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PREPARATION OF CELLULOSE ESTERS

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This invention relates to the preparation of cellulose esters, and relates more particularly to the pretreatment of cellulosic material whereby said material is rendered more reactive toward subsequent treatments, and to the preparation of organic acid esters of cellulose from said pretreated cellulosic material.

In the production of organic acid esters of cellulose, cellulosic material is usually esterrified with an organic acid anhydride in the presence of an esterification catalyst and an organic acid which acts as a solvent for the cellulose ester. It has been customary to pretreat the cellulosic material before esterification to render said material more reactive during the esterification step. Various expedients have been proposed to carry out such pretreatment. In some instances the cellulosic material is pretreated with alkaline swelling agents, and in other instances the cellulosic material is pretreated with lower aliphatic acids in either liquid or vapor form. These pretreatments have been of some value in increasing the reactivity of the cellulosic material, but even when such pretreatments are employed the time necessary for esterification has ranged from 2 to 7 hours, or more. Moreover, the time necessary to carry out the pretreatment has ranged from 2 to 5 hours, or more, so that the total time necessary for pretreatment and esterification has ranged from 4 to 12 hours, or more. As a result, it has hitherto been necessary to carry out both the pretreatment and the esterification on a batch basis requiring a large number of individual reactors, thus involving 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 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 on a continuous basis.

Another object of this invention is to provide a process for preparing organic acid esters of cellulose in which cellulosic material is subjected to a two-stage pretreatment prior to esterification.

A still further object of this invention is to provide a two-stage process for pretreating cellulosic material.

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

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In its broadest aspect this invention comprises a process for the preparation of organic acid esters of cellulose from cellulosic material, in which the cellulosic material is subjected to a two-stage pretreatment prior to esterification. In the first stage of the pretreatment the cellulosic material is treated with a lower aliphatic acid, and in the second stage the cellulosic material is treated for a period not exceeding about 15 minutes with an additional quantity of a lower aliphatic acid containing substantially all, namely from about 5 to 15 parts by weight of the esterification catalyst which will be employed during the subsequent esterification for each 100 parts by weight of the cellulosic material. Thereafter, an organic acid anhydride is added to the mixture formed during the pretreatment and esterification proceeds rapidly to completion. The lower aliphatic acid employed during the pretreatment acts as a solvent for the cellulose ester, forming a clear dope of satisfactory viscosity.

During both stages of the pretreatment the pretreating agents must be so distributed as to reach all of the cellulosic material. If any of the cellulosic material is left untreated, it will not be esterified during the esterification period, producing a cloudy dope containing unesterified particles.

While our 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 the simple and mixed lower aliphatic acid esters including cellulose propionate, cellulose butyrate, cellulose acetate propionate and cellulose acetate butyrate. In addition, it is applicable to the preparation of such organic acid esters of cellulose as cellulose acetate stearate, as well as to the benzoic acid ester of cellulose.

The process of the present invention may be applied to any suitable cellulosic material, such as, cotton linters, or wood pulps or the like from which the lignin, pentosan, resins and similar constituents have been removed, as, for example, purified 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, staws such as linseed and hempseed straw, grasses, peanut hulls, bark, etc. The cellulosic material may be pretreated

in the form of a mass of loose fibers, or in the form of a sheet, strip or board.

Any of the lower aliphatic acids including acetic, propionic and butyric acids may be employed during the first pretreating stage in concentrations ranging from about 80 to 100% by weight and in quantities ranging from about 15 to 75 parts by weight for each 100 parts by weight of the cellulosic material. When the proportion of lower aliphatic acid is either larger or smaller than the preferred range, it has been found that the reactivity of the pretreated cellulosic material and the clarity of the final dope decreases rapidly. 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, depending upon the efficiency with which the pretreating agent is distributed, may range from 2 seconds, or even less, to any desired value. Although shorter pretreating periods during this stage are preferred as being most efficient in the use of equipment and personnel, longer pretreating periods are not objectionable since they do not affect unfavorably the properties of the pretreated cellulosic material.

