

UNITED STATES PATENT OFFICE

2,622,080

METHOD FOR THE MANUFACTURE OF HIGH BUTYRYL CELLULOSE ESTERS

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No Drawing. Application June 5, 1950,
Serial No. 166,292

7 Claims. (Cl. 260—229)

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This invention relates to a process of making high butyryl cellulose esters in which cellulose fiber is activated by treatment with water, the water is replaced by a lower aliphatic alcohol, formic acid, acetic acid, a low molecular weight ester or ketone or acetonitrile, followed by replacement of the water-displacing liquid with butyric acid free of catalyst.

It is well known that cellulose is more readily susceptible to acylation if it is first pretreated or activated. Most of the pretreatment processes heretofore have involved a preliminary soaking of the cellulose with acetic acid, either with or without catalyst. Of recent years the value of aqueous acids for that purpose has been recognized. However, cellulose which has been treated with aqueous acid or water and which has a high moisture content is difficult to properly esterify with acid anhydride due to the vigorous nature of the reaction which occurs when water and acid anhydride are contacted in the presence of catalyst. The pretreatment of cellulose with water, followed by displacement of the water from the cellulose with acetic acid prior to its use in the esterification process has been suggested, but in the case of the manufacture of high butyryl cellulose esters the acetic acid which ordinarily has been employed for that purpose decreases the proportion of butyryl which can be introduced into the cellulose. If butyric acid is employed directly for the purpose of displacing the water in the cellulose, the time of esterification materially exceeds that necessary for the esterification of cellulose activated by our process.

One object of our invention is to provide a method for activating cellulose in a rapid manner preparatory to butyrylation. Another object of our invention is to provide a process for activating fibrous cellulose in sheet form in which the convenient sheet form is retained throughout the activation preparatory to butyrylation. A further object of our invention is to provide a process for activating cellulose preparatory to butyrylation in which the cellulose when ready for esterification is substantially free of moisture. A still further object of our invention is to provide a method of activating fibrous cellulose in sheet form whereby the cellulose is rendered more reactive for the preparation of cellulose esters having a high butyryl content than is obtained with a single stage method. Other objects of our invention will appear herein.

Our invention in its broadest aspects com-

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prises applying moisture to a fibrous cellulose sheet at a temperature of 70–100° C. whereby the cellulose is quickly and uniformly activated, followed by replacing the water with one of the following displacing liquids: methanol, ethanol, acetone, formic acid, acetic acid, acetonitrile, methyl formate and methyl ethyl ketone, which procedure is followed by the replacement of the displacing liquid with butyric acid. This sheet which has thus been activated is then employed in an esterification in which butyric anhydride is employed as an esterifying anhydride, thereby obtaining a high quality cellulose ester having a high butyryl content.

A convenient method for activating cellulose in accordance with our invention is to pass the cellulose in sheet form in a continuous manner over a series of suction boxes by the procedure illustrated in our Patent No. 2,484,455. In the first part of the treatment the cellulose sheet has water at a temperature of 70–100° C. sucked therethrough for a time of at least 10–20 seconds. Any time greater than this will give the same effect but ordinarily is unnecessary and cuts down the rapidity of the operation. After the cellulose has been thoroughly moistened in this fashion and suction has been applied thereto, the sheet, with or without passing through pressure rolls, is then subjected to a sucking through of a displacing liquid, such as one of the liquids mentioned heretofore, this treatment being continued until the moisture is substantially all displaced from the cellulose. This treatment need only take 10 to 20 seconds although here again a longer time may be used if for any reason the individual operator desires to use a longer period at this point. After the moisture has been displaced from the cellulose sheet, the cellulose, with or without treatment with pressure rolls, is then subjected to treatment with butyric acid, such as by sucking the butyric acid through the sheet thereby removing the displacing liquid. The butyric acid employed contains little or no moisture and may be used as is, or in some cases it may be desirable to incorporate a small proportion of catalyst therein, which operation distributes the catalyst uniformly throughout the cellulose sheet.

