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MODIFICATION OF CELLULOSE WITH VAPOROUS EPIHALOHYDRIN USING TWO DISTINCT STEPS OF REACTION CATALYSIS

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ABSTRACT OF THE DISCLOSURE

The disclosure describes a process for treating textiles and the like to impart increased wet and dry crease recovery which includes treating the material with an epihalohydrin such as epichlorohydrin in the presence of an acid catalyst such as zinc fluoborate and treating the resulting product with an alkaline material such as sodium hydroxide. The material may then be cured by heat treatment.

This invention relates to a process for treating fibrous materials to impart improved properties thereto. More particularly, the invention relates to a process for treating fibrous textile materials to impart both wet and dry crease recovery, and to the resulting products.

Specifically, the invention provides a new and improved process for treating fibrous materials, and preferably cellulose textile fabrics to impart both wet and dry crease recovery using the same basic chemical reactant, which comprises treating the textile material with an epihalohydrin or material which liberates an epihalohydrin in the presence of an acid acting catalyst, and then treating the resulting material with an aqueous alkaline material. The invention further provides fibrous materials having both wet and dry crease recovery and good tensile strength.

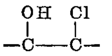
Many fabrics, and particularly those prepared from cotton and rayon, have rather poor resilience, i.e., they are easily creased or wrinkled. This is generally true both in the wet and dry state. Thus, many fabrics are wrinkled after being tumble dried or when they are drip dried. In order to overcome this dificulty, it has been common practice to treat the fabric with various chemicals and synthetic resins to effect cross-linking with the fabric. While this has been satisfactory in some cases to effect an improvement in wet or dry crease recovery, no good technique has been found that will give excellent improvement in both wet and dry crease recovery at the same time. In addition, many of the treatments which are directed to both wet and dry crease recovery raise other problems, such as chlorine-retention and discoloration after the bleaching, excessive loss of tensile strength and in some cases are prohibitive in cost.

It is therefore an object of the invention to provide a new process for treating fibrous materials to improve properties thereof. It is a further object to provide a new process for treating fibrous material to impart both wet and dry crease recovery. It is a further object to provide a new economical process for imparting both dry and wet crease recovery employing only one basic reactant. It is a further object to provide a new process for imparting dry and wet crease recovery to textile fabrics without causing excessive loss of tensile strength. It is a further object to provide a new process for treating textiles that can be used on a continuous manner and in a short period of time. It is a further object to provide a new process for imparting wet and dry crease recovery which imparts no chlorine-retention properties. It is a further object to provide a process for imparting wet and dry crease recovery at a low cost. These and other objects of the invention will be apparent from the following detailed description thereof.

It has now been discovered that these and other objects may be accomplished by the new process of the invention which comprises treating the fibrous material with an epihalohydrin or material which liberates an epihalohydrin in the presence of an acid acting catalyst, and treating the resulting product with aqueous alkaline material. It has been unexpectedly found that this new process using only the epihalohydrin as the chief reactant imparts both wet and dry crease recovery to the fibrous material. In addition, this is accomplished without any excessive loss of tensile strength. Further advantage is also found in the fact that the process is operable in a continuous manner and at a low cost.

That the above-noted results could be obtained was quite surprising because it was expected heretofore that the acid catalyst would not effect sufficient cross-linking with the cellulose molecule and epichlorohydrin, and that only the wet crease recovery of the caustic treatment would be obtained.

