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CELLULOSE ETHERS OF 3,4 EPOXY 1-BUTENE AND THEIR OXIDATION PRODUCTS

David M. Musser, Orange, N. J., assignor to Pacific Mills, Boston, Mass., a corporation of Massachusetts

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8 Claims. (Cl. 260—231)

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This invention relates to the treatment of cellulosic materials for the purpose of increasing their chemical reactivity, and to the products obtained.

The invention is particularly concerned with the preparation of cellulosic material characterized by the presence of an ethylenic linkage attached to the cellulose molecule, thereby imparting to the cellulosic material the typical chemical reactivity of materials containing double bond linkages of the ethylenic type. Preferably, establishment of this linkage is accomplished without decreasing the hydroxyl content of the cellulosic material and desirably by establishing a hydroxylated carbon atom linked directly to a double bond carbon atom so that the ethylenic linkage possesses the very high degree of reactivity characteristic of double bonds in close proximity to a hydroxyl group.

It is an object of the invention to increase the chemical reactivity of cellulosic materials particularly for the purpose of rendering the cellulosic material susceptible to further chemical treatment in the production of durable finishes, as in the textile field. A further object of the invention is to produce cellulosic material of increased reactivity without reduction of the hydroxyl content of the cellulose. Another object of the invention is the production of cellulosic textiles having durable finishes with the aid of double bond reactions.

It is well known in the art to coat and impregnate fabrics with materials such as synthetic resins, starch, waxes, soaps and quaternary ammonium compounds for the purpose of improving their appearance and hand. Finishes of this kind impart to textiles desirable properties such as crush resistance, water repellence, softness, stiffness, etc. These coated or impregnated fabrics have an improved appearance when new, and therefore possess a very strong sales appeal. However, finishes resulting from coating and impregnating techniques are not of a permanent nature, as they will not withstand repeated launderings, washings, dry cleaning, etc. In many instances, one simple laundering will completely remove all the original desirable properties of the finish. The treatment can be repeated after each such laundering or dry cleaning but such after-treatment is usually expensive and rarely feasible.

A truly permanent textile finish may be accomplished only by chemical reaction of a finishing compound with the cellulose of the fabric. For example, durable finishes have been attained by

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reacting finishing compounds with free hydroxyl groups of the cellulose provided that the reactions involved are not of a reversible nature and that the products thereof are not susceptible to hydrolysis. Obviously finishes of this type are limited to those which result from the application of compounds which will react with hydroxyl groups.

The present invention provides a treatment whereby cellulosic fabrics may be supplied with finishes formed with compounds not chemically reactive with cellulose hydroxyl groups by first producing an unsaturated cellulose derivative containing a double bond, preferably in close proximity to a hydroxyl group, and thereafter treating the cellulose derivative with any of a variety of compounds that react with the derivative at the double bond.

A double bond or ethylenic linkage as above described attached to the cellulose molecule in accordance with this invention retains all of its characteristics of chemical reactivity, i. e. is susceptible to oxidation, halogenation, alkylation, polymerization, cross linkages, additive reactions, etc.

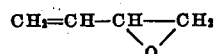
Such a double bond derivative may be produced by reacting the cellulosic material with a gaseous or low boiling point (i. e. under 300° F.) epoxy alkene in the presence of an alkali to form a hydroxy alkylene ether of cellulose, wherein the hydroxyl group is attached to a carbon atom linked to a double bond carbon atom, e. g., to form the 2-hydroxy- Δ^3 -butenyl ether of cellulose,



and then washing and drying the cellulosic material. The following are examples of treatment:

Example I

Cellulosic fabric (desized and boiled off) was immersed at room temperature in aqueous solution containing 20% sodium hydroxide, passed through squeeze rolls to remove excess alkali; then subjected in vacuum chamber to 3, 4-epoxy-1-butene,



20% based on weight of dry fabric, at 15 mm. pressure and at 50° C.; soured in 5% sulfuric acid at 25° C., washed in water until free of acid, and dried.

Example II

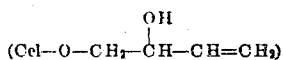
Cellulosic fabric (desized and boiled off) was immersed at room temperature in aqueous solu-

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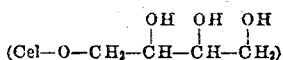
tion containing 20% sodium hydroxide, passed through squeeze rolls to remove excess alkali; then subjected in chamber containing a reflux condenser continuously to 3,4-epoxy-1-butene, vaporized by application of heat to the chamber; scoured in 15% acetic acid, washed, and dried.

The time of treatment may vary. Usually 15 to 30 minutes will suffice, but if a higher degree of reaction is desired, longer exposure may be given.

The treated fabrics of Examples I and II display characteristic reactivity of materials carrying an ethylenic linkage in proximity to a hydroxyl group. For example, when these fabrics are submitted to mild oxidation with agents such as a dilute solution of potassium permanganate or the like, additional hydroxyl groups are attached to the carbon atoms at the double bond converting the 2-hydroxy- Δ^3 -butenylether of cellulose



into the 2,3,4-trihydroxybutyl ether of cellulose



Such oxidation is indicated in cases where textile finishes exhibiting great affinity for water are desired. On the other hand, where excellent water-repellency together with soft finish is desired, short or long chain alkyl groups may be attached to the molecule by reacting with the double bond or ethylenic linkage. Other treatments involving double bond reactions such as halogenation and polymerization may be given these fabrics.

Treatment of cellulosic materials with epoxy alkenes as herein described therefore affords a highly convenient basic treatment preparatory to subsequent treatment with a variety of compounds, some of which at least are non-reactive with native cellulose, for imparting any of numerous different finishes, as desired, to such materials.

I claim:

1. A method of improving the chemical re-

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activity of cellulosic fibrous material containing free hydroxyl groups which comprises reacting said material in the presence of an alkali with 3,4-epoxy-1-butene.

2. The 2-hydroxy- Δ^3 -butenyl ether of cellulose.

3. A cellulosic fibrous material comprising 2-hydroxy- Δ^3 -butenyl ether of cellulose.

4. The method of treating cellulosic material which comprises reacting said material in the presence of an alkali with 3,4-epoxy-1-butene.

5. The method of treating cellulosic material which comprises reacting said material in the presence of an alkali with 3,4-epoxy-1-butene to form a cellulose ether containing a double bond and thereafter treating the material to saturate said double bond.

6. The method of treating cellulosic material which comprises reacting said material in the presence of an alkali with 3,4-epoxy-1-butene to form a cellulose ether containing a double bond and thereafter oxidizing said material at said double bond.

7. 2,3,4-trihydroxybutyl ether of cellulose.

8. A cellulosic fibrous material comprising 2,3,4-trihydroxybutyl ether of cellulose.

DAVID M. MUSSER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,502,379	Dreyfus	July 22, 1924
1,941,278	Schorger	Dec. 26, 1933
2,120,513	Stahn	June 14, 1938
2,131,120	Schlack	Sept. 27, 1938
2,131,145	Schlack	Sept. 27, 1938
2,164,248	Lawrie et al.	June 27, 1939
2,238,949	Schlack	Apr. 22, 1941

FOREIGN PATENTS

Number	Country	Date
415,052	Great Britain	Aug. 14, 1934
467,992	Great Britain	June 28, 1937