PREPARATION OF ORGANIC ACID ESTERS OF CELLULOSE


No Drawing. Application October 7, 1954
Serial No. 461,008
5 Claims. (Cl. 260—229)

This invention relates to the preparation of organic acid esters of cellulose and relates more particularly to an improved process for the preparation of organic acid esters of cellulose which may be carried out in a continuous manner.

In the preparation of organic acid esters of cellulose by the esterification of cellulose with an organic acid anhydride, it is customary to pretreat the cellulose to increase its reactivity and thereby shorten the time required for the esterification. It has recently been suggested that the pretreatment of the cellulose, which may be cotton linters or wood pulp, be carried out in a plurality of stages, one of which includes the treatment of the cellulose with a lower aliphatic acid and a later one of which includes the treatment of the cellulose with a mixture of a lower aliphatic acid and an esterification catalyst, such as sulfuric acid. Prior to these two stages of the pretreatment, the cellulose may be pretreated with water. Cellulose that has been pretreated in accordance with the multi-stage process has an extremely high reactivity and may be esterified with an organic acid anhydride in an extremely short period of time. This pretreatment process accordingly lends itself to the preparation of organic acid esters of cellulose in a continuous manner.

When the foregoing pretreatment process is applied to a mixture of cotton linters and wood pulp, and particularly such a mixture containing about 25 and 90% by weight of wood pulp, it is found that the pretreated cellulose does not have a uniformly high reactivity. As a result, when such a mixture is pretreated and then esterified, the time required for complete esterification, as evidenced, for example, by the clearing of the esterification mixture, becomes quite long so that it is no longer feasible to carry out the pretreatment and esterification in a continuous manner. Since it is common to employ a mixture of cotton linters and wood pulp as the source of cellulose in the preparation of organic acid esters of cellulose, the failure of this pretreatment process to work on such a mixture seriously limits the utility thereof.

The failure of the multi-stage pretreatment process to work effectively on a mixture of cotton linters and wood pulp is most surprising. When the pretreatment of cellulose prior to esterification is carried out in a single stage, as by the treatment of the cellulose with a lower aliphatic acid, the efficiency of the pretreatment in increasing the reactivity of the cellulose is independent of whether cotton linters, wood pulp, or a mixture of the two is employed as the source of cellulose.

It is an important object of this invention to provide a process for the preparation of organic acid esters of cellulose from cellulose comprising a mixture of cotton linters and wood pulp wherein the cellulose is subjected to a multi-stage pretreatment process prior to esterification.

Other objects of this invention will be apparent from the following detailed description and claims.

According to the present invention, organic acid esters of cellulose are prepared from cellulose comprising a mixture of cotton linters and wood pulp, and particularly from such a mixture containing between about 25 and 90% by weight of wood pulp, by separately pretreating the cotton linters and wood pulp by a multi-stage pretreatment process, mixing the pretreated cotton linters and wood pulp, and esterifying such mixture with an organic acid anhydride. When the cotton linters and the wood pulp are pretreated separately and then mixed, the reactivity of the cellulose in the resultant mixture is uniformly high. As a result, the esterification of said mixture proceeds rapidly and the entire process lends itself to operation in a continuous manner.