After the treatment of the cellulose sheet in the manner described, it is preferably broken up and employed in an esterification in which butyryl predominates so that a high butyryl cellulose ester results.

We have found that the method of activation

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described herein in which the water is displaced with a displacing liquid and this displacing liquid is then displaced with butyric acid that the time of esterification is appreciably lessened as compared with an activation method in which the moisture is replaced directly by the butyric acid. In case a short esterification period is maintained, quality of the first stage dope as obtained with the two-stage displacement sequence is appreciably better than when butyric acid is used directly to remove water from the sheet. For instance, in comparative esterifications in one case using the sequence of water displacement with acetic acid, and then with butyric acid, and in a second case the sequence of water and displacement with butyric acid, the time of esterification was appreciably shortened in the first case using butyric anhydride as the esterifying agent under substantially the same esterification conditions. The cellulose employed in accordance with our process may be either cotton linters or refined woodpulp. However, as the latter material is ordinarily marketed in sheet form, our method of activation is especially adapted for woodpulp pretreatment.

Some procedures where cellulose treated in accordance with our invention is useful, are for instance processes in which pulp sheet after activation and while wet with one part of butyric acid (such as results after pressing) is picked apart and then charged to an esterification mixer to which a butyrylating mixture had been added, such as where the reaction mass having an initial temperature of 35-40° C. is of the following composition:

	Parts
Cellulose (dry weight basis)-----	1
Butyric acid-----	1
Butyric anhydride-----	3
Acetic anhydride-----	.7
Butyric acid-----	.2
Sulfuric acid-----	.03

By controlling the temperature and agitating for a time of 4-6 hours, a high butyryl cellulose acetate butyrate is obtained. If only butyric acid and anhydride is employed, a cellulose butyrate is obtained.

The following examples illustrate our invention:

Example I

One part of a sheet of acetylation grade refined wood pulp was treated using a vacuum of 4 cm. of mercury under the sheet by pulling there-through the following liquids in the order and for the times indicated:

100 parts distilled water at 80° C.-----seconds--	30
25 parts of methanol at 30° C.-----do-----	15
25 parts of butyric acid at 30° C.-----do-----	7
100 parts of butyric anhydride containing 0.3% sulfuric acid at -10° C.-----seconds--	70

The unpressed sheet was then placed in an esterification vessel containing 6.5 parts of acetic anhydride and 10.6 parts of butyric acid per 9 parts of cellulose at 0° C. Enough butyric anhydride was added to make the total anhydride 26 parts per 9 parts of cellulose. The reaction mass was mechanically agitated while cooling until a viscous reaction product was obtained. The mass was then diluted with 108 parts of 96.5% acetic acid per 9 parts of cellulose and was mechanically agitated whereupon the physical characteristics thereof were determined as re-

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gards haze, color and fiber. The haze was determined as 36, the fiber as 5, and the color as 130.

The haze reading is determined as the depth in centimeters through which a standard stainless steel wire can be seen as it is lowered into the dope. Color is measured as p. p. m. of platinum as chloroplatinate by comparison with color standards containing enough cobalt chloride to give the proper red content for color comparison with the cellulose ester reaction mass. The fiber readings are in parts of unesterified fiber per million parts of mass being examined.

Example II

The procedure of Example I was repeated except that formic acid was employed as the liquid to displace the water. The values of the resulting product were: haze, 28; color, 150; and fiber, 30.

Example III

Example I was repeated except that acetone was employed instead of methanol. The values obtained were: haze, 28.5; color, 150; and fiber, 15.

Example IV

A sheet of acetylation grade refined cotton linters was activated by drawing through the sheet the following liquids in the order listed, in one case the fatty acid being acetic acid, and in a second case, butyric acid:

100 parts of water at 80° C.
50 parts of fatty acid at 80° C.
25 parts butyric acid at 30° C.

