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PRETREATMENT FOR ESTERIFICATION OF CELLULOSE IN ATTENUATED FORM

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FIG. 1.

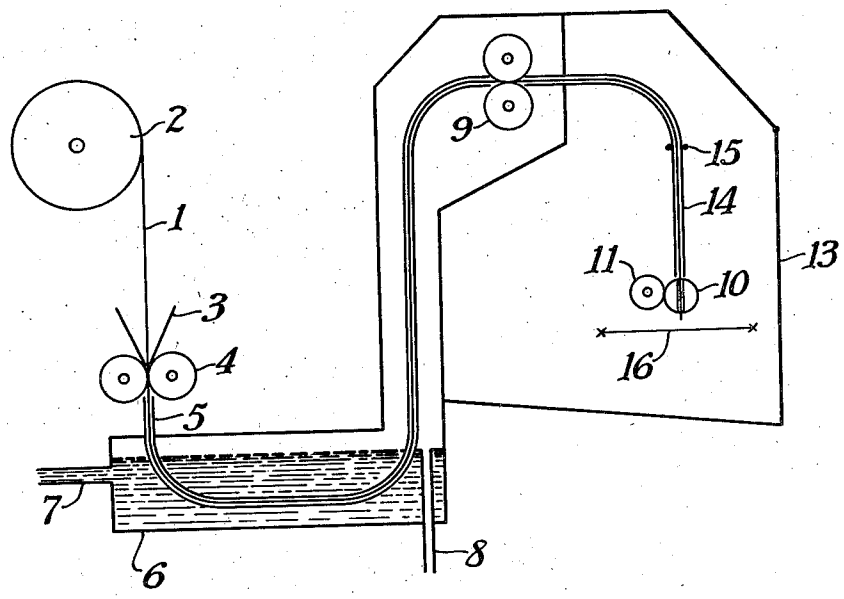
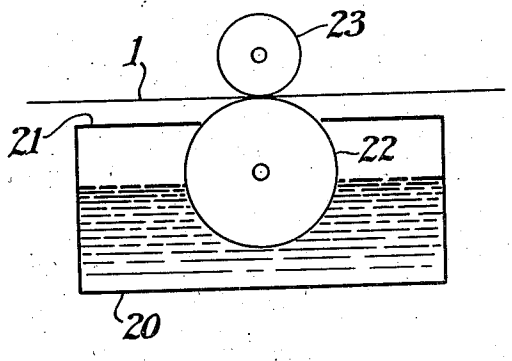


FIG. 2.



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PRETREATMENT FOR ESTERIFICATION OF CELLULOSE IN ATTENUATED FORM

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9 Claims. (Cl. 260—229)

The present invention relates to the treatment of cellulose in attenuated form, such as a sheet, with a suitable pretreatment bath, such as one consisting of one or more lower fatty acids of which at least 40% is acetic acid, enclosing the treated cellulose in suitable containers and allowing it to stand until activated to the desired extent. The cellulose may then be acylated.

This application is a continuation-in-part of my application Serial No. 81,323 filed May 22, 1936.

Ordinarily in the manufacture of cellulose acetate or other cellulose esters, it is customary to pretreat the cellulose with a lower fatty acid either with or without a small amount of catalyst. The pretreatment of the cellulose is usually carried out in the same vessel in which the subsequent esterification is carried out. This method has the disadvantage of requiring the use of an esterification vessel for a relatively long period of time for each batch of cellulose acetate so that the production in the equipment is restricted thereby. If, on the other hand, a separate vessel is employed for the pretreatment of the cellulose, difficulties arise in transferring the pretreated cellulose quantitatively from the pretreatment bath to the reaction vessel.

One object of my invention is to provide a pretreatment for cellulose having a shorter mixer cycle and thereby greatly increasing the capacity of a given amount of esterification equipment. Another object of my invention is to provide a process in which the cellulose, which is to be used for making cellulose esters containing higher acyl will get a better pretreatment. Another object of my invention is to provide a pretreatment process which is more efficient and easily controlled than that carried out with an excess of liquid. A still further object of my invention is to provide a method of pretreatment in which less handling of the cellulose is necessary than was formerly the case in the preparation of cellulose esters.

I have found that cellulose may be uniformly pretreated by contacting a sheet of the cellulose with a pretreatment bath consisting of one or more lower fatty acids containing at least 40% of acetic acid and then, with the sheet in only a moist condition, storing it in a closed container at the temperature and for the length of time desired. It is preferable to compact the treated sheet, such as by rolling it up tightly or cutting it and piling the cut sheets, before or at the time it is put into the container thus further economizing upon equipment. Thus it becomes unnecessary to use the esterification vessel in pretreating the cellulose. The cellulose may thereafter be introduced directly into the reaction mixture without any serious physical disintegration being necessary. Also the cellulose may be given a most satisfactory pretreatment without a large excess of acetic acid being present therein, which is quite important where the subsequent esterification involves the use of reagents in a high proportion to the acetic acid.

