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HERBERT E. MARTIN, JAMES W. ELDER, AND LINWOOD N. ROGERS, OF CUMBERLAND, MARYLAND, ASSIGNORS TO CELANESE CORPORATION OF AMERICA, A CORPORATION OF DELAWARE

PROCESS OF MAKING ORGANIC ESTERS OF CELLULOSE

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This invention relates to the preparation of organic esters of cellulose, particularly cellulose acetate, by a process that is not only more expeditious than the prior processes but also produces a superior product.

An object of our invention is to provide a process for the esterification and particularly the acetylation of cellulose, which process shortens the period of time required for making such organic esters of cellulose.

Other objects of our invention will appear in the following detailed description.

It has been proposed to pretreat cellulosic material by various methods for rendering the same more reactive to esterifying agents, whereby cellulose esters of superior properties may be formed. We have found that if a cellulosic material is both pretreated and prehydrolized, the cellulosic material may be esterified rapidly, and cellulose esters of superior properties are formed.

In accordance with our invention, we pretreat a cellulosic material, then prehydrolize the same, and then esterify the pretreated and prehydrolized cellulosic material.

The cellulosic material that is to be treated in accordance with our invention may be any suitable cellulosic material commonly employed for making cellulose esters. Examples of such cellulosic material are cotton, cotton linters, purified wood pulp, reconstituted cellulose, etc.

The pretreatment process comprises the treatment of the cellulosic material with a suitable proportion of a lower fatty acid such as formic acid or acetic acid or with a mineral acid such as hydrochloric acid. The formic or acetic acid may be applied to the cellulosic material in any suitable manner, either in the form of a liquid, or in the form of a vapor. One mode of pretreatment comprises the agitation of the cellulosic material with a relatively small amount of glacial acetic acid in a suitable apparatus, say a horizontal type of agitator. Instead of glacial acetic acid, weaker acetic acid of from 50% to 90% strength may be used.

Instead of employing the organic acid in the liquid state, pretreatment may be effected by subjecting the cellulosic material to the vapors of the acid, such as acetic acid, formic acid or hydrochloric acid, the vapors being employed either alone or in admixture with an inert gaseous carrier, such as air, nitrogen, carbon dioxide, etc., or the vapors may be generated by soaking the cellulosic materials in concentrated or dilute acids and subsequently passing air or other inert gas through the materials. Preferably after pretreatment, air or other inert gas is passed through the materials in order to remove the acid wholly or partially.

The temperature of the pretreatment may be boiling temperatures of the organic acid used, or it may be below such temperature, and may be ordinary temperature or even below ordinary temperature. The time of treatment may be varied from one hour to five hours or more, depending on the concentration, amount, and nature of the organic acid used, and the temperature employed. The amount of the lower fatty acid used may be varied within wide limits, but we have found that if glacial acetic acid is used, excellent results are obtained by employing 10 to 30 parts of the glacial acetic acid to 100 parts of the cellulose.

After the cellulosic material has been subjected to a pretreatment process, it is then given a "prehydrolysis" treatment. This "prehydrolysis" comprises subjecting the cellulosic material to a bath containing the liquids normally used for esterifying cellulose, but which bath contains little or no catalysts for promoting the esterification, so that practically no esterification takes place. During this prehydrolysis treatment, any water that may be contained in the cellulosic material is destroyed, and probably the cellulose is hydrolized to some extent. The mixture of cellulosic material and prehydrolysis bath is stirred for a while and then a small amount of alkaline material or alkaline salts of weak acids, e. g. sodium acetate, may be added to neutralize all or part of the trace of acid catalyst that is present, and the mass is then further stirred. As stated, the prehydrolysis bath contains a mixture of liquids such as are used for esterifying cellulose

minus the necessary catalysts. Thus, if cellulose acetate is to be made, the prehydrolysis bath will contain acetic anhydride and a solvent or diluent such as glacial acetic acid or benzol.

After the "prehydrolysis", the esterification process is initiated. During the prehydrolysis, no cooling is necessary although it may be used. The mixture is then cooled to some extent to a temperature sufficiently low so that the temperature during esterification does not exceed a certain maximum, say 60° C. The esterifying catalysts, such as sulfuric acid, is then added and the esterification process now proceeds. Due to the prior treatments, the cellulosic material is in a very reactive and uniform condition, so that upon addition of the catalysts, a very smooth and quick reaction takes place. In the case of the acetylation of cellulose, the temperature rises in the course of 30 minutes from 8° or 10° C. to about 42° to 45° C. At the peak temperature, the acetylation process is practically completed. The reacting mass is then cooled and is then subjected to the normal procedure of ripening, etc.

The process may be employed for preparing various organic esters of cellulose such as cellulose acetate, cellulose formate, cellulose propionate or cellulose butyrate. However, further details will be given with respect to the manufacture of cellulose acetate and the properties of cellulose acetate produced in accordance with our invention.