After the first pretreating stage, it may be desirable, in certain instances, to permit the cellulosic material to stand for at least about 2 minutes before continuing with the pretreatment. This allows the lower aliphatic acid to diffuse through the mass or thickness of cellulosic material and into the cellulose fibers, particularly when the cellulosic material is in the form of a sheet, strip or board. In a continuous process, the necessary interval of time may be obtained by applying the pretreating agents at spaced points and moving the cellulosic material from one point to the other at a given speed.

The first pretreating stage is followed, in the second pretreating stage, by the treatment of the cellulosic material for a period not exceeding about 15 minutes with an additional quantity of a lower aliphatic acid containing substantially all, namely from about 5 to 15 parts by weight of the esterification catalyst for each 100 parts by weight of the cellulosic material. The lower aliphatic acid is preferably employed in concentrations ranging from about 95 to 100% by weight and in quantities ranging from about 200 to 600 parts by weight for each 100 parts by weight of the cellulosic material.

Various esterification catalysts may be employed during the pretreatment in accordance with the process of this invention, but sulfuric acid is preferred for this purpose since it produces a cellulosic material having the highest reactivity in the shortest period of time. In addition to sulfuric acid, the esterification catalyst may also be phosphoric acid, zinc chloride or any other of the catalysts that are well known for this purpose.

Both stages of the pretreatment may be carried out at room temperature or at temperatures above or below room temperature. However, pretreatment at temperatures above or below room temperature is somewhat less desirable owing to the necessity for artificially heating or cooling the pretreating agents and the cellulosic material.

In the pretreating processes hitherto proposed, no special care has been needed to insure that all of the cellulosic material will come into contact with the pretreating agents, since the pretreating periods have ranged from two hours upwardly. However, if the high concentration of catalyst employed in the second pretreating stage of this invention were to be left in contact with a cellulosic material for two hours, or more, it would cause a serious degradation of the cellulosic material as a result of which the cellulosic material would no longer be suitable for the production of organic acid esters of cellulose. Accordingly, the time of pretreatment during the second stage which may be as low as about 2 seconds, or less, must be limited to not more than about 15 minutes. It is, therefore, particularly important that during this extremely short pretreating period, the pretreating agent be distributed so as to reach all of the cellulosic material to avoid the production of a cloudy dope containing unesterified particles.

Although it has previously been suggested that a loose mass of cellulosic fibers be stirred continuously or intermittently to distribute the pretreating agent during pretreatment, the degree of stirring has been relatively slight since the pretreating periods have ranged from two hours upwardly. During this extended period of time a considerable amount of diffusion and vaporization of the pretreating agent occurs, insuring that all of the cellulosic material will be reached thereby. When, however, the pretreating period is reduced to not more than about 15 minutes or even as low as 2 seconds, or less, more vigorous means are necessary to insure a thorough distribution of the pretreating agent. Various expedients may be employed to achieve this thorough distribution. For example, when a loose mass of cellulosic fibers is employed the cellulosic fibers and the pretreating agent may be introduced into a stirrer equipped with paddle wheels operating at speeds ranging from about 50 to 1200 R. P. M., or more, for a suitable period of time. When employing equipment of this type it is important to avoid the presence of dead spots in which a portion of the cellulosic fibers may remain during the pretreating period without coming into contact with the pretreating agent. The cellulosic fibers and the pretreating agent may also be introduced into a pulp beater or a pulp refiner of the type employed in paper manufacture which will fibrillate the cellulosic fibers during pretreatment as is more fully disclosed in our copending application, Serial Number 47,324, filed September 1, 1948. The same or different types of apparatus may be employed to distribute the pretreating agents over the cellulosic material during the two stages of the pretreatment. If desired, an interval of about 2 minutes, or more, may be permitted to elapse between the first and second stages of the pretreatment to allow the pretreating agent to diffuse through the cellulosic material.

