves contacting it with an aqueous solution of hydrazine. The textile is allowed to remain in contact with the solution until the polyepoxide is cured, that is, until it is rendered insoluble so that it is not removable from the textile by laundering. The time for cure will vary depending on several factors as set forth below. The concentration of hydrazine in the solution may be varied from about 0.1 to about 10%, the higher concentrations in this range giving the faster cure. The hydrazine solution may be maintained at a temperature from room temperature (25° C.) up to the boiling point (100° C.), the rate of cure being increased with increasing temperature. Taking into account these factors, the time for cure may involve a period of about from 0.5 to 72 hours. It is preferred to adjust the hydrazine to a pH of about 7 to 11 since too high pH's may cause degradation of woolen textiles. The pH may be adjusted by adding salts of hydrazine such as hydrazine sulphate or chloride; acids such as sulphuric, hydrochloric, or phosphoric; salts such as sodium sulphate, ammonium chloride, sodium bisulphate, monosodium phosphate, etc.

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 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, epichlorhydrin 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 epichlorhydrin; others are epibromhydrin, epiodohydrin, 3-chloro,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, penterythritol, 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-dihydroxy-diphenyl 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' - dihydroxy-dinaphthyl)-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-3,4 - epoxybutoxy) diphenyl dimethylmethane; 1,3 - bis(4,5 - epoxybutoxy) - 5 - chlorobenzene; 1,4-bis(3,4 - epoxybutoxy)-2-chlorocyclohexane; 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; 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 glycerol and diglycidyl ether, the reaction product of sorbitol and bis(2,3-epoxy-2-methylpropyl)ether, the reaction product of pentaerythritol and 1,2,4,5-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. A particularly preferred type of polyepoxide polyether is that prepared by reacting epichlorhydrin with 2,2-bis(parahydroxyphenyl)propane. The structure of these compounds is illustrated by the formula:



wherein  $n$  varies between zero and about 10, corresponding to a molecular weight about from 350 to 8,000.

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.

The polyepoxide is preferably applied to the textile material in the form of a solution or dispersion to ensure uniform impregnation of the fibrous elements. Aqueous solutions may be used, for example, where the selected polyepoxide is soluble in this medium. In many cases other volatile solvents may be required such as acetone, benzene, alcohol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, dioxane, etc., depending on the property of the agent in question. It is often preferred to apply the polyepoxides in the form of aqueous emulsions prepared by application of any of the known emulsification techniques. A preferred procedure is to dissolve the polyepoxide in a suitable quantity of alcohol or other volatile organic solvent and add this solution to water with vigorous agitation. In this way contact of the solution with water will precipitate the

polyepoxide in minute particles which will be relatively easy to emulsify. To assist in forming and maintaining the emulsion, one may add a small proportion of a conventional emulsification agent. For this purpose one may employ agents such as soaps, long-chain alkyl sulphates, long-chain alkyl benzene sulphonates, alkyl esters of sulphosuccinic acid, etc., typical examples being sodium lauryl sulphate, sodium alkyl ( $\text{C}_{10}$ - $\text{C}_{20}$ ) benzene sulphonate, sodium dioctylsulphosuccinate, etc. Preferably, emulsifying agents of the non-ionic type are employed, for example sorbitan laurate, polyoxyethylene ether of sorbitan monostearate, polyoxyethylene ether of sorbitan distearate, sorbitan trioleate, isoocetyl phenyl ether of polyethylene glycol, and so forth. Other suspending agents as gums, gelatin, pectin, soluble starch, dextrans, etc., can be used to keep the polyepoxide in suspension. It is obvious that the proportion of polyepoxide in the solution or dispersion may be varied as necessary to deposit on the textile material the desired percentage of polyepoxide.

In the preferred modification of the invention, the polyepoxide and hydrazine are successively applied to the textile. If desired, however, both agents may be applied simultaneously. To this end the textile is impregnated with a polyepoxide dispersion, preferably an aqueous emulsion of the polyepoxide, to which is added about from 0.1 to 10% of hydrazine. In this way the polyepoxide is cured by the hydrazine as it is absorbed onto the fibers of the textile.

