

UNITED STATES PATENT OFFICE

1,962,829

PRODUCTION OF MIXED ESTERS OF CELLULOSE IN AN ESTER OF A HALOGENATED FATTY ACID

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No Drawing. Application October 3, 1931,
Serial No. 566,799

19 Claims. (Cl. 260-101)

The present invention relates to the production of the mixed organic esters of cellulose such as cellulose acetate-stearate in which an ester of a halogenated fatty acid is employed as the solvent.

It has been previously known to employ the halogenated lower fatty acids such as chloracetic acid as a solvent in esterification baths, which are quite satisfactory except for the fact that they are very corrosive which obviously leads to deterioration of equipment and accompanying contamination of the product.

We have now found that the esters of the halogenated fatty acids exhibit the valuable solvent properties of the halogenated fatty acids without the accompanying disadvantageous property of those acids of being highly corrosive. We have found that the esters of the halogenated fatty acids are suitable as solvents for various types of esterification processes such as, for example, those in which partially deacetylated cellulose acylates such as commercially available acetone soluble hydrolyzed cellulose acetate are employed as the initial cellulosic material. On the other hand these esters of halogenated fatty acids are also suitable for use as solvents in reaction mixtures for the esterification of cellulose itself.

Our solvent permits of use in the production of mixed esters of cellulose in which either acid anhydrides such as acetic anhydride or the high fatty acid anhydrides are employed.

Our solvent is of especial value in the esterification of the lower fatty acid esters of cellulose with the higher fatty acid anhydrides such as stearic anhydride as there are few solvents in which both of these materials are compatible. As pointed out previously chloracetic acid which is suitable as a solvent for a mixture of a higher fatty acid anhydride and a lower ester of cellulose is corrosive and severe on the reaction vessels. However we have found that the esters of the halogenated fatty acids will dissolve both lower fatty acid esters of cellulose and the higher fatty acid anhydrides without the corrosive effect on equipment, which is characteristic of the solvents previously employed, which makes it eminently suitable as a solvent in esterification processes in which higher fatty acid anhydrides are employed.

The following specific examples illustrate the application of our invention to esterification processes. It is to be understood however that our invention is not limited to the details given in those examples.

Example I

About 50 lbs. of an acetone-soluble cellulose

acetate having an acetyl content of about 38% was introduced into an esterifying bath comprising about 400 lbs. of methyl chloracetate, 100 lbs. of stearic anhydride and 1 lb. of benzene sulfonic acid and the whole was agitated and maintained at about 80° F. until a sample from the bath showed that the product formed was soluble in hot toluene. The solution was then poured into isopropyl ether to precipitate out the product, which was washed with isopropyl ether all as disclosed in Malm and Fordyce application Serial No. 553,646 and dried. A cellulose acetate-stearate having a stearyl content of about 40% was obtained.

Example II

About 50 lbs. of bleached cotton tissue was placed in an esterifying bath comprising about 250 lbs. of commercial stearic acid, 150 lbs. of acetic anhydride, 400 lbs. of ethyl chloracetate and .5 lb. of perchloric acid and the whole was agitated and maintained at 60-65° C. until a clear dope resulted (about 5 hours). The product was precipitated out from the reaction mass by pouring into iso-propyl ether. It was then washed with isopropyl ether and dried. The ester formed was a cellulose acetate-palmitate-stearate (palmitic acid being present in commercial stearic acid) and was soluble in acetone.

Example III

About 50 lbs. of cellulose acetate having an acetyl content of 38% was treated with an esterification bath comprising about 50 lbs. of propionic anhydride, 400 lbs. of methyl chloracetate and 1 lb. of benzene sulfonic acid at about 80° F. with vigorous stirring. When a sample showed that the product was soluble in ethylene chloride, the solution was poured into methyl alcohol, washed with alcohol and dried. A cellulose acetate-propionate soluble in acetone, ethylene chloride, and ethyl acetate was obtained.

Altho the alkyl esters of the halogenated fatty acids such as methyl, ethyl or propyl chloracetate are the preferred solvents for use in esterification baths, nevertheless any other compatible liquid aliphatic ester of the halogenated fatty acids which is suitable may be employed as a solvent in baths for the esterification of cellulose or cellulosic materials, for example the esters of halogenated fatty acids with other mono- or polyhydroxy alcohols may be employed as solvents in esterification baths. Also the esters of the bromoacetic and iodo-acetic acids may find use as solvents according to the present invention however

at present because of the availability of the chloroacetic acids and the usefulness of their esters, it is preferred to employ the esters of the chloroacetic acids in that connection.