My method of pretreating cellulose may consist in providing the cellulose in the form of a continuous sheet or batting and treating the sheet with a lower fatty acid containing a large proportion of acetic acid, either by passing it through the lower fatty acid bath or over a roll moistened with the acid and, if necessary, squeezing the sheet so that about ¼ to 2 parts by weight of the liquid remains therein for every part of cellulose, after which the sheet is, for instance, wound tightly into a roll and the roll is stored either alone or with other rolls in a closed container at the desired temperature and for the desired length of time. This treatment activates the sheet so that it is readily reacted upon by the esterification mixture and weakens the sheet sufficiently so that it is easily disintegrated upon being introduced directly into the esterification vessel containing a stirring device. Thus long soaking of the sheet in an excess of acid is avoided and the amount of pretreatment equipment is reduced to a minimum. The sheet is just as effectively pretreated by my novel method as by soaking in excess acid for the reason that the acid vapors in the enclosed vessel thoroughly permeate every fiber and do the work of a great excess of liquid with much greater economy.

Instead of rolling up the sheet, it may be folded, or cut into pieces and stacked, or some other procedure may be used to bring it together into a compact mass.

It is desirable in order to obtain uniform pretreatment that the acid with which the sheet is treated be kept at the temperature at which the pretreatment is to be carried out. This pretreatment temperature is determined by the amount of activation or the decrease of the cuprammonium viscosity of the cellulose in the pretreatment which it is desired to obtain. For instance, in the manufacture of cellulose acetate where a small amount of catalyst is to be employed, a cellulose of low viscosity is desirable as the starting material for the esterification in order to prevent gelling of the dope formed. Unless the cellulose for preparing cellulose acetate is a low viscosity material, the pretreatment should be carried out

for a longer time or at a higher temperature, such as about 180–220° F., unless large amounts of catalyst are used in the esterification. If, however, the pretreatment is to be followed by another pretreatment employing a catalyst before the acetylation (as I may sometimes do), such a high temperature would be unnecessary as the second pretreatment with a catalyst will serve to lower the viscosity. Where the cellulose is to be used in an esterification in which gelling of the reaction mixture after the esterification is not liable to occur, such as in the esterification of cellulose in a bath containing propionyl or butyryl or a chlorinated hydrocarbon such as ethylene chloride or methylene chloride as the solvent, or when a cellulose having a low viscosity is pretreated, the function of the pretreatment should be primarily to swell the fibers and make them more readily susceptible to esterification rather than to lower the cuprammonium viscosity. In this case where the lowering of the cuprammonium viscosity is not necessary, shorter time of pretreatment or lower pretreatment temperatures, such as 100° F. or ordinary room temperature (70° F.) or some temperature therebetween may be employed. If it is desired to retain the viscosity of a high viscosity cellulose the procedure for merely swelling the fibers only should be employed. In the latter two instances one would be guided merely by the extent of activation of the cellulose necessary or desirable in such instances; experience with subsequent esterification readily indicates the amount of activation required for the specific cellulose being employed.

My pretreatment method may be employed for pretreating any type of cellulose which can be formed into sheets having sufficient mechanical strength to be led over rollers and wound into a sheet as will be described hereinafter. At the present time, cotton and refined wood pulp, such as refined sulfite pulp, are the most commonly employed starting materials for the preparation of cellulose esters. Wood pulp and cotton linters are frequently prepared in sheet form and, therefore, are particularly adaptable to my process.

The liquid employed for pretreating in accordance with my invention should contain a considerable proportion of acetic acid. If either propionic or butyric acid are present it is necessary that the fatty acids of more than 2 carbon atoms constitute not more than 60% of the liquid. It is desirable that the pretreatment liquid be concentrated acid and, for economical reasons, that it contain not more than 10% of a substance that will react with acetic anhydride, such for instance as water or alcohols. The remainder of the liquid should constitute lower fatty acid except in some cases where it is desirable to add a small amount of acylation catalyst such as concentrated sulfuric acid to the pretreatment liquid.