According to the first phase of process of the invention, the textile material is treated with an epihalohydrin or material which liberates an epihalohydrin. The epihalohydrins to be used in the process include those halo-substituted monoepoxy compounds, such as, for example, epichlorohydrin, epibromohydrin, 2,3-epoxy-2-methyl-1-chloroprene, 2,3-epoxy-1-chlorobutane, 2,3-epoxy-1-bromo-butane, 2,3-epoxy-1- chloropentane, and the like. The materials wihch liberate epichlorohydrins when in an alkaline medium, i.e., materials having a



$$-\overset{\displaystyle OH}{\overset{|}{C}}-\overset{\displaystyle Cl}{\overset{|}{C}}-$$

group in place of the 1,2-epoxy group, include, among others, the dihalohydrins as 1,3-dichloro-2-hydroxypropane, 1,3-dibromo-2-hydroxypropane, 1,3-dichloro-2-hydroxybutane, 1,3-dichloro-2-hydroxypentane, 2-methyl-1,3-dichloro-2-hydroxypropane and the like, and mixtures thereof. Epichlorohydrin is particularly preferred.

According to the process of the invention, the above-noted treatment is accomplished in the presence of an acid-acting catalyst. This catalyst may be an organic and inorganic acid or salt thereof. Examples of this include, among others, oxalic acid, lactic acid, succinic acid, acetic acid, maleic acid, phosphoric acid, boric acid, sulfonic acid, perchloric acid, persulfuric acid, p-toluenesulfonic acid, sulfuric acid, zinc fluoborate, copper fluoborate, zinc persulfate, cupric arsenite, cupric chlorate, cupric chromate, cupric dichromate, cupric fluosilicate, cupric nitrate, zinc nitrate, cupric sulfate, cobaltic chlorostannate, cobaltous fluoborate, cobaltous fluosilicate, cobaltous sulfite, chromic sulfate, chromic nitrate, lead borate, lead chlorate, lead phosphate, barium chlorate, barium phosphate, magnesium fluosilicate, magnesium chloride, magnesium perchlorate, magnesium nitrate fluoborate, cadmium arsenate, cadmium borate, cadmium perchlorate, cadmium phosphate, aluminum arsenate, aluminum chlorate, aluminum nitrate, aluminum fluoborate, nickel phosphate, nickel selenate, nickel sulfate, silver sulfate, silver nitrate, silver thiosulfate, stannic fluoborate, strontium chlorate, titanium sulfate, vanadium sulfate, zinc chlorate, zinc fluosilicate, zinc permanganate, zinc phosphate, zinc sulfate, zirconium sulfate, aluminum phosphate, aluminum sulfate, vanadium nitrate, vanadium sulfate, vanadium fluoborate, vanadium selenate, bismuth phosphate, ferric phosphate, ferric pyrophosphate, ferric sulfate, ferrous sulfite, ferrous perchlorate, mercuric arsenate, mercuric chromate, mercuric sulfate, mercurous chlorate, mercurous fluoborate, nickel fluoborate, nickel arsenate and the like, and mixtures thereof.

Particularly preferred catalysts are the organic and inorganic acids and salts of the group consisting of organic mono- and dicarboxylic acids containing up to 10 carbon atoms, inorganic acids containing at least one element of the group consisting of halogen atoms, oxygen sulfur, nitrogen and phosphorous, and metal salts of metals having an atomic weight between 10 and 240, and acids of the formula

$$H_a[(X)_w(Z)_y]$$

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 $(X)_w(Z)_z$.

Coming under special consideration are the inorganic acids and salts thereof and preferably those having an acidity of at least 10^{-4}.

The above-noted catalysts are preferably employed as an aqueous solution. The strength of the solutions may vary but preferably vary from about 1% to 15% by weight. Generally, the lower concentrations tend to give high dry recovery with less loss of strength. Preferred concentrations vary from about 1% to 5%.

The impregnation with the aqueous acid catalyst may be accomplished by any suitable means, such as, for example, by dipping, spraying, padding and the like. It is generally preferred to pass the fibrous material into and through the aqueous solution as by padding. The amount of wet pick-up will vary with the different cases, but generally is preferred to have a wet pick-up varying from about 20% to 100%.

The temperature of the acid catalyst solution as well as the temperature of the fibrous material to be impregnated may vary, but in general, it is preferred to have both at about ambient temperature. In some cases, cure may be speeded by employing the fibrous material at high temperatures, say from about 20° C. to 80° C.

