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PREPARATION OF ORGANIC ACID ESTERS OF CELLULOSE

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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 in a continuous manner.

In the preparation of organic acid esters of cellulose by the esterification of a cellulosic material, it is customary to pretreat the cellulosic material before esterification to increase its reactivity and thereby reduce the total esterification time. This pretreatment may, for example, be effected by mixing the cellulosic material for a period of several hours with a lower aliphatic acid in either liquid or vapor form. Following the pretreatment, the cellulosic material is entered into an esterification mixture comprising an organic acid anhydride, a diluent or a solvent for the ester being formed and an esterification catalyst.

The reaction which takes place when the pretreated cellulosic material is entered into the esterification mixture is strongly exothermic and tends to raise the temperature of said mixture. If the temperature is permitted to rise unchecked, it will cause a degradation of the cellulose molecule, resulting in the production of an organic acid ester of cellulose of extremely low viscosity that is not suited for the preparation of filaments and films. To prevent such a degradation of the cellulose molecule, the esterification mixture is cooled initially to a low temperature and, in addition, external cooling is applied to the reaction mixture with the object of further controlling the temperature thereof. Usually, the heat generated during the esterification is permitted to cause a gradual and controlled increase in the temperature of the reaction mixture over a period of several hours to a peak of 35 to 50° C. At this stage of the esterification, a part of the cellulosic material is not completely esterified. Accordingly, the reaction mixture is held at the peak temperature for an additional period of several hours until all of the cellulosic material is fully esterified.

Since both the pretreatment and the esterification require several hours, it has hitherto not been practical to carry on these steps in a continuous manner. Instead, it has been necessary to carry on both the pretreatment and esterification on a batch basis, requiring a large number of individual reactors, thus involving a great deal of labor and a large capital outlay.

It is an important object of this invention to provide a process for preparing organic acid esters of cellulose which will be free from the

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foregoing and other disadvantages of the processes hitherto employed for this purpose and which will be especially simple and efficient in operation.

A further object of this invention is the provision of a process for preparing organic acid esters of cellulose which may be carried out in a continuous manner.

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

According to this invention, the cellulosic material is conditioned so that it has a moisture content of between about 5 and 8% by weight, or preferably between about 6.5 and 8.0% by weight, and the conditioned cellulosic material is then subjected to a pretreatment in two stages. In the first stage of the pretreatment, the cellulosic material is treated with a lower aliphatic acid. Then, after an interval of at least about 2 minutes, the cellulosic material is treated for a period not exceeding about 15 minutes with an additional quantity of a lower aliphatic acid containing from about 5 to 15 parts by weight, for each 100 parts by weight of the cellulosic material, of an esterification catalyst.

I have found that by means of this novel process, the time necessary for the pretreatment may be reduced materially from that previously necessary. In addition, the reactivity of the cellulosic material is greatly increased so that the esterification of the pretreated cellulosic material proceeds to completion more rapidly than heretofore. The reactivity of the pretreated cellulosic material is so great that, despite external cooling, the heat liberated by the exothermic esterification reaction raises the temperature of the esterification mixture to values high enough to cause a degradation of the cellulose molecule. To prevent such an excessive increase in temperature during esterification, the pretreated cellulosic material is cooled so as to cause at least a portion of the lower aliphatic acid present therein to freeze.

The pretreated cellulosic material, containing the frozen lower aliphatic acid, is then brought into contact with an organic acid anhydride which has been cooled to a temperature below about 10° C. The temperature of the mixture so formed is permitted to rise to a value of between about 15 and 25° C., and is held within said temperature range of between about 15 and 25° C. for a period of from about 1 to 10 minutes. The temperature of the esterification mixture is then permitted to rise further to a value of from

about 30 to 65° C., with the application of external heat, if necessary, and it is held within said temperature range until the esterification is complete. I have found that the major portion of the cellulosic material is esterified without suffering any appreciable loss in viscosity during the initial stages of the esterification, i. e. while the temperature of the reaction mixture is below about 25° C. When the temperature is raised, the relatively small proportion of unesterified cellulosic material still present is esterified rapidly without in any way impairing the properties of the organic acid ester of cellulose being produced.