The process of the invention is particularly adapted to the treatment of wool, but is also advantageously applicable to other textiles including mohairs; animal hair; silk; fibers made from proteins such as zinc, caesin, peanut protein, soybean protein, keratins, etc.; cotton; regenerated cellulose; viscose; linen; cellulose acetate, etc. The textile material may be in the form of fibers, threads, yarns, woven or knitted fabrics, garments, etc.

The invention is further demonstrated by the following illustrative examples.

#### Example I

An aqueous emulsion was prepared containing 10% polyepoxide, 10% toluene, and 0.5% of the dioctyl ester of sodium sulfosuccinic acid. The poly-epoxide was a commercial product consisting essentially of the diglycidyl ether of 2,2-bis(parahydroxyphenyl)propane.

The above emulsion was padded onto pieces of white woolen cloth. The cloth was then dried in air. The pickup of polyepoxide was 3.5% based on the weight of the cloth.

The polyepoxide cloth was divided into two samples. Each of these samples was immersed for 72 hours at 25° C. in a hydrazine solution as set forth below.

Solution 1: 5% hydrazine in water, adjusted to pH 10.5 by addition of hydrazine sulphate.

Solution 2: 1% hydrazine in water, adjusted to pH 10.1 with hydrazine sulphate.

The treated samples of cloth and a sample of untreated cloth (control) were subjected to tests to determine their shrinkage characteristics. In these tests the cloth samples were subjected to a laundering operation wherein the cloth was violently agitated in an "Accelerator" for 3 minutes at 0.5% solution of sodium oleate at 40° C. with a cloth to solution ratio of 1 to 35. The area of the cloth was measured before and after laundering. The washing tests were carried out in duplicate. The results are tabulated below, the shrinkage values being averages of the duplicate tests.

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Also, samples of the cloths were tested to determine their flexural rigidity by the cantiliver method ASTM D-1388-55T. In this test, a higher value denotes a stiffer fabric.

The results are tabulated below:

Sample	Hydrazine conc. in solution, Percent	Color	Flexural rigidity, mg.-cm.	Area shrinkage, Percent
Control.....	0	white.....	130	50.0
1.....	5	white, unchanged.	151	1.0
2.....	1	do.....	160	0

*Example II*

Samples of white woolen cloth were impregnated with the polyepoxide emulsion described in Example I. In this case a lesser amount of the emulsion was padded on the cloth to provide a polyepoxide pickup of 2.5%.

The polyepoxide-impregnated cloth was then immersed in an aqueous solution containing 0.5% hydrazine (no buffer was used in this case, pH of the solution was 9.0). The solution was held at 90° C. and the cloth immersed therein for 4 hours.

The treated cloth was tested for shrinkage by the method described in Example I. The area shrinkage was found to be zero. It was also observed that the treated cloth was white in color and had a soft resilient hand.

Having thus described the invention, what is claimed is:

1. The method of imparting shrink resistance to a textile without significant impairment of its hand which comprises impregnating the textile with about from 0.5% to 10% of its weight of a polyepoxide containing at least two epoxy groups per molecule and contacting the

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polyepoxide-impregnated textile with hydrazine to cure and insolubilize the polyepoxide on the textile fibers.

2. The method of imparting shrink resistance to wool without significant impairment of its hand which comprises impregnating wool with about from 0.5% to 10% of its weight of a polyepoxide containing at least two epoxy groups per molecule and being free from functional groups other than hydroxyl groups and epoxy groups and contacting the polyepoxide-impregnated wool with an aqueous solution of hydrazine to cure and insolubilize the polyepoxide on the wool fibers.

3. The process of claim 2 wherein the polyepoxide is a polyglycidyl ether of 2,2-bis(parahydroxyphenyl)propane.

4. A shrink resistant textile of substantially unimpaired hand comprising textile fibers carrying a hydrazine-cured deposit of a polyepoxide containing at least two epoxy groups per molecule, in an amount about from 0.5% to 10% of the weight of the textile.

5. Shrink resistant wool of substantially unimpaired hand comprising wool carrying a hydrazine-cured deposit of a polyepoxide containing at least two epoxy groups per molecule and being free from functional groups other than hydroxyl groups and epoxy groups, in an amount about from 0.5% to 10% of the weight of the wool.

6. The product of claim 5 wherein the polyepoxide is a polyglycidyl ether of 2,2-bis(parahydroxyphenyl)propane.

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