It is also desirable in some cases to employ wetting agents in the acid catalyst to assist in speeding the cure. These agents may be any of the known cationic, anionic or non-ionic materials and may have a great variety of different compositions. Preferred materials include the ionic agents and especially those having a polar structure including a hydrophilic (predominantly hydrocarbon) residue and a charged ionic radical thereon; such anionic surface active compounds include alkalai metal and nitrogen-base soaps of higher fatty acids, such as potassium, and sodium hyristate, laurate, palmitate, oleate, stearate, ammonium stearate, etc., as well as salts of long-chain aliphatic amines and quarternary ammonium bases, such s lauryl amine hydrochloride, stearyl amine hydrochloride, and the like. Examples of the non-ionic agents include the partial esters of polyhydric alcohols and fatty acids, such as the hexitane and hexitide esters as sorbitan monolaurate, hydroxypolyoxyalkylene ethers of the above-described partial esters as the polyethylene glycol ethers of sorbitan monolaurate, the hydroxypolyoxyalkylene ethers of phenols as the reaction product of ethylene oxide and bisphenol-A and the like and mxtures thereof. These materials are preferably employed in amounts varying from about .1% to 25% by weight, and still more preferably from 1% to 5% by weight.

The material impregnated with the acid catalyst solution is then treated with the above-noted epihalohydrins or material which liberates epihalohydrin. This is preferably accomplished by exposing the impregnated material to hot vapors of the epihalohydrin or material which liberates epihalohydrins. The temperature of the vapors may vary over a wide range, but will generally range from the refluxing temperature of the epihalohydrin to about 50 to about 100° C. in excess thereof. In the case of epihalohydrin, the preferred temperatures range from about 240° F. to 275° F.

The length of time for exposing the impregnated material to the hot vapors will vary depending on the strength of acidic solution and temperatures of the vapors. The period of exposure in all cases will not be more than a few minutes, and preferably between 15 seconds to about five minutes. Using epichlorohydrin and acidic solutions of concentration of 2.5% to 10%, reaction times vary from about 30 seconds to three minutes.

A great variety of different techniques may be used to expose the impregnated fibrous material to the hot vapors of the epihalohydrin or material liberating epihalohydrins. The fibrous material, for example, may be hung or suspended in the presence of the hot vapors of the epihalohydrin or material liberating epihalohydrins brought about by refluxing the said epihalohydrin or material liberating the epihalohydrins. In another technique, the fibrous material may be hung in a chamber and the hot vapors continuously passed over or around the fibrous material.

After the impregnated material is removed from the curing zone, it may then be washed with cold water to stop the reaction and to remove any excess epihalohydrin or other material. Washing is preferably accomplished by use of water or water and detergents at temperatures of say 15° C. to 30° C.

The second phase of the process is to subject the above-noted textile material which has previously been exposed to the epihalohydrin and acid acting catalyst to aqueous alkaline material. This may be accomplished while the fibrous material is still wet or after it has been dried say at temperatures of 50° C. to 100° C.

The alkaline material employed may be of any type as long as it has a pKb value of at least 10^{-5}. Preferred examples include sodium and potassium hydroxide, and sodium orthosilicate.

The concentration of the alkaline solution to be employed may vary over a wide range. In general, the concentration varies from about 1% to 25% by weight. The higher concentrations tend to give higher wet crease recovery in a shorter cure time and are generally preferred.

The impregnation with the alkaline solution may be accomplished by any suitable means, such as, for example, by dripping, spraying, padding and the like. It is generally preferred to pass the fibrous material into and through the aqueous solution as by padding. The amount of wet pick-up will vary with the different cases, but generally it is preferred to have a wet pick-up varying from about 20% to 100%.