In accordance with my invention, the time required for both the pretreatment and esterification of the cellulosic material may be reduced to as little as 10 minutes, or even less. Accordingly, the pretreatment and esterification may be readily carried out in a continuous manner.

While my invention will be described in connection with the preparation of cellulose acetate, it is to be understood that it is also applicable to the preparation of other organic acid esters of cellulose such as, for example, cellulose propionate, cellulose acetate-propionate, cellulose butyrate, cellulose acetate-butyrate and the like.

The process of the present invention may be applied to any suitable cellulosic material such as, for example, cotton linters or wood pulps or the like from which the lignin, pentosan, resins and similar constituents have been removed, as for example, sulfite pulp, sulfate pulp or soda pulp. In addition, there may be employed cellulosic material derived from other sources such as bamboo, reeds, jute, esparto, bagasse, straws such as linseed and hempseed straw, grasses, peanut hulls, bark, etc. The cellulosic material may be employed in the form of a mass of loose fibers, or in the form of a sheet of matted cellulosic fibers, which sheet may be forwarded continuously while the several treating media are applied thereto.

Before the cellulosic material is pretreated, it must be conditioned so that it has a moisture content of between about 5 and 8% by weight, or preferably between about 6.5 and 8.0% by weight. This conditioning may be readily effected by spraying the required quantity of water onto the cellulosic material, or by passing the cellulosic material through a chamber maintained at a high humidity by the injection therein of steam or water. I have found that if the moisture content of the cellulosic material drops below the value specified, the pretreatment and esterification will both require a considerably longer period of time. I have also found that the addition of water to the lower aliphatic acid employed for pretreating the cellulosic material is not equivalent to the presence of moisture in the cellulosic material in that it does not reduce the time required for pretreatment and esterification. If, on the other hand, the moisture content of the cellulosic material rises above the value specified, the excess water will hydrolyze a portion of the organic acid anhydride employed for the esterification, necessitating the use of larger quantities of anhydride and liberating a great deal of heat which will tend to cause an undesirable increase in the temperature of the esterification mixture.

Any of the lower aliphatic acids including acetic, propionic and butyric acids, or mixture thereof, may be employed during the first pretreating stage in concentrations ranging from about 80 to 100% by weight, the remainder being water, and in quantities ranging from about 15 to 75 parts by weight for each 100 parts by weight of the cellulosic material. If desired, up to about 2 parts by weight of an esterification catalyst may be added to the lower aliphatic acid for each 100 parts by weight of the cellulosic material. The time of pretreatment during the first stage is not critical and may range from as little as 2 minutes, or even less, to any desired value. Although shorter pretreating periods during this stage are preferred as being most efficient, longer pretreating periods are not objectionable since they do not affect unfavorably the properties of the pretreated cellulosic material. The lower aliphatic acid may be applied to the cellulosic material at room temperature or at a temperature above or below room temperature, but is preferably applied at a temperature of from about 30 to 40° C. for best results.

After the first pretreating stage and before the second pretreating stage, an interval of at least about 2 minutes is permitted to elapse, during which time the lower aliphatic acid enters into the fibers of the cellulosic material. This interval may be kept to a minimum by bringing the cellulosic material to a temperature ranging from about 40 to 80% C. In a continuous process, the necessary interval of time between the first and second pretreating stages may be obtained by applying the pretreating agents at spaced points and forwarding the cellulosic material from one point to another at a given speed.

The first pretreating stage is followed by the second pretreating stage wherein the cellulosic material is treated for a period not exceeding about 15 minutes with an additional quantity of a lower aliphatic acid containing from about 5 to 15 parts by weight of an esterification catalyst for each 100 parts by weight of the cellulosic material. If a longer pretreating period is employed, there is the danger that the high concentration of esterification catalyst will degrade the cellulose molecule and thereby cause an excessive reduction in the viscosity of the final product, rendering the same unsuitable for the preparation of filaments and films. The lower aliphatic acid is employed in concentrations ranging from about 95 to 100% by weight, the remainder being water, and in quantities ranging from about 200 to 600 parts by weight for each 100 parts by weight of the cellulosic material. The lower aliphatic acid containing the esterification catalyst may be applied to the cellulosic material at room temperature or at a temperature above or below room temperature.