The multi-stage pretreatment of the cotton linters and the wood pulp may be carried out in the manner described in U. S. Patents Nos. 2,603,634, 2,603,635, 2,603,636, 2,603,637, and 2,603,638. As the initial step in the pretreatment, the cellulose may be conditioned to bring its water content to between about 2 and 10 parts by weight, or preferably between about 3 and 8 parts by weight for each 100 parts by weight of cellulose. Following this step, the cellulose has added thereto between about 20 and 100 parts by weight of a lower aliphatic acid for each 100 parts by weight of cellulose, preferably in the presence of between about 3 and 20 parts by weight of water for each 100 parts by weight of the cellulose. The necessary amount of water present in the cellulose, the lower aliphatic acid, or both. There is then added to the cellulose, without displacing any of the materials previously added thereto, a mixture of a lower aliphatic acid and an esterification catalyst, such as sulfuric acid. Such mixture contains between about 35 and 300 parts by weight of the lower aliphatic acid and between about 3 and 15 parts by weight of esterification catalyst for each 100 parts by weight of cellulose. The pretreated cotton linters and the pretreated wood pulp are then mixed and esterified with an organic acid anhydride. The esterification of the pretreated cellulose should normally take place within a period of about 15 minutes from the time the mixture of lower aliphatic acid and esterification catalyst is added to the cellulose to avoid an excessive degradation of the cellulose molecules by the esterification catalyst. Prior to the esterification, the pretreated cellulose may be cooled to freeze at least a portion of the lower aliphatic acid present therein. The frozen acid, which should comprise at least about 30% of the total acid, absorbs the heat that is liberated during the strongly exothermic esterification reaction and tends to prevent an excessive rise in the temperature of the reaction mixture which would degrade the cellulose molecule.

The multi-stage pretreatment of the cellulose may also be carried out by successively forcing the treating reagents through the cellulose. When the pretreatment is carried out in this manner, the cellulose should be in the form of a sheet so as to permit the same to be handled readily. The sheet of cellulose is first treated with water so as to thoroughly saturate the same. Then, with or without an intermediate pressing step to remove some of the water from the sheet, a lower aliphatic acid is forced through the sheet to displace the water therefrom. The sheet, with or without an intermediate pressing step, has then forced through a mixture of a lower aliphatic acid and an esterification catalyst to displace the lower aliphatic acid therefrom. The so pretreated cotton linters and wood pulp are then mixed and esterified with an organic acid anhydride.
to the esterification, the pretreated cellulose may be cooled to freeze at least a portion of the lower aliphatic acid present therein for the reasons set out above.

The lower aliphatic acids that are employed during the pretreatment are formic acid, acetic acid, propionic acid, and butyric acid, as well as mixtures thereof. It is preferred, when making lower aliphatic acid esters of cellulose, to employ a pretreating acid having the same organic radical as will be present in the ester formed.

The esterification of the pretreated cellulose may be carried out in the presence of a solvent for the ester being formed, which solvent may be the pretreating acid. In this case, the organic acid ester of cellulose will be obtained in the form of a solution. Alternatively, there may be present during the esterification a non-solvent diluent for the organic acid ester of cellulose being formed, in which case the ester will be obtained in the form of a fibrous mass suspended in the esterification mixture.

The process of this invention is useful whenever it is desired to prepare organic acid esters of cellulose from cellulose comprising a mixture of cotton linters and wood pulp. However, it is especially useful when there is present in such mixture between about 25 and 90% by weight of wood pulp, since it is in this range that the greatest difficulty is experienced in obtaining a rapid esterification of all the pretreated cellulose.

The process of this invention will now be described in connection with the production of cellulose acetate which is commercially the most important organic acid ester of cellulose at the present time. It may also be used for the production of cellulose propionate, cellulose butyrate, cellulose acetate formate, cellulose acetate propionate, and cellulose acetate butyrate.

The following example is given to illustrate the invention further.

**Example**

To 4 parts by weight of cotton linters (dry basis) containing 6% by weight of water, there are added 1.4 parts by weight of glacial acetic acid and the whole is stirred for 15 minutes at 25°C. There is then added to the cotton linters a mixture containing 0.24 part by weight of sulfuric acid and 2.8 parts by weight of acetic acid and the whole is stirred for 3 minutes more at 25°C. At the same time, 4 parts by weight of wood pulp (dry basis) containing 7% by weight of water are pretreated in identical manner. The cotton linters and the wood pulp are then blended and the whole is esterified with a mixture containing 24 parts by weight of acetic anhydride, 26.6 parts by weight of acetic acid and 0.6 parts by weight of sulfuric acid. The esterification requires a total of 23 minutes to complete as evidenced by the clearing of the esterification mixture. When the cotton linters and wood pulp are blended before the pretreatment, the esterification requires a total of 36 minutes to complete. The esterification of cotton linters alone requires 27 minutes and the esterification of wood pulp alone requires 23 minutes when the pretreatment is effected in the same manner.

