Patented Apr. 27, 1943 2,317,767

UNITED STATES PATENT OFFICE

2,317,767

CELLULOSE FATTY ACID ESTERS

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No Drawing. Application April 26, 1939, Serial No. 270,161. In Germany May 12, 1938

3 Claims. (Cl. 260—227)

The present invention relates to the production of fibrous fatty acid esters of cellulose.

It is known to produce fibrous esters of cellulose, for instance cellulose acetate, by reacting cellulose with an esterifying agent, for instance acetic acid anhydride, in the presence of a non-solvent for the cellulose ester formed, for instance carbon tetrachloride, benzene, toluene, aliphatic and aromatic ethers and the like, and in the presence of sulfuric acid as a catalyst. Since esterification of cellulose in the fibrous form is still more difficult than producing cellulose esters in solution, it was necessary to use large amounts of the sulfuric acid catalyst and/or to subject the cellulose to particular pre-treatment processes with water, aqueous sulfuric acid or lyes in order to carry out the reaction. However, cellulose esters prepared in the presence of large quantities of sulfuric acid are of insufficient stability. The presence of large quantities of water, on the other hand, caused the esterification to proceed very inhomogeneously, and a pre-treatment with sulfuric acid or lyes caused degradation of the cellulose, so that the cellulose esters produced according to the said known methods were not of the highest quality.

We have now found that fatty acid esters of cellulose in fibrous form can be produced in a very simple and economical manner by treating cellulose with an esterifying mixture consisting of a fatty acid anhydride, a non-solvent for the cellulose ester formed and less than 1% of sulfuric acid. As an example, the concentration may be between 0.5–1% of sulfuric acid. The cellulose used in this process may have been pre-treated with a fatty acid, for instance with glacial acetic acid, but it is not to be pre-treated, as in the previous processes, with water, sulfuric acid or lyes. The reaction is carried out at elevated temperatures, temperatures between 30 and 70° C. being preferred. It was rather unexpected that in spite of the great difficulties in esterifying cellulose in the fibrous form, fibrous cellulose esters of uniform solubility, high viscosity and excellent mechanical properties could be obtained within normal reaction periods in the presence of such small quantities of the catalyst. It is especially advantageous that when preparing fibrous cellulose esters according to our new process no special stabilizing treatment is necessary.

The other reaction conditions like regulation of the temperature during the reaction, the relative proportions of and the way of adding the esterifying mixture may be varied, as desired for any particular purpose, within the above defined limits. The process is suitable as well for the production of fibrous cellulose acetate as of fibrous esters of cellulose with higher saturated and unsaturated fatty acids, fibrous mixed esters and ether-esters of cellulose etc.

Our process is more fully illustrated by the following examples, without being limited thereto, the parts being by weight:

Example 1

100 parts cellulose of normal humidity, for instance bucked and bleached cotton linters, which have been pre-treated in known manner with 50 parts glacial acetic acid, are introduced into an acetylating mixture of 350 parts acetic acid anhydride, 400 parts carbon tetrachloride and 0.7 part concentrated sulfuric acid. The temperature is raised to 65° C. in the course of about 3 hours. When the reaction mixture has been kept at that temperature for about 10 hours, esterification is complete; a sample will then clearly dissolve in a mixture of methylene chloride-methyl alcohol (9:1). When the viscosity of the sample corresponds to the desired value, the sulfuric acid catalyst is neutralized, for instance by adding a basic salt or an organic base to the mixture; the neutralizing agent may be dissolved in glacial acetic acid. The excess acetic acid anhydride may be destroyed by adding water to the mixture; but this is not absolutely necessary. The reaction mass is then pressed or centrifuged, the non-solvent still present therein is distilled off with water and the fibrous cellulose acetate is thereupon worked up as usual, for instance by deacidifying, bleaching, washing and drying.

Example 2

100 parts of bucked and bleached cotton linters of normal humidity having been pre-treated with 50 parts glacial acetic acid are introduced into a mixture of 350 parts acetic acid anhydride, 400 parts toluene and 0.9 part concentrated sulfuric acid. The reaction temperature is raised in the course of 3 hours to 60° C. and kept at that value until esterification is complete. After about 15 hours from the introducing of the cellulose a clearly soluble fibrous cellulose triacetate of normal viscosity has been formed. It is worked up as described in Example 1.

Example 3

100 parts bucked and bleached cotton linters of normal humidity having been pre-treated in

the usual manner with glacial acetic acid are introduced into a mixture of 350 parts acetic acid anhydride, 1000 parts carbon tetrachloride and 0.8 part concentrated sulfuric acid. The mixture is heated in the course of about 3 hours to 70° C. and is kept at this temperature until esterification is complete. After about 10 hours a clearly soluble fibrous cellulose triacetate is formed which may be worked up similarly as described in Example 1.

We claim:

1. In the production of fibrous fatty acid esters of cellulose from cellulose which has been pretreated with a lower fatty acid, the modification which comprises reacting the cellulose with an esterifying mixture consisting of a lower fatty acid anhydride, an organic diluent which is a non-solvent for the cellulose ester formed, and an amount of sulfuric acid up to 1% based on the weight of the cellulose as a catalyst at a temperature between 30 and 70° C., the esterification being carried out until the cellulose ester formed dissolves in a mixture of methylene chloride-methylene alcohol (9:1).

2. In the production of fibrous fatty acid esters of cellulose from cellulose which has been pretreated with a lower fatty acid, the modification which comprises reacting the cellulose with an acetylating mixture consisting of acetic acid anhydride, an organic diluent which is a non-solvent for the cellulose acetate formed, an amount of sulfuric acid up to 1% based on the weight of the cellulose as a catalyst at a temperature between 30 and 70° C., the esterification being carried out until the cellulose acetate formed dissolves in a mixture of methylene chloride-methyl alcohol (9:1).

3. In the production of fibrous fatty acid esters of cellulose, the modification which comprises reacting cellulose which has been pretreated with glacial acetic acid, with an acetylating mixture consisting of acetic acid anhydride, an organic diluent which is a non-solvent for the cellulose acetate formed, and between 0.5 to 1% sulfuric acid based on the weight of the cellulose as a catalyst at a temperature between 30 and 70° C., the esterification being carried out until the ester dissolves in a mixture of methylene chloride-methyl alcohol (9:1).

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