When yarns are made from ordinary cellulose acetate, the yarns or fabrics produced therefrom become delustered when subjected to the action of boiling water or boiling dilute soap solutions. However, yarns or fabrics made of cellulose acetate made in accordance with our invention are highly resistant to the action of boiling water or boiling soap solutions, so that yarns or fabrics made of cellulose acetate prepared in accordance with our invention can be treated for a much longer time in such hot aqueous baths without losing their luster appreciably. This property of resistance to delustering in boiling water or soap solutions is of great benefit, for instance in the dyeing or cleaning of such yarns or fabrics.

To further illustrate our invention but without in any way being limited thereto, the following detailed description of one mode of carrying out the same is given:

Example

The cellulosic material is first subjected to a pretreatment process which comprises, for instance spraying 20 lbs. of glacial acetic acid onto 100 lbs. of cotton linters. The mixture is stirred in a wooden vessel of the horizontal type for a period of time which may be up to three hours. While the pretreatment is going on, the acetylizer proper is charged with 500 to 600 lbs. say, 560 lbs. of a mixture of glacial acetic acid and acetic anhydride, the acetic anhydride comprising 38 to 39% of the mixture. This mixture of acetic anhydride and glacial acetic acid also contains about 2 oz. of sulfuric acid. The mixture is then cooled to about 8° C.

After pretreatment the cellulosic material is added to the acetylizer containing the acetic acid and acetic anhydride. The temperature soon rises from about 8 to 15° C., and as soon as the latter temperature is reached, 2 oz. of sodium carbonate are added to the mass. Stirring is continued for about an hour and then the temperature is reduced to about 8° C. This part of the process comprises the prehydrolysis treatment.

To cause acetylation, a mixture containing 13 to 16 lbs. say, 14½ lbs. of sulfuric acid and 100 lbs. of a mixture of acetic anhydride and glacial acetic acid of the strength mentioned above, is now added. The temperature rises in the course of about 25 minutes to about 43° C., which is the peak of the reaction. The acetylation reaction is now practically complete and there are practically no visible fibres in the mass. The mass is then cooled down and ripened in any suitable manner to the normal acetone soluble stage.

The term prehydrolysis used in the specification and claims refers to the treatment described, and it is to be understood that the term does not necessarily mean that hydrolysis actually takes place in the treatment.

It is to be understood that the foregoing detailed description is given merely by way of illustration and that our invention is in nowise limited thereto.

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

1. In the method of making organic esters of cellulose, the steps of subjecting cellulose to pretreatment with a lower fatty acid and then to a pretreatment with an organic acid anhydride in the absence of sufficient catalyst to cause esterification of the cellulose.

2. In the method of making cellulose acetate, the steps of subjecting cellulose to pretreatment with a lower fatty acid and then to a pretreatment with acetic anhydride and a liquid diluent in the absence of sufficient catalyst to cause esterification of the cellulose.

3. In the method of making cellulose acetate, the steps of subjecting cellulose to pretreatment with acetic acid and then to a pretreatment with acetic anhydride and a liquid diluent in the absence of sufficient catalyst to cause esterification of the cellulose.

4. The method of preparing organic esters of cellulose comprising subjecting cellulose to pretreatment by agitating the same with a relatively small amount of a lower fatty acid, then prehydrolizing the cellulose by subjecting the cellulose to a bath containing

acetic anhydride, which bath does not contain sufficient catalyst to cause appreciable esterification, whereby prehydrolysis takes place, and then adding an esterification promoting catalyst to cause esterification.

5. The method of preparing cellulose acetate comprising subjecting cellulose to pretreatment by agitating the same with a relatively small amount of a lower fatty acid, then prehydrolizing the cellulose by subjecting the cellulose to a bath containing acetic anhydride, which bath does not contain sufficient catalyst to cause appreciable acetylation, whereby prehydrolysis takes place, and then adding an acetylation promoting catalyst to cause acetylation.

6. Method of preparing cellulose acetate comprising subjecting cellulose to pretreatment by agitating the same with a relatively small amount of acetic acid, then prehydrolizing the cellulose by subjecting the cellulose to a bath containing acetic anhydride, which bath does not contain sufficient catalyst to cause appreciable acetylation, whereby prehydrolysis takes place, and then adding an acetylation promoting catalyst to cause acetylation.

7. Method of preparing cellulose acetate comprising subjecting cellulose to pretreatment by agitating the same with a relatively small amount of acetic acid, then prehydrolizing the cellulose by subjecting the cellulose to a bath containing acetic anhydride, which bath does not contain sufficient catalyst to cause appreciable acetylation, whereby prehydrolysis takes place, and then adding sulfuric acid to cause acetylation.

8. Method of making cellulose acetate of high clarity and/or deluster resistant properties comprising mixing 100 parts of cotton linters with substantially 20 parts of glacial acetic acid, then mixing the mixture with substantially 500 to 600 parts of a mixture containing glacial acetic acid and acetic anhydride and then adding from 13 to 16 parts of sulfuric acid and substantially 100 parts of a mixture of glacial acetic acid and acetic anhydride.

9. A two-stage process of rendering cellulose more reactive towards esterification, comprising first treating the same with an organic acid and then with organic acid anhydride in the absence of sufficient catalyst to cause esterification of the cellulose.

In testimony whereof, we have hereunto subscribed our names.

HERBERT E. MARTIN.
JAMES W. ELDER.
LINWOOD N. ROGERS.