On the other hand, when a sheet, strip or board of cellulosic material is employed, the pretreating agents may be applied to one or both surfaces of said sheet, strip or board by spraying, dipping, roller coating or other similar manner. It is important, in this case, to allow a time interval to elapse between the first and second stages of pretreatment to permit the pretreating agent employed during the first stage to diffuse through the cellulosic material. After the second pretreating agent is applied, the sheet, strip or board of cellulosic material may be fed directly into an acetylizer. However, if desired, the sheet, strip or board may first be disintegrated in an agitator, by means of a rapidly rotating wire brush or in any

other manner before being fed to the acetylizer.

To test the adequacy with which a given procedure distributes the pretreating agents through the cellulosic material during either of the two pretreating stages, a small amount of a dye such as amethyst violet may be added to the pretreating agent during a trial run. When the cellulosic material is uniformly colored or is substantially free from undyed particles at the end of the trial run, the procedure for distributing the pretreating agents is adequate for the purpose of this invention.

Esterification may be carried out by mixing from about 180 to 370 parts by weight of an organic acid anhydride for each 100 parts by weight of cellulosic material with a mixture of the cellulosic material and the pretreating agents. The organic acid anhydride, the cellulosic material containing the pretreating agents, or both may be precooled before being mixed, if desired, or they may be employed at room temperature, or above. Esterification proceeds rapidly and is completed in from about 2 to 10 minutes, or less. The lower aliphatic acid acts as a solvent for the cellulose ester yielding a clear dope of satisfactory viscosity. After esterification is completed, the cellulose ester may be ripened, precipitated by the addition of water to the dope, stabilized, if desired, and dried.

When the process of this invention is employed, it is possible to carry out the pretreatment and esterification on a continuous rather than on a batch basis, since the time required for both treatments is sufficiently short to render a continuous process feasible.

The following examples are given as illustrative of this invention.

Example I

A mixture of 100 parts by weight of cotton linters and 35 parts by weight of glacial acetic acid are stirred for 5 minutes in a cylindrical mixer equipped with horizontal paddle wheels operating at 50 R. P. M. An additional 286 parts by weight of glacial acetic acid containing 14 parts by weight of 100% sulfuric acid are introduced into the mixer and stirring continued for 2 minutes. The cotton linters and pretreating agents are introduced into 215 parts by weight of acetic anhydride precooled to 0° C. Esterification proceeds smoothly with the temperature rising to 65° C. at the end of 3 minutes, at which time there is obtained a clear dope of satisfactory viscosity.

Example II

A mixture of 100 parts by weight of cotton linters, 35 parts by weight of glacial acetic acid and 0.5 part by weight of 100% sulfuric acid are stirred for 5 minutes in a cylindrical mixer equipped with horizontal paddle wheels operating at 50 R. P. M. An additional 286 parts by weight of glacial acetic acid containing 13.5 parts by weight of 100% sulfuric acid are introduced into the mixer and stirring continued for 2 minutes. The cotton linters and pretreating agents are introduced into 215 parts by weight of acetic anhydride precooled to 0° C. Esterification proceeds smoothly with the temperature rising to 65° C. at the end of three minutes, at which time there is obtained a clear dope of satisfactory viscosity.

Example III

A mixture of 100 parts by weight of cotton linters, 35 parts by weight of glacial acetic acid and 0.5 part by weight of 100% sulfuric acid are stirred for 5 minutes in a mixer equipped with horizontal paddle wheels operating at 50 R. P. M. An additional 285 parts by weight of acetic acid and 13.5 parts by weight of 100% sulfuric acid are introduced into the cotton linters and the whole run between the plates of a conventional pulp grinder operating at 3600 R. P. M. with the clearance between the plates set at 0.10 inch to fibrillate the cellulosic material. The mixture of fibrillated cellulosic material and pretreating agents is introduced into 215 parts by weight of acetic anhydride precooled to —14° C. Esterification proceeds smoothly with temperature rising to 51° C. at the end of 7 minutes at which time there is obtained a clear dope of satisfactory viscosity.

Example IV

A mixture of 100 parts by weight of cotton linters and 35 parts by weight of glacial acetic acid are stirred for 10 seconds in a cylinder mixer equipped with paddle wheels operating at 1200 R. P. M. The mixture is allowed to stand for 5 minutes, whereupon an additional 285 parts by weight of glacial acetic acid containing 14 parts by weight of 100% sulfuric acid are introduced into the mixer and stirring continued for 30 seconds. The cotton linters and pretreating agents are introduced into 230 parts by weight of acetic anhydride precooled to —10° C. Esterification proceeds smoothly yielding a clear dope of satisfactory viscosity at the end of three minutes.

