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METHOD OF PREPARING CELLULOSE FOR
ACYLATIONCarl J. Malm, Rochester, N. Y., assignor to East-
man Kodak Company, Rochester, N. Y., a cor-
poration of New JerseyNo Drawing. Application April 16, 1938,
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11 Claims. (Cl. 260—101)

My invention relates to the pretreatment of cellulose with a small amount of a mixture of acetic acid and sulfuric acid together with anhydride in an amount only sufficient to destroy the water present in the acetic acid and the cellulose, in which the temperature is initially below that which will cause acylation.

This application is a continuation-in-part of my applications Serial No. 526,121, filed March 28, 1931 and No. 168,966, filed October 14, 1937.

My invention is concerned with the type of pretreatment in which $\frac{1}{4}$ –2 parts of liquid is employed on every part of cellulose. A satisfactory pretreatment process using a small amount of pretreating liquid is that described and claimed in my application Serial No. 168,966. This pretreatment comprises impregnating cellulose in attenuated form with the pretreatment liquid either by contacting the cellulose with a surface wet with the pretreatment liquid or by immersing the cellulose in the liquid and pressing out the excess and then allowing the cellulose to stand preferably under enclosed conditions for a time sufficient to activate the cellulose to the desired degree. In a pretreatment process using a small proportion of liquid to cellulose, it is desirable to have anhydrous conditions as this makes the pretreatment more efficient and makes it easier to control the subsequent esterification.

One object of my invention is to provide a pretreatment process in which substantially no water is present. Another object of my invention is to provide a process of activating cellulose which will not cause haze in the final product.

If cellulose is pretreated with a small amount of pretreating liquid, the efficiency of the pretreatment is lessened by the moisture which is present, due to the decrease in the superacidity of the catalyst. The amount of moisture for a given proportion of liquid to cellulose is governed by the moisture content of the cellulose. If the fatty acid used is not highly concentrated, the moisture in the cellulose is still more effective in lessening the activating power of the pretreatment.

If the cellulose is pretreated under ordinary conditions using a small proportion of pretreating liquid except that acetic anhydride or the like is added to destroy the water, the anhydride reacts with the cellulose to a sufficient extent to cause haze and lack of clarity in the final product.

I have found that if the cellulose is contacted with a pretreating liquid containing acid anhydride so that the amount of pretreating liquid retained contains approximately just sufficient an-

hydride to destroy the moisture in the cellulose and the air at such a temperature that no esterification occurs prior to the activation proper, a product is obtained which is free of haze. After the water has been destroyed the temperature is allowed to rise to that suitable for pretreating cellulose and the mass is allowed to stand for the time desired.

If the pretreatment is carried out by the contact method in which every part of cellulose absorbs $\frac{1}{2}$ part of liquid, the pretreating liquid and preferably the place of operation is maintained at a temperature which will avoid esterification of the cellulose by the anhydride in the pretreating bath. This temperature is governed by the proportion of catalyst present as explained at another point herein. The cellulose, preferably in the form of a sheet, passes over a roll, the lower part of which contacts the pretreatment liquid. It is desirable that the roll have an uneven or embossed surface to provide more liquid than would a smooth surface. Good contact of the sheet with the wet roll may be assured by pressure upon the opposite side of the sheet such as would be obtained by a guide roll thereon. By passing the sheet over this roll, it is rotated so that the pretreatment liquid is uniformly distributed on the sheet.

The sheet is preferably formed into a roll or a compact mass and placed in an enclosed container in which the pretreatment temperature prevails. Before the sheet is formed into a roll or compact mass, it is passed between heated rolls to bring the temperature of the moistened sheet up to that desired for the pretreatment. The details of this method are given in my application Serial No. 168,966, filed October 14, 1937.

In a pretreatment process such as that described above in which each part of cellulose absorbs $\frac{1}{2}$ part of pretreating liquid, approximately .11 part of acetic anhydride is needed in every $\frac{1}{2}$ part of pretreating liquid to destroy the water if the cellulose has a moisture content of 2%. If the cellulose has a moisture content of 5%, approximately .28 part of acetic anhydride is needed in every $\frac{1}{2}$ part of pretreating liquid.