- 5 The term "cellulosic material" as employed herein, is intended to define both partially esterified cellulose esters and materials such as cotton linters, pulp, etc. which are composed mainly of cellulose.
- 10 Various mixed esters of cellulose are possible according to our process by merely substituting for the fatty acids or anhydrides employed in the examples equimolecular proportions of other fatty acids or anhydrides, the groups of which are desired in the cellulose molecule. For instance, in
- 15 Example I given herein instead of 100 lbs. of stearic anhydride, 70 lbs. of lauric anhydride may be employed and in that case the resulting product would be a cellulose acetate-laurate. If a
- 20 cellulose propionate (or butyrate) -higher acylate is desired the starting material should obviously be a partially esterified cellulose propionate (or butyrate) instead of the cellulose acetate which is employed in the examples. Typical ex-
- 25 amples of esters which may be prepared according to our invention, by methods analogous to those shown in the examples, are:

- 30 Cellulose acetate-propionate
Cellulose acetate-butyrate
Cellulose acetate-laurate
Cellulose acetate-stearate
Cellulose acetate-oleate
Cellulose propionate-stearate
35 Cellulose butyrate-stearate.

What we claim as our invention and desire to be secured by Letters Patent of the United States:

1. The esterification of cellulosic material with an aliphatic acid compound in the presence of an
- 40 alkyl ester of a halogenated acetic acid which is a liquid solvent of the cellulose ester formed.
2. The esterification of cellulosic material with an aliphatic acid compound in the presence of an ester of a halogenated acetic acid which is a li-
- 45 quid solvent of the cellulose ester formed selected from the groups consisting of the methyl, the ethyl, and the propyl esters of the halogenated acetic acids.
3. The esterification of cellulosic material with
- 50 an aliphatic acid compound in the presence of an alkyl ester of a chloroacetic acid.
4. The esterification of cellulosic material with an aliphatic acid compound in the presence of methyl chloroacetate.
- 55 5. In the production of a mixed ester of cellulose, the step which comprises treating cellulosic material with an esterifying bath comprising a fatty acid anhydride and an alkyl ester of a halo-
- 60 genated acetic acid which is a liquid solvent of the cellulose ester formed.
6. In the manufacture of a mixed ester of cellulose, the step which comprises treating cellulosic material with an esterifying bath comprising a fatty acid anhydride and an alkyl ester of chloroacetic acid.
- 65 7. In the manufacture of a mixed ester of cel-

lulose, the step which comprises treating cellulosic material with an esterifying bath comprising a fatty acid anhydride and methyl chloroacetate.

8. The process of making mixed esters of cellulose which comprises esterifying a partially esterified lower fatty acid ester of cellulose with the anhydride of a higher fatty acid in the presence of an alkyl ester of a halogenated acetic acid which is a liquid solvent of the cellulose ester formed.

9. The process of making mixed esters of cellulose which comprises esterifying a partially esterified lower fatty acid ester of cellulose with the anhydride of a higher fatty acid in the presence of an alkyl ester of a chloroacetic acid.

10. The process of making mixed esters of cellulose which comprises esterifying a partially esterified lower fatty acid ester of cellulose with the anhydride of a higher fatty acid in the presence of methyl chloroacetate.

11. The process of making mixed esters of cellulose which comprises esterifying a partially esterified cellulose acetate with a higher fatty acid anhydride in the presence of an alkyl ester of a halogenated acetic acid which is a liquid solvent of the cellulose ester formed.

12. The process of making mixed esters of cellulose which comprises esterifying a partially esterified cellulose acetate with a higher fatty acid anhydride in the presence of an alkyl chloroacetate.

13. The process of making mixed esters of cellulose which comprises esterifying a partially esterified cellulose acetate with a higher fatty acid anhydride in the presence of a methyl chloroacetate.

14. The process of making cellulose acetate-stearate which comprises esterifying a partially esterified cellulose acetate with stearic anhydride in the presence of an alkyl ester of a halogenated acetic acid which is a liquid solvent of the cellulose ester formed.

15. The process of making cellulose acetate-stearate which comprises esterifying a partially esterified cellulose acetate with stearic anhydride in the presence of an alkyl chloroacetate.

16. The process of making cellulose acetate-stearate which comprises esterifying a partially esterified cellulose acetate with stearic anhydride in the presence of a methyl chloroacetate.

17. The esterification of cellulosic material with an aliphatic acid compound in the presence of an alkyl ester of monochloroacetic acid.

18. The process of making mixed esters of cellulose which comprises esterifying a partially esterified lower fatty acid ester of cellulose with the anhydride of a higher fatty acid in the presence of an alkyl ester of monochloroacetic acid.

19. The process of making a mixed ester of cellulose which comprises esterifying a partially esterified cellulose acetate with a higher fatty acid anhydride in the presence of methyl monochloroacetate.

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