Example V

Strips of cotton sheet are passed continuously through a spray chamber containing two spaced sets of spray nozzles arranged in such a manner that the sprayed liquid impinges equally and uniformly on both sides of the sheet. From the first set of spray nozzles, glacial acetic acid is sprayed onto the sheets in an amount equal to 35 parts by weight for each 100 parts by weight of cellulosic material. The sheets travel for five minutes before reaching the second set of spray nozzles from which a mixture containing 95% by weight of glacial acetic acid and 5% by weight of 100% sulfuric acid is sprayed onto the sheets in an amount equal to 300 parts by weight of said mixture for each 100 parts by weight of cellulosic material. Thereafter, the sheets are disintegrated by means of a rotating metal brush and the cellulosic material is esterified in the manner outlined in Example IV. Esterification proceeds smoothly yielding a clear dope of satisfactory viscosity at the end of two minutes.

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 our invention.

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

1. In a process for the preparation of organic acid esters of cellulose from cellulosic material wherein the esterification proceeds rapidly, 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 said pretreatment comprising the addition to the cellulosic material containing the lower aliphatic acid of a further quantity of a lower aliphatic acid containing all of an esterification catalyst which will be employed during the sub-

sequent esterification of the cellulosic material without displacing any of the lower aliphatic acid contained in the cellulosic material, and esterifying the pretreated cellulosic material within a period of less than about 15 minutes after the addition thereto of the further quantity of lower aliphatic acid containing the esterification catalyst.

2. Process according to claim 1, wherein cellulose acetate is produced and acetic anhydride is employed as the esterifying agent.

3. In a process for the preparation of organic acid esters of cellulose from cellulosic material wherein the esterification proceeds rapidly, 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 said 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, and esterifying the pretreated cellulosic material within a period of less than about 15 minutes after the addition thereto of the further quantity of lower aliphatic acid containing the esterification catalyst.

4. Process according to claim 3, wherein there is an interval of at least about 2 minutes between the two stages of the pretreatment to permit the diffusion of the lower aliphatic acid through the cellulosic material.

5. Process according to claim 3, wherein acetic acid is employed as the pretreating acid.

6. Process according to claim 3, wherein sulfuric acid is employed as the esterification catalyst.

7. Process according to claim 3, wherein from about 15 to 75 parts by weight of lower aliphatic acid for each 100 parts by weight of cellulosic material are employed during the first stage of the pretreatment, and from about 200 to 600 parts by weight of lower aliphatic acid for each 100 parts by weight of cellulosic material are employed during the following stage of the pretreatment.

8. Process according to claim 7, wherein acetic acid is employed as the pretreating acid, and sulfuric acid is employed as the esterification catalyst.

9. In a process for the preparation of cellulose acetate from cellulosic material wherein the esterification proceeds rapidly, 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 said 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, and esterifying the pretreated cellulosic material with acetic anhydride within a period of less than about 15 minutes after the addition thereto of the further quantity of lower aliphatic acid containing the esterification catalyst.

10. Process according to claim 9, wherein there is an interval of at least about 2 minutes between the two stages of the pretreatment to permit the diffusion of the lower aliphatic acid through the cellulosic material.

11. Process according to claim 9, wherein acetic acid is employed as the pretreating acid.

12. Process according to claim 9, wherein sulfuric acid is employed as the esterification catalyst.

13. Process according to claim 9, wherein from about 15 to 75 parts by weight of lower aliphatic acid for each 100 parts by weight of cellulosic material are employed during the first stage of the pretreatment, and from about 200 to 600 parts by weight of lower aliphatic acid for each 100 parts by weight of cellulosic material are employed during the following stage of the pretreatment.

14. Process according to claim 9, wherein acetic acid is employed as the pretreating acid, and sulfuric acid is employed as the esterification catalyst.

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