If the pretreatment is carried out by the immersion method, the pretreating liquid and preferably the place of operation is maintained at a temperature which will avoid esterification of the cellulose by the anhydride, which temperature is governed by the proportion of catalyst used. The proportion of anhydride to employ in the pretreating liquid is calculated on the basis of the proportion of liquid taken up by the cellulose be-

fore the pressing. For instance, if the cellulose is so absorbent that it will soak up 5 parts of liquid, there need be only .28 part of anhydride in 5 parts of liquid for treating a cellulose having 5% moisture.

After the cellulose has been immersed, it is preferably led to press rolls which reduces the content of liquid to about 2 parts per part of cellulose. It is desirable that the pressed out liquid be not returned to the pretreating liquid unless it is fortified again with anhydride. After pressing, the cellulose is allowed to stand, preferably in an enclosed container at the pretreatment temperature for the desired time. For instance, at 90° F. with the maximum proportion of catalyst practicable for an acetic acid pretreatment, 2 hours are usually sufficient.

The temperature necessary to avoid esterification by the pretreating liquid depends on the proportion of catalyst present. If 500 lbs. of cellulose is pretreated with pretreating liquid having 2000 cc. of sulfuric acid (sp. gr. 1.84) the temperature should be not greater than 65° F. until the anhydride is used up to avoid esterifying action on the cellulose. It is preferable not to cool much below 65° F. when glacial acetic acid is the predominant organic acid as crystallization will occur at too low a temperature. Therefore 2000 cc. of catalyst per 500 lbs. of cellulose will be about the limit when pretreating with only glacial acetic acid in accordance with my invention. When effective amounts of other acids, such as propionic or butyric, are present, thus preventing crystallization except at much lower temperatures, a higher proportion of catalyst can be employed and a temperature may be used which will prevent esterification.

If 500 cc. of sulfuric acid is used for every 500 lbs. of cellulose, the temperature should not go above 75° C. until the anhydride is used up. Processes using other proportions of catalyst should be correspondingly governed as to temperature.

If propionic acid or butyric acid is used in sufficient amount in the pretreatment to prevent the crystallization of acetic acid, lower temperatures are not impractical and therefore greater proportions of catalyst may be used and esterifying action can be prevented by means of lower temperatures. It is preferred that at least 40% of the organic acid employed in the pretreatment liquid be acetic. The acetic acid formed by the reaction of acetic anhydride with water should be included in calculating the proportion of acetic acid present in the pretreating liquid.

After the cellulose has been allowed to stand for the desired time, it is then ready for esterification. For instance, after the cellulose has been pretreated by the contact method of pretreatment in which each part of cellulose takes up 1/2 part of pretreating liquid, it may be led into a mixture of 3,000 lbs. of 99.8% acetic acid and 1,400 lbs. of 85% acetic anhydride per 500 lbs. of original cellulose. The mixture of acetic acid and anhydride is preferably cooled to 65° F. or below before introducing the pretreated cellulose therein to permit good control of the reaction. The temperature is then permitted to rise gradually to a maximum of 100° F. where it is kept until a solution free of grain, fiber and haze is obtained.

The cellulose acetate formed may then be hydrolyzed by adding sufficient 50% aqueous acetic acid to the reaction mass to destroy all the acetic anhydride present and have about 10% water present. If it is desired to speed up the

hydrolysis, additional catalyst may be mixed with the acid which is added. The mass may be allowed to stand at 100° F. until a cellulose acetate having the desired acetyl is obtained.

If mixed esters, such as the acetate-propionates or the acetate-butyrate of cellulose, are desired, some propionic or butyric acid may be used in the pretreatment or, if desired, acetic acid may be the only organic acid used in the pretreatment and the propionic or butyric acid may be added with the esterifying reagents.

The most convenient cellulose material to employ in my process is refined wood pulp because it is usually provided in sheet form. Other esterifiable cellulose materials, such as cotton linters, etc. may be employed preferably after having been sheeted first to facilitate handling.

I claim:

1. A method of preparing cellulose material for esterification which comprises impregnating the cellulose with a mixture of acetic and sulfuric acids containing about, but not appreciably more than, sufficient lower organic acid anhydride to destroy the water present, at a temperature at which the union of anhydride with water will take place but below that at which esterification will occur and, after the anhydride is all used up, raising the temperature to that which will cause activation of the cellulose and maintaining that temperature for the time desired.