It is to be understood that the foregoing detailed description is merely given by way of illustration and that many variations may be made therein without departing from the spirit of our invention.

Having described our invention, what we desire to secure by Letters Patent is:

1. A process for the production of organic acid esters of cellulose by the esterification of cellulose comprising a mixture of cotton linters and wood pulp, which comprises separately pretreating the cotton linters and wood pulp by a multi-stage pretreating process in which one stage of the pretreatment comprises the treatment of the cellulose with a lower aliphatic acid, and a later stage of the pretreatment comprises the treatment of the cellulose with a mixture of a lower aliphatic acid and an esterification catalyst, blending the pretreated cotton linters and the pretreated wood pulp, and esterifying the blended pretreated cellulose.

2. A process for the production of organic acid esters of cellulose by the esterification of cellulose comprising a mixture of cotton linters and wood pulp containing between about 25 and 90% by weight of wood pulp, which comprises separately pretreating the cotton linters and wood pulp by a multi-stage pretreating process in which one stage of the pretreatment comprises the treatment of the cellulose with between about 20 and 100 parts by weight of a lower aliphatic acid for each 100 parts by weight of cellulose and a later stage of the pretreatment comprises the treatment of the cellulose with a mixture of between about 35 and 300 parts by weight of a lower aliphatic acid and between about 3 and 15 parts by weight of an esterification catalyst for each 100 parts by weight of cellulose, blending the pretreated cotton linters and the pretreated wood pulp, and esterifying the blended pretreated cellulose.

3. A process for the production of cellulose acetate by the esterification of cellulose comprising a mixture of cotton linters and wood pulp, which comprises separately pretreating the cotton linters and wood pulp by a multi-stage pretreating process in which one stage of the pretreatment comprises the treatment of the cellulose with a lower aliphatic acid, and a later stage of the pretreatment comprises the treatment of the cellulose with a mixture of a lower aliphatic acid and sulfuric acid as an esterification catalyst, blending the pretreated cotton linters and the pretreated wood pulp, and esterifying the blended pretreated cellulose.

4. A process for the production of cellulose acetate by the esterification of cellulose comprising a mixture of cotton linters and wood pulp containing between about 25 and 90% by weight of wood pulp, which comprises separately pretreating the cotton linters and wood pulp by a multi-stage pretreating process in which one stage of the pretreatment comprises the treatment of the cellulose with a lower aliphatic acid, and a later stage of the pretreatment comprises the treatment of the cellulose with a mixture of a lower aliphatic acid and sulfuric acid as an esterification catalyst, blending the pretreated cotton linters and the pretreated wood pulp, and esterifying the blended pretreated cellulose.

5. A process for the production of cellulose acetate by the esterification of cellulose comprising a mixture of cotton linters and wood pulp containing between about 25 and 90% by weight of wood pulp, which comprises separately pretreating the cotton linters and wood pulp by a multi-stage pretreating process which comprises the treatment of the cellulose with a lower aliphatic acid, and a later stage of the pretreatment comprises the treatment of the cellulose with a mixture of a lower aliphatic acid and sulfuric acid as an esterification catalyst, blending the pretreated cotton linters and the pretreated wood pulp, and esterifying the blended pretreated cellulose.

6. A process for the production of cellulose acetate by the esterification of cellulose comprising a mixture of cotton linters and wood pulp containing between about 25 and 90% by weight of wood pulp, which comprises separately pretreating the cotton linters and wood pulp by a multi-stage pretreating process which comprises the treatment of the cellulose with a lower aliphatic acid, and a later stage of the pretreatment comprises the treatment of the cellulose with a mixture of a lower aliphatic acid and sulfuric acid as an esterification catalyst, blending the pretreated cotton linters and the pretreated wood pulp, and esterifying the blended pretreated cellulose.

**References Cited** in the file of this patent

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