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CYRIL J. STAUD AND JAMES T. FUESS, OF