Thus, it is preferred that the pretreatment liquid be nearly anhydrous as the moisture in the cellulose will tend to dilute the acid to some extent; it is preferable that it should be of at least 90% concentration unless the cellulose should have such a small moisture content that no dilution from that moisture would occur. In that case the concentration could be a few per cent below 90% and an economical pretreatment would occur. In other words, my pretreatment method is effective with any concentration or mixture of lower fatty acids and still obtain the result of low equipment cost; however, the limitations given above have been found to be the most practical for the reason that if one allows much water in the pretreatment liquid it merely means that such water (carried over into the esterification) reacts with and uses up more expensive anhydrides in the esterification liquid and makes the esterification difficult to control because of development of reaction heat. Also as the acids above 2 carbon atoms are increased in the pretreatment (above the limitation given) the time or temperature of the pretreatment has to be increased in order to obtain the desired activation.

If desired an acylation catalyst may be present in small amount in the pretreatment bath especially if appreciable reduction of the viscosity of the cellulose is desired. The catalyst may be sulfuric acid, perchloric acid or the like and may be present in an amount up to 5% of the pretreatment liquid.

Apparatus which may be employed for pretreating cellulose, in accordance with my invention, is illustrated by the attached drawing. The method of impregnating the cellulose may be governed by the amount of pretreatment acid which it is desired should be in direct contact with the cellulose during the time of treatment. The cellulose sheet may be treated either by passing the sheet through the pretreatment acid (soaking treatment) followed by squeezing out the excess and/or by passing it over a surface which has been moistened with pretreating acid from which it will absorb the liquid (contact treatment). The soaking treatment is primarily adapted to a treatment in which it is desired that the cellulose contain 1 to 2 parts by weight of the pretreating liquid for every part of cellulose. If, however, the use of a smaller content of the liquid in the cellulose is desired, such as about ½ part or even less of acid to every part of cellulose, the method, in which the cellulose sheet contacts a surface wet with the pretreating acid is suitable.

Fig. 1 illustrates an apparatus in which the soaking of the cellulose sheet in the pretreating liquid is accomplished. The cellulose sheet **1** which is to be pretreated comes rolled-up on the feed roll **2** from which it is led into the apparatus. This is done by feeding the end of the sheet into a guide funnel **3** where the drive rolls **4** start the sheet on its course through the apparatus. In order to direct the sheet through the apparatus, guide plates **5** are provided. There are several sets of these plates provided to direct the sheet. It is preferred that the outer guide plates extend beyond the edges of the sheet and that the space through which the sheet moves be closed by a vertical strip to limit the motion of the sheet in a sidewise direction. After the sheet passes through the drive rolls and into the guide plates, it is led into a vat **6** containing the pretreating liquid such as glacial acetic acid. A sufficient level of the pretreating acid to assure good soaking is maintained by conducting the acid as needed into the vat through the feed pipe **7**. The vat is also provided with an overflow **8** to prevent the level of the acetic acid becoming too high. It is preferred that the sheet contact the pretreating acid long enough to thoroughly saturate the sheet. The temperature of the bath should be held constant and is preferably that at which it is desired that the pulp be treated.

The flow of acid to the bath may be regulated manually or automatically controlled or, if desired, a circulating system with a separate tank or pump may be used. If a circulating tank is used, the bath may overflow into it continuously and make-up acid may be added at appropriate intervals to the circulating system.

The soaked cellulose sheet is then led to the squeeze rolls 9 by which the excess acid is removed. By the arrangement shown, the excess acid squeezed out is returned to the vat containing the pretreating acid. The squeeze rolls should preferably admit of adjustment so that the pressure which is exerted by them upon the sheet can be varied in accordance with the amount of acid which it is desired should remain in the sheet. From the squeeze rolls the sheet is further directed through the guide plates and to the slot in the wind-up roll 10 by means of the swinging guide plates 14 which are hinged at points 15. This wind-up roll is driven by a drive roll 11 of the floating-friction type. The passage of the sheet through the slot of the wind-up roll may be noted by a photo-electric cell unit 16 at this point. By this means the rotation of the drive roll 11 may be started at the proper moment and also the guide plates 14 may be swung clear of the roll of cellulose sheet upon the wind-up roll 10 as it increases in size. Instead of having a photo-electric unit and automatic control, starting of the rotation of the drive roll 11 and the swinging up of the guide plates 14 may be manually operated. When the entire sheet has passed through the apparatus and has been wound upon the wind-up roll, it may be removed from the apparatus through the hinged air-seal plate 13. As a slightly decreased pressure is preferably maintained within the apparatus, this air-seal plate is desirable to avoid drawing a large quantity of air into the apparatus. The roll after removal from the apparatus is placed in a closed container adapted to contain either one roll or a number of rolls. To facilitate handling, it is desirable that the container be mounted on wheels so that it may be easily moved about. After the roll has been enclosed for the required time and at the desired temperature, the sheet may be then led into an esterification mixer to be esterified forming an organic acid ester of cellulose.