Any of the known esterification catalysts may be employed for pretreating the cellulosic material in accordance with this invention, but it is preferred to employ sulfuric acid for this purpose since it produces a cellulosic material having the highest reactivity in the shortest period of time.

The pretreating agents may be applied to the cellulosic material in any desired manner. For example, they may be sprayed or rolled onto the cellulosic material, or when the cellulosic material is in sheet form, they may be applied as a continuous film from a perforated or slotted conduit extending the width of the sheet.

During the second pretreating stage, the cellulosic material is cooled to a temperature below the freezing point of the lower aliphatic acid employed for the pretreatment and is held at this temperature until at least about 30% of the lower aliphatic acid is frozen. When acetic acid is employed for the pretreatment, the cellulosic mate-

rial is cooled to below about 15° C. to effect the freezing of the acid. The pretreated cellulosic material, containing the frozen lower aliphatic acid, is esterified by treatment with from about 200 to 250 parts by weight, for each 100 parts by weight of the cellulosic material, of an organic acid anhydride which has been cooled to a temperature of below about 10° C. If desired, up to about 100 parts by weight of lower aliphatic acid and 2 parts by weight of esterification catalyst, may be added to the organic acid anhydride, with a corresponding reduction in the quantities of said materials employed during the second pretreating stage. The temperature of the esterification mixture is permitted to rise to a value of between about 15 and 25° C. and is held within said temperature range for a period of from about 1 to 10 minutes. The temperature of the esterification mixture is then permitted to rise further to a value of from about 30 to 65° C., with the application of external heat, if necessary, and it is held within said temperature range of from about 30 to 65° C. until the esterification is complete, which normally takes about 2 to 15 minutes. The temperature of the esterification mixture may be permitted to rise continuously during the esterification, provided that it remains within the range of values set forth above for the time specified.

After the esterification is complete, a sufficient quantity of water is added to the esterification mixture to convert any remaining organic acid anhydride to the corresponding acid, following which the cellulose ester, preferably after the addition of a further quantity of water, is permitted to hydrolyze or ripen to impart the desired solubility characteristics thereto. The cellulose ester is then precipitated from the esterification mixture, washed to free it from acids and other impurities, stabilized, if necessary, washed again and finally dried.

The following example is given to illustrate this invention further.

Example

A mass of willowed cotton linters is passed continuously at a rate of 5 parts by weight per minute through a cylindrical mixer equipped with stirrer blades and having a length to give a total retention time of the cotton linters in the mixer of 2 minutes. A sufficient quantity of water is sprayed into the mixer to bring the moisture content of the cotton linters to 7.5% by weight. The so-conditioned cotton linters are entered continuously into a second cylindrical mixer equipped with stirrer blades and with a jacket through which a heating medium is passed to raise the temperature of the cotton linters to 35° C. As the conditioned cotton linters enter the second cylindrical mixer, they are sprayed with acetic acid in an amount of 35 parts by weight of acid for each 100 parts by weight of cotton linters. The cotton linters remain in the second cylindrical mixer for 2 minutes and are then entered continuously into a third cylindrical mixer equipped with stirrer blades and a jacket to maintain the temperature of the pretreated cotton linters at 35° C. As the cotton linters enter the third cylindrical mixer, they are sprayed with a mixture of acetic acid and sulfuric acid in an amount of 172 parts by weight of acetic acid and 14 parts by weight of sulfuric acid for each 100 parts by weight of cotton linters. The cotton linters are held in the third cylindrical mixer for 2 minutes with a cooling medium passed through the jacket to reduce the temperature of the pretreated cotton linters to 15° C. and freeze at least a portion of the acetic acid.

From the third mixer, the pretreated cotton linters are entered continuously into a first acetylizer equipped with stirrer blades and with a jacket through which a cooling medium is passed to control the temperature of the esterification mixture to a maximum of 25° C. Simultaneously, there is entered into the first acetylizer a mixture of acetic anhydride and acetic acid cooled to −15° C. in an amount of 249 parts by weight of acetic anhydride and 166 parts by weight of acetic acid for each 100 parts by weight of cotton linters. After 2 minutes in the first acetylizer, the cotton linters are entered continuously into a second acetylizer equipped with stirrers and with a jacket through which a heating medium is passed to bring the temperature of the esterification mixture to 45° C. The esterification mixture remains in the second acetylizer for 6 minutes and is discharged therefrom in the form of a clear viscous dope that may be neutralized, hydrolyzed, precipitated and washed in a manner well known in the art.