The alkaline impregnated material is then subject to curing conditions. These conditions may vary within certain limits. The cure may be accomplished at lower temperatures over an extended period, e.g., at ambient temperature overnight, or by exposing the treated material to elevated temperatures for a few minutes. It is generally preferred to effect the cure by heating to say 100° C. to 150° C. for from 1 minute to 20 minutes. Particularly preferred conditions vary from 1 to 5 minutes at 100° C.

The curing may be conducted in an aqueous or anhydrous condition. In the anhydrous cure, the fibrous materials may be simply hung in a forced hot air oven. The aqueous cure consists of sandwiching the treated material between two layers of plastic, such as polyethylene, rolling the material on a wooden dowel and sealing the ends so that no moisture can be lost. It is generally preferred to effect an anhydrous cure as by handing in a forced hot air oven.

After curing, the materials are preferably washed with water, then with an acidic solution as with acetic acid and then dried at ambient or higher temperatures.

The material obtained by the above-described process will have the same appearance and feel as before the treatment but will demonstrate excellent wet and dry crease recovery and other desired properties. The material will also have satisfactory strength and non-chlorine retentive properties.

The products treated as above may then be utilized for any of the intended applications. The textile materials, for example, may be used in the manufacture of dresses, drapes, upholsteries, shoe fabrics, carpets, coats, shirts, uniforms, shoes, towels, cords, construction fabrics and the like. The use will, in many cases, determine the amount of the epihalohydrin or material liberating the epihalohydrin to be applied to the textile material. The paper having improved strength may be used for various applications as in wrappings, containers, cards and the like. The wood products having improved dimensional stability may be used for conventional structural operations and the like.

The above-described process may be utilized for the treatment of any fibrous material and preferably cellulose fibrous material. The textile materials may be woven and non-woven fabrics, threads, gauze, yarn, cord, string, netting, and the like. The process also includes treatment of materials which have been pretreated, e.g., mercerized, dyed, resin-treated. By cellulosic is meant material which has any part, and preferably at least 10%, derived from cellulosic materials, such as natural cellulose such as cotton, linen, and the like, and other as viscose, supraammoniumrayon, and other regenerated cellulose, as well as mixtures of any of the foregoing as well as mixtures with wood synthetics as fibers derived from acrylonitrile (Orlon-100% acrylonitrile polymer), vinylidine cyanide polymers, polyamides (nylon-super polyamides), polyester-polyamides, polymers prepared from corn protein and formaldehyde, as well as copolymers of the above monomers as, for example, Acrilan (85% acrylonitrile and 15% vinyl acetate), Dynel (60% vinyl chloride and 40% acrylonitrile), Saran (85% vinylidene chloride and 15% vinyl chloride), and other synthetic fabrics or fibers prepared from polyalkylenes as polyethylene, polypropylene, polyurethanes, mineral fibers (Fiberglas), and alginic materials as alginate rayon.

The preferred materials to be employed in the process include those textile materials containing at least 10% cellulosic materials and preferably those derived from cotton and rayon.

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 crease recovery values reported in some of the examples were determined by the standard AATCC test (66–1959T) and tensile strengths were obtained on 1" strips with an Instron (Federal Specification CCC–T–191b, Method 5102). Appearance ratings were determined by comparison with the Monsanto plastic standards (AATCC Test 88A–1964T). All tests were carried out at 65±2% relative humidity and 70±2°. Specimens were conditioned 4 hours at standard conditions before physical testing. The wet crease recovery values were determined by soaking the fabric in water for 5 minutes and then blotting before testing.

EXAMPLE I

Bleached mercerized 80 x 80 count cotton print cloth was impregnated with an aqueous solution of 2% zinc fluoborate at a wet pick-up of 100% (based on the weight of the dry fabric using a Morrison laboratory 3-roll padder. The impregnated fabric is then introduced into a chamber containing hot (240–242° F.), vapors of epichlorohydrin. The contact time was about 5 minutes. The fabric was then rinsed in cold water to quench the reaction and to remove unreacted epichlorohydrin. The fabric was then washed in hot water and dried by hanging in air at a constant temperature.