Fig. 2 illustrates a modified apparatus in which the cellulose sheet may be moistened with the pretreating acid instead of being dipped or soaked. This would make unnecessary the vat 6 and the squeeze rolls 9 which are necessary in the dipping process. This modified treating apparatus consists of a vat of pretreating acid 20 provided with a cover 21 with an opening sufficient for the top part of the treating wheel 22 to protrude. It is preferred that there also be an idling roll 23 directly above the treating wheel 22 to ride upon the surface of the cellulose sheet and thus assure a good contact between the sheet and the acid present on the roll 22. The amount of acid which will be taken-up by the cellulose sheet, using this apparatus, will depend upon the surface speed of the roll, the surface of the roll and the level of the pretreating acid in the vat. Thus, increasing the speed or increasing the level of the liquid would result in increased soaking-up of the acid by the cellulose sheet. In order to still further increase the amount of pretreating acid presented to the cellulose sheet by roll 22, an embossed surface may be employed.

In the use of the apparatus of Fig. 1, it is desirable that the drive rolls 4, the squeeze rolls 9 and the wind-up rolls 10 be synchronized to run at a constant surface speed. The surface speed of the wind-up roll 10 depends on the drive roll 11 and does not vary with the size of the roll which has collected on wind-up roll 10.

Although the operation of this apparatus has been explained with reference to the processing of individual sheets, the operation may be made continuous by providing a cellulose sheet of continuous length. In that case, of course, after the wind-up roll 10 contains a roll of treated cellulose of desired size, it will be necessary to cut the sheet at this point and insert a new wind-up roll. The following examples illustrate processes in which cellulose sheets are pretreated in accordance with the present invention:

Example I

25 lbs. of refined wood pulp, having a high alpha cellulose content which is in the form of a roll of a narrow sheet of considerable length was passed through a bath containing glacial acetic acid (at room temperature) and through squeeze rolls which were adjusted so that the sheet after rewinding into a roll weighed approximately 50 lbs. The roll was then kept in an air-tight, stainless-steel container for about 12 hours at room temperature. This sheet was then led off from this roll into a mixer containing 10 lbs of acetic acid, 140 lbs. of propionic acid, 75 lbs. of 85% acetic anhydride and 110 cc. of sulfuric acid, the reaction mixture having previously been cooled to 60° F. The reaction temperature was permitted to rise to a maximum temperature of about 100–110° F. over a period of about 4 hours whereupon a clear viscous solution of cellulose acetate propionate was obtained. The resulting ester may be hydrolyzed or directly precipitated out in any desired manner, such as by pouring into aqueous acetic acid as described and claimed in my Patent No. 2,030,883.

Example II

25 lbs. of cellulose, having a 2½% cuprammonium viscosity of 250 centipoises, which was in sheet form and upon a roll, was led into an acetic acid bath kept at a temperature of about 180° F. The excess acetic acid was squeezed out leaving 25 lbs. of acid in the sheet and it was wound tightly onto a roll and kept at about 180° F. for approximately 6 hours. The sheet was then led into an esterification vessel containing 150 lbs. of glacial acetic acid, 75 lbs. of 85% acetic anhydride and 80 cc. of sulfuric acid which mixture had been cooled to 55° F. The temperature was allowed to rise to 90–95° F. over a period of approximately 3 hours. After treating for another hour a clear and viscous dope consisting of cellulose acetate in solution in the spent esterification mixture was obtained.

The length and width of the cellulose sheets employed in my invention may be those found most convenient. The width, for instance, would be governed by the width of the dipping apparatus and by the size of the opening of the mixer in which the acetylation is carried out. The length of the sheet would depend upon the roll size which could be most readily handled. For the ordinary mixer a sheet having 20'' width has been found to be quite suitable.

It is preferred to employ a cellulose sheet, dried down to a low moisture content, such as about 2%. The roll of cellulose sheet may be standardized as to size at that desirable for a single charge of cellulose for the esterification mixer. If the mixers are small, the charge of cellulose used may be from 25 to 100 lbs. If the esterification mixers are of good size, the roll of cellulose sheet might be as great as 500 lbs. However, instead of having the entire charge for a mixer in one sheet, it might be desirable to use

smaller rolls and employ more than one roll of treated cellulose sheet for each charge.

