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INSOLUBILIZED CELLULOSE ETHER

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2 Claims. (Cl. 260—232)

1

This invention deals with a method whereby cellulose is utilized in desired forms or shapes. It concerns a method in which cellulose derivative is rendered soluble and applied or shaped from solution, whereupon the resulting form is rendered insoluble. The invention also concerns the products which are thus obtained. These comprise a cross-linked form of a cellulose ether which is peculiar to this invention.

It has been proposed to convert cellulose to hydroxyethyl cellulose or carboxyalkyl cellulose ethers which are soluble in alkali solutions, deposit modified cellulose therefrom in the form of films or foils, and set the deposited film or foil with acid. Such material, however, remains water-sensitive and capable of re-solution in alkali solutions.

A method has now been found by which a cellulose derivative in a soluble state may be shaped or deposited in a desired form and then rendered insoluble, even in alkaline solutions. This method comprises treating cellulose with an alkali hydroxide to form alkali cellulose, reacting the alkali cellulose with isobutylene oxide to form an alkali-soluble product, forming a solution thereof in an alkali solution, forming a desired shape or form therefrom, removing alkali from said shape or form, treating it with a soluble cobalt salt, and heating the thus treated shape or form to insolubilize the cellulosic material.

The cellulose may thus be formed as a coating or film, as on a woven or knitted fabric, or it may be cast as an integral object, such as a foil or unsupported film. The coating is useful as a textile finish, for example, while the film may be used as a modified cellulose sheet or other formed cellulosic object.

As a source of cellulose for use in this process, there may be used cotton linters, purified wood pulp, rayon waste, or the like.

When cellulose is treated with a solution of a strong alkali, it is converted at least in part to so-called alkali-cellulose. For this purpose, there may be used relatively strong solutions of sodium hydroxide, potassium hydroxide, or strong quaternary ammonium hydroxides such as benzyl trimethyl ammonium hydroxide or dibenzyl dimethyl ammonium hydroxide. Alkali solutions of 10% up to 50% or more may be used. Although the conversion to alkali cellulose is rapid, it is often desirable to allow the alkali cellulose to age in a closed container. An inert atmosphere improves the nature of the final product.

Excess alkali may be removed, as by draining

2

or centrifuging, if desired, although this is not essential.

Isobutylene oxide is then reacted with the alkali cellulose. This reaction may be accelerated by warming, temperatures from 20° C. to 60° C. being useful, 25° C. to 40° C. being preferred. When about 0.05 to about 0.5 mol of isobutylene oxide has reacted per glucose unit, the cellulose becomes soluble in solutions of about 5% to about 15% of a strong alkali, such as sodium hydroxide.

This solution may be applied to a textile base to form a coating thereon. The alkali may be destroyed with acid, a dilute solution such as a 2% to 10% solution of acetic or sulfuric acid being effective in destroying the alkali and depositing the cellulosic material. Instead of a coating, a foil may be formed by deposition of solution on a metal or ceramic ware plate or roll. Similarly, the cellulosic material may be formed as a filament rod or other shaped object by injection into an acidic coagulating bath, or solid objects may be cast by other methods. The formed or shaped objects at this stage are still water-sensitive and capable of being redissolved by a strong alkali in solution.

The formed or shaped object may, however, now be rendered insoluble by treatment with a cobalt salt, which is most readily applied from about 0.05% to about 4% aqueous solution of such salts as cobalt chloride, cobalt nitrate, or cobalt acetate, followed by heating. At temperatures of 120° to 150° C., the cellulosic materials become quite insoluble in four hours to less than one hour.

In the application of a cobalt salt, the use of a buffering salt, such as sodium or potassium acetate, is helpful in controlling the conditions of reaction. A high concentration of cobalt hastens the insolubilizing action but may cause dry strength of the product to be slightly decreased. The presence of sodium acetate as a typical buffer in a molecular proportion from about 0.5 to about 0.9 that of the concentration of the cobalt salt gives a good balance and assures insolubilizing action without deleterious action of cobalt on cellulose.

The process of this invention is illustrated by the following typical preparations.

Example 1

One hundred seventy parts of purified wood pulp was mixed with four hundred parts of a 20% sodium hydroxide solution in a closed vessel. This mixture was left standing in a closed con-

tainer for forty-four hours at about 30° C. It was then placed in a Werner-Pfleiderer mixer and treated with 144 parts of isobutylene oxide. The resulting mixture was worked at 38°–40° C. for six hours and left standing for fifteen hours with the temperature between 38° and 30° C. This product was washed with a 50% methanol solution until caustic was removed and, after being dried, was obtained in the form of white flakes. A solution was prepared from these by suspending 160 parts of flakes in 1840 parts of 8% sodium hydroxide solution and reducing the temperature of the suspension to —5° C. A syrupy, water-white solution resulted.

This solution was poured over a glass plate, which was then passed under a doctor blade set at twenty-four mils clearance. The film on the plate was dried, whereafter the alkali was destroyed in the dried film by immersion in a 5% hydrocarbon acid solution. The film was then stripped from the plate and cut into sections. Some of these were dried and then heated in an oven at 135° C. for four hours. Other were dipped into a 0.5% cobalt chloride solution and then dried and heated at 135° C. for four hours.