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

Having described my invention, what I desire to secure by Letters Patent is:

1. In a process for the preparation of organic acid esters of cellulose from cellulosic material, the steps which comprise subjecting the cellulosic material to a multi-stage pretreatment prior to esterification, one stage of said pretreatment comprising the addition to the cellulosic material of a lower aliphatic acid and another stage of the pretreatment comprising the addition to the cellulosic material containing the lower aliphatic acid of a further quantity of a lower aliphatic acid containing from about 5 to 15 parts by weight of an esterification catalyst for each 100 parts by weight of cellulosic material without displacing any of the lower aliphatic acid contained in the cellulosic material, freezing at least a portion of the lower aliphatic acid contained in the cellulosic material, and esterifying the cellulosic material containing the frozen lower aliphatic acid and all the pretreating agents within a period of less than about 15 minutes after the addition thereto of the lower aliphatic acid containing the esterification catalyst.

2. Process according to claim 1, wherein at least about 30% by weight of the lower aliphatic acid in the cellulosic material is frozen.

3. Process according to claim 1, wherein the esterification is effected by first holding the esterification mixture at a temperature of from about 15 to 25° C., and then holding said mixture at a temperature of from about 30 to 65° C. until the esterification is complete.

4. Process according to claim 1, wherein from about 15 to 75 parts by weight of acetic acid for each 100 parts by weight of cellulosic material are employed during the initial stage of the pretreatment, from about 200 to 600 parts by weight of acetic acid for each 100 parts by weight of cellulosic material are employed during the subsequent stage of the pretreatment, and sulfuric acid is employed as the esterification catalyst.

5. Process according to claim 4 wherein at least about 30% of the acetic acid in the cellulosic material is frozen and wherein the esterification is

effected by first holding the esterification mixture at a temperature of from about 15 to 25° C. for a period of from about 1 to 10 minutes, and then holding said mixture at a temperature of from about 30 to 65° C. until the esterification is complete.

6. In a process for the preparation of cellulosic acetate from cellulosic material, the steps which comprise subjecting the cellulosic material to a multi-stage pretreatment prior to acetylation, one stage of said pretreatment comprising the addition to the cellulosic material of a lower aliphatic acid and another stage of the pretreatment comprising the addition to the cellulosic material containing the lower aliphatic acid of a further quantity of a lower aliphatic acid containing from about 5 to 15 parts by weight of an acetylation catalyst for each 100 parts by weight of cellulosic material without displacing any of the lower aliphatic acid contained in the cellulosic material, freezing at least a portion of the lower aliphatic acid contained in the cellulosic material, and acetylating the cellulosic material containing the frozen lower aliphatic acid and all the pretreating agents within a period of less than about 15 minutes after the addition thereto of the lower aliphatic acid containing the acetylation catalyst.

7. Process according to claim 6, wherein at least about 30% by weight of the lower aliphatic acid in the cellulosic material is frozen.

8. Process according to claim 6, wherein the acetylation is effected by first holding the acetylation mixture at a temperature of from about 15 to 25° C., and then holding said mixture at a temperature of from about 30 to 65° C. until the acetylation is complete.

9. Process according to claim 6, wherein from about 15 to 75 parts by weight of acetic acid for each 100 parts by weight of cellulosic material are employed during the initial stage of the pretreatment, from about 200 to 600 parts by weight of acetic acid for each 100 parts by weight of cellulosic material are employed during the subsequent stage of the pretreatment, and sulfuric acid is employed as the acetylation catalyst.

10. Process according to claim 9 wherein at least about 30% of the acetic acid in the cellulosic material is frozen and wherein the acetylation is effected by first holding the acetylation mixture at a temperature of from about 15 to 25° C. for a period of from about 1 to 10 minutes, and then holding said mixture at a temperature of from about 30 to 65° C. until the acetylation is complete.

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