After the pretreatment has occurred, it is probably desirable to know the amount of pretreating liquid which is present therein, to aid in making-up an esterification bath of the desired composition. This may be determined by weighing the treated roll, the amount of the pretreating liquid present therein, being the difference between that weight and the weight of the cellulose sheet before its treatment.

Thus, I have provided a pretreatment method requiring a minimum of equipment and space, a minimum of pretreating liquid and a minimum of handling of the cellulose. Regardless of the kind of pretreating liquid employed and regardless of the amount of liquid initially deposited in the cellulose sheet, the liquid diffuses and vaporizes and thoroughly permeates every fiber of cellulose during the time that it is contained in the enclosed vessel in which it is put. I have further found that the effectiveness of the pretreatment is not determined by employing larger amounts of pretreating liquid; in other words the dipping step which more thoroughly saturates the cellulose fibers does not give any more effective activation of the cellulose than does the contact step where the cellulose is allowed to take up only a small amount of pretreating liquid, nor is the time or temperature of pretreatment changed by so doing. In fact where a catalyst is employed in the pretreating liquid, the contact method is preferable because it allows a minimum of selective absorption of the catalyst from the organic acid and distributes the catalyst more evenly in the cellulose.

Compacting the cellulose following impregnation with pretreating liquid is not necessary for effectiveness of the process but is desirable to cut down the number and size of containers necessary to handle a given quantity of cellulose. In other words the cellulose containing pretreating liquid may be placed loosely in the vessels, stacked in vessels, rolled and placed in vessels or tamped in, depending upon the equipment available. The only essential step is that the cellulose containing pretreating liquid be enclosed in a chamber or vessel for a time and at a temperature sufficient to make it readily esterifiable.

I claim:

1. The method of pretreating cellulose to prepare it for esterification which comprises impregnating cellulose in attenuated form with a pretreatment liquid essentially consisting of lower fatty acid of which at least 40% is acetic acid, enclosing the impregnated cellulose in a container and allowing it to stand for the desired time and at the desired temperature until the cellulose is sufficiently pretreated for esterification.

2. The method of pretreating cellulose to prepare it for esterification which comprises impregnating cellulose in attenuated form with a bath essentially consisting of concentrated lower fatty acid of which at least 40% is acetic acid, enclosing the impregnated cellulose in a container and allowing it to stand for the desired time and at the desired temperature until the cellulose is sufficiently pretreated for esterification.

3. The method of pretreating cellulose to prepare it for esterification which comprises impregnating cellulose in attenuated form with a bath essentially consisting of concentrated acetic acid, enclosing the impregnated cellulose in a container and allowing it to stand for the desired time and at the desired temperature until the cellulose is sufficiently pretreated for esterification.

4. The method of pretreating cellulose to prepare it for esterification which comprises impregnating cellulose in attenuated form with a pretreatment liquid essentially consisting of lower fatty acid of which at least 40% is acetic acid, compacting and enclosing the impregnated cellulose in a container and allowing it to stand for the desired time and at the desired temperature until the cellulose is sufficiently pretreated for esterification.

5. The method of pretreating cellulose to prepare it for esterification which comprises impregnating cellulose in attenuated form with a bath essentially consisting of ¼–2 parts of concentrated lower fatty acid of which at least 40% is acetic acid, enclosing the impregnated cellulose in a container and allowing it to stand for the desired time and at the desired temperature until the cellulose is sufficiently pretreated for esterification.

6. The method of pretreating cellulose to prepare it for esterification which comprises impregnating cellulose in attenuated form with a bath essentially consisting of ¼–2 parts of concentrated lower fatty acid of which at least 40% is acetic acid and a small amount of acylation catalyst, enclosing the impregnated cellulose in a container and allowing it to stand for the desired time and at the desired temperature until the cellulose is sufficiently pretreated for esterification.

7. The method of pretreating cellulose to prepare it for esterification which comprises impregnating cellulose in attenuated form with a bath essentially consisting of lower fatty acid of which at least 40% is acetic, forming the cellulose into a mass, enclosing it in a container and allowing it to stand at approximately 100° F. until the cellulose is sufficiently pretreated for esterification.

8. The method of pretreating cellulose which comprises contacting a cellulose sheet with concentrated acetic acid so as to leave ¼–2 parts of acetic acid by weight for every part of cellulose, winding the sheet into the form of a roll and allowing the roll to stand at 100° F. for a desired time.

9. The method of pretreating cellulose which comprises contacting a cellulose sheet with a pretreatment bath comprising concentrated acetic acid and a small amount of acylation catalyst so as to leave ¼–2 parts of the bath for every part of cellulose, winding the sheet into the form of a roll and allowing the roll to stand at 100° F. for a desired time.

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