After the various strips had been conditioned at 21° C. in an atmosphere at 65% relative humidity, tensile strengths were determined. Strips dried but not heated and strips dried and heated, all without catalyst, showed tensile strengths of about nine kilograms per square millimeter when dry and about 0.3 kilogram per square millimeter when wet. After immersion of strips in the cobalt solution, there was no significant change upon drying at 21° C., but the strips heated at 135° C. had tensile strengths of about eight kilograms per square millimeter when dry and 2.2 kilograms per square millimeter when wet. This was about a seven-fold increase in wet strength.

Example 2

As another example illustrating this invention, one hundred seventy parts of α-cellulose was mixed with four hundred parts of 20% aqueous sodium hydroxide solution, and this mixture was aged for thirty-six hours in a closed container at room temperature. Thereto seventy-two parts of isobutylene oxide was added and mixed in a Werner-Pfleiderer mixer at 21° C. for six hours The reaction mixture was then left standing overnight and washed with about 120 parts of acetic acid diluted with 120 parts of water. The insoluble portions was washed with water until free from acetic acid and dried at room temperature.

A portion of eighty parts of the dried product was dissolved in 920 parts of 8% sodium hydroxide solution. After this mixture had been chilled to —5° C., a clear solution was obtained having a viscosity of 2500 centipoises.

The solution was forced through an orifice 0.25'' x 0.03'' into a bath composed of 15% sulfuric acid, 8% of sodium sulfate, 5% of glucose, and 1.0% of cobalt chloride ($CoCl_2 \cdot H_2O$), and the cellulose ether was thus coagulated or precipitated in the form of a ribbon. This ribbon was washed with water, dried, and baked at about 130° C. for about four hours. A water and alkali-insoluble product was thus obtained.

Example 3

One hundred seventy parts of a purified α-cellulose and four hundred parts of 20% sodium hydroxide solution were mixed and allowed to stand in a closed container at 30° for twenty-four hours. The mixture was then placed in a Werner-Pfleiderer mixer, and 144 parts of isobutylene oxide was added and mixed at 40° C. for six hours. The batch was then neutralized by addition of 10% acetic acid, which resulted in the precipitation of the hydroxyisobutyl ether of cellulose. This was washed thoroughly with water and dried in an oven at 75° C. There was obtained 184 parts of a white flaky solid which, according to analysis, contained 445.2% carbon and 6.46% hydrogen. This corresponds to about 0.08 hydroxyisobutyl group per glucose unit. A solution was prepared by suspending 160 parts of dried flakes in 1840 parts of 8% sodium hydroxide solution and chilling to 0° to —5° C. The resulting solution was a syrupy, water-white solution having a viscosity of 950 centipoises.

The preparation of films was done by spinning the above solution through a slit 0.01'' by 0.25'' into a bath having the following composition:

15% sulfuric acid
8% sodium sulfite
5% corn syrup
72% water

The ribbon obtained was washed thoroughly and then soaked for one hour in a solution containing 4.0% cobaltous chloride hexahydrate and 1.0% sodium acetate. The films were suspended on a frame so that they could shrink in only the transverse direction and were dried at room temperature and then cured by being placed in an oven at 150° C. for two hours. The dry film had cross-sectional dimensions of 0.89 mm. x .037 mm. The dry tensile strength was 10.1 kilograms per square millimeter. The wet strength was 3.3 kilograms per square millimeter.

Example 4

As yet another example of the preparation of the products of this invention, 170 parts of purified cellulose was taken up in four hundred parts of a 20% caustic soda solution and aged twenty-four hours in a closed vessel. Thereupon, 108 parts of isobutylene oxide was run in and the mixture worked mechanically for six hours at 40° C. in a closed Werner-Pfleiderer mixer. The material was left standing overnight. It was then washed with methanol to remove excess alkali and dissolved in an 8% caustic soda solution. Analysis of the solid cellulose ether showed the presence of 0.08 hydroxyisobutyl group per glucose unit.

The solution was forced through an orifice as in the previous example into a similar acid bath containing about 2% of cobalt chloride. After the ribbon was washed and dried, it was baked at 140° C. for two hours. The product was insoluble in sodium hydroxide solutions.

We claim:

1. A process for insolubilizing an alkali-soluble cellulose ether formed by reacting alkali cellulose with isobutylene oxide and removing alkali therefrom, which comprises treating said cellulose ether with a solution of a water-soluble cobalt salt and heating the thus-treated cellulose ether at 120° to 150° C. until the said ether is insoluble.

2. A process for insolubilizing an alkali-soluble cellulose ether prepared by reacting an alkali cellulose with 0.2 to 0.8 mole of isobutylene oxide per glucose unit of the cellulose and removing alkali therefrom, which comprises treating said cellulose ether with 0.04% to 4% aqueous solution of a soluble cobalt salt and heating the thus-treated

cellulose ether at a temperature of 120° to 150° C. until insoluble.

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

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Certificate of Correction

Patent No. 2,498,208 February 21, 1950

ALVA L. HOUK ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 3, line 20, for the word "hydrocarbon" read *hydrochloric*; line 23, for "Other" read *Others*; line 53, for "portions" read *portion*; line 63, for "($CoCl_2 \cdot H_2O$)" read *($CoCl_2 \cdot 6H_2O$)*; column 4, line 9, for "445.2%" read *45.2%*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 23rd day of May, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.