A sheet was then pressed between stainless steel rolls so that it consisted of equal parts of cellulose and acid. Eighteen parts of sheet composed of nine parts of cellulose and nine parts of butyric acid were placed in the following mixture having a temperature of 38° C.:

	Parts
Butyric anhydride-----	26
Acetic anhydride-----	6.5
Butyric acid-----	1.5
Sulfuric acid-----	.27

The mixture was agitated while using surrounding baths thereon having the following temperatures:

38° C. bath for 15 minutes
10° C. bath for 20 minutes
30° C. bath for 3 hours
35° C. bath for 1 hour

The reaction mass was diluted with 108 parts of 96.5 per cent acetic acid. It was thoroughly mixed to a homogeneous system in one-half hour, and the following readings were made on each of the two batches which were prepared by this method. These readings as regards the two batches were as follows, taking two separate readings for each:

	Clarity (cm.)	Viscosity	Color	Fiber
Acid used in displacement step (#2 above):				
Acetic-----	23.5	23	55	30
	22.5	24	60	30
Butyric-----	6.0	13	(1)	2,500
	5.0	21	(1)	2,500

¹ Too much fiber.

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Example V

The preceding example was repeated except that the first displacement of water used 250 parts of solvent as shown in the following table. The results obtained with various solvents are as follows, the figures given being the averages of dope from two esterifications:

	Temperature displacement liquid, ° C.	Clarity (cm.)	Viscosity	Color	Fiber
Solvent: Methanol	30	20	20	70	15
Nitriles: Acetonitrile	30	18	14	75	40
Ketones:					
Acetone	30	19.5	22	70	220
Methyl ethyl ketone		16	24	65	625

	Degrees	Clarity (cm.)	Viscosity	Color	Fiber
Esters:					
Methyl formate	20	18	12	75	35
Methyl acetate	30	15	27	70	50
Ethers:					
Ethyl ether	20	12	8	75	300
Isopropyl ether	20	10	11	75	750
Hydrocarbons: Benzene	30	9	16	70	525

In each of the examples given above, the reaction masses can be precipitated by running this dilute acetic acid accompanied by agitation and the precipitated cellulose esters can then be separated from the liquid in each case.

What we claim and desire to secure by Letters Patent of the United States is:

1. A process of activating cellulose for the formation of butyryl containing cellulose esters comprising subjecting the cellulose in sheet form to a water wetting, displacement of the water by a displacement agent selected from the group consisting of methanol, ethanol, formic acid, acetic acid, acetone, acetonitrile, methyl ethyl ketone, and methyl formate, and following this displacement with a second displacement of the organic reagent with butyric acid.

2. A process of activating cellulose for the preparation of butyryl containing cellulose esters comprising subjecting the cellulose in sheet form to wetting with water, displacement of the water with methanol, and then displacing the methanol with butyric acid.

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3. A process of activating cellulose for the preparation of butyryl containing cellulose esters comprising subjecting the cellulose in sheet form to wetting with water, displacement of the water with acetonitrile, and then displacing the acetonitrile with butyric acid.

4. A process for preparing a cellulose acetate butyrate comprising activating cellulose in sheet form by a sequence consisting of water wetting, displacement of the water with a displacement agent selected from the group consisting of methanol, ethanol, formic acid, acetic acid, acetone, acetonitrile, methyl ethyl ketone, and methyl formate, and then a second displacement with butyric acid, and then esterifying the so treated cellulose with a butyrylation mixture comprising butyric anhydride and esterification catalyst.

5. A process of activating cellulose for the preparation of butyryl containing cellulose esters comprising subjecting the cellulose in sheet form to wetting with water, displacement of the water with acetic acid, and then displacing the acetic acid with butyric acid.

6. A process of activating cellulose for the preparation of butyryl containing cellulose esters comprising subjecting the cellulose in sheet form to wetting with water, displacement of the water with acetone, and then displacing the acetone with butyric acid.

7. A process of activating cellulose for the preparation of butyryl containing cellulose esters comprising subjecting the cellulose in sheet form to wetting with water, displacement of the water with formic acid, and then displacing the formic acid with butyric acid.

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