2. A method of preparing cellulose for esterification which comprises impregnating the cellulose with a mixture of acetic and sulfuric acids in the presence of approximately sufficient acetic anhydride to destroy the water present, at a temperature below that at which the cellulose will be acylated and, after the anhydride is all used up, raising the temperature to that which will cause activation of the cellulose and maintaining that temperature for the time desired.

3. A method of preparing cellulose for esterification which comprises impregnating the cellulose in attenuated form with concentrated lower fatty acid, of which at least 40% is acetic acid, containing sulfuric acid and about, but not substantially more than, sufficient lower fatty acid anhydride to destroy the water present, at a temperature which will prevent reaction of the anhydride with the cellulose but not with the water, and after the anhydride is all used up, raising the temperature to that which will cause activation of the cellulose and maintaining that temperature for the time desired.

4. A method of preparing cellulose for esterification which comprises impregnating the cellulose in attenuated form with concentrated fatty acid, of which at least 40% is acetic acid, containing sulfuric acid and about, but not substantially more than, sufficient acetic anhydride to destroy the water present, at a temperature which will prevent reaction of the anhydride with the cellulose but not with the water, and after the acetic anhydride is all used up, raising the temperature to that which will cause activation of the cellulose and maintaining that temperature for the time desired.

5. A method of preparing cellulose for esterification which comprises impregnating the cellulose in attenuated form with glacial acetic acid, containing sulfuric acid of about, but not substantially more than, sufficient acetic anhydride to destroy the water present, at a temperature which will prevent reaction of the anhydride with the cellulose but not with the water, and, after the anhydride is all used up, raising the temper-

ature to that which will cause activation of the cellulose and maintaining that temperature for the time desired.

5 6. A method of preparing cellulose for esterification which comprises contacting the cellulose in attenuated form with concentrated lower fatty acid, of which at least 40% is acetic acid, containing sulfuric acid and about, but not substantially more than, sufficient lower fatty acid anhydride to destroy the water present, at a temperature which will prevent reaction of the anhydride with the cellulose but not with the water, and after the anhydride is all used up, raising the temperature to that which will cause activation of the cellulose and maintaining that temperature for the time desired.

20 7. A method of preparing cellulose for esterification which comprises contacting the cellulose in attenuated form with glacial acetic acid, containing sulfuric acid and about, but not substantially more than, sufficient acetic anhydride to destroy the water present, at a temperature which will prevent reaction of the anhydride with the cellulose but not with the water, and after the anhydride is all used up, raising the temperature to that which will cause activation of the cellulose and maintaining that temperature for the time desired.

30 8. A method of preparing cellulose for esterification which comprises impregnating the cellulose in sheet form with concentrated lower fatty acid, of which at least 40% is acetic acid, containing sulfuric acid and about, but not substantially more than, sufficient lower fatty acid anhydride to destroy the water present, at a temperature which will prevent reaction of the anhydride with the cellulose but not with the water, and after the anhydride is all used up, raising the temperature to that which will cause activation of the cellulose and maintaining that temperature for the time desired.

40 9. A method of preparing refined wood pulp

cellulose for esterification which comprises impregnating the pulp cellulose in attenuated form with concentrated lower fatty acid of which at least 40% is acetic acid, containing sulfuric acid and about, but not substantially more than, sufficient acetic anhydride to destroy the water present, at a temperature which will prevent reaction of the anhydride with the cellulose but not with the water, and after the anhydride is all used up, raising the temperature to that which will cause activation of the wood pulp cellulose and maintaining that temperature for the time desired.

15 10. A method of preparing refined wood pulp cellulose for esterification which comprises impregnating the pulp cellulose in sheet form with concentrated lower fatty acid of which at least 40% is acetic acid, containing sulfuric acid and about, but not substantially more than, sufficient acetic anhydride to destroy the water present, at a temperature which will prevent reaction of the anhydride with the cellulose but not with the water, and after the anhydride is all used up, raising the temperature to that which will cause activation of the wood pulp cellulose and maintaining that temperature for the time desired.

25 11. A method of preparing an acetyl cellulose which comprises impregnating cellulose in sheet form with glacial acetic acid, containing sulfuric acid and about, but not substantially more than, sufficient acetic anhydride to destroy the water present, at a temperature which will prevent reaction of the anhydride with the cellulose but not with the water, subsequently raising the temperature to that which will cause activation and maintaining that temperature until the cellulose is readily esterifiable and reacting on the cellulose with acetic anhydride in the presence of a catalyst until the cellulose dissolves in the reaction mixture.

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