The dried fabric is then passed with an aqueous sodium hydroxide solution of concentration 10% by weight for a 100% wet pick-up. The resulting material was then cured, some in an aqueous state and others in an anhydrous state. The aqueous cure consisted of sandwiching the fabric between two layers of polyethylene, rolling around a wooden dowel and sealing such that no moisture would be lost. In the anhydrous cure, the samples were hung in a forced hot air oven. Two sets of cure conditions were used, (1) overnight at ambient temperature, and (2) 15 minutes at 200° F. After curing the samples were washed, scoured with acetic acid, dried and conditioned for testing.

The results of the test are shown in the table below:

	Crease recovery angles	
Condition of cure	Wet	Dry
15 minutes 200° F.:		
Aqueous	296	247
Anhydrous	300	265
Epichlorohydrin only	239	231
Untreated	166	182

EXAMPLE II

Example I is repeated with the exception that the zinc fluoborate is replaced with each of the following: aluminum sulfate, zinc chloride, zinc nitrate and magnesium sulfate. Related results are obtained.

EXAMPLE III

Example I is repeated with the exception that the exposure time with the various epichlorohydrin is changed to the following: 1 minute, 3 minutes and 10 minutes. Related results are obtained.

EXAMPLE IV

Example I is repeated with the exception that the concentration of the caustic in the final step is changed to the following: 5%, 15%, and 25%. Related results are obtained.

EXAMPLE V

Example I is repeated with the exception that the cotton fabric is replaced by a mixture of 50% cotton and 50% Dacron. Related results are obtained.

EXAMPLE VI

Example I is repeated with the exception that the cotton fabric is replaced by rayon. Related results are obtained.

EXAMPLE VII

Bleached mercerized cotton broadcloth was impregnated with a 10% w. aqueous solution of zinc silicofluoride at a 100% wet pick-up. The fabric was then exposed to epichlorohydrin vapors (240° F.) for five minutes. The fabric was then rinsed in hot water and dried.

The dried fabric was padded at 100% wet pick-up with a 10% w. aqueous sodium orthosilicate solution and placed on a pin frame. The frame was placed in a forced hot air oven for three minutes at 250° F. The fabric was removed from the frame, water washed and dried at ambient temperature before testing. The following results were obtained.

Appearance ratings:	
Drip	4.6
Tumble	4.2
Spin and line	4.1
Crease recovery angles:	
Wet	274
Dry	242
Filling tensile loss (percent)	57

I claim as my invention:

1. A process for treating a cellulose fabric to impart increased wet and dry crease recovery thereto which comprises impregnating the fabric with a solution of an acid catalyst; reacting the fabric with epichlorohydrin by exposing it to vapors thereof at a temperature equal to or greater than the normal reflux temperature of epichlorohydrin; washing the fabric to remove excess reagents therefrom; impregnating the fabric with a solution of an

alkaline material having a pKb value of at least 10^{-5} and curing the impregnated fabric.

2. A process as in claim **1** wherein the cellulosic textile fabric is cotton fabric.

3. A process as in claim **1** wherein the acid catalyst is a metal salt catalyst.

4. A process as in claim **1** wherein the acid catalyst is employed in a concentration of 1% to 10% by weight of solution.

5. A process as in claim **1** wherein the alkaline material employed is NaOH.

6. A process as in claim **1** wherein the curing step is conducted at a temperature between 50° C. and 150° C. for a few minutes.

7. A process as in claim **6** wherein the acid catalyst is zinc fluoborate.

8. A process as in claim **6** wherein the exposure to the vapors epichorohydrin is from 2 to 5 minutes.

9. A process as in claim **6** wherein the concentration of the caustic is 5% to 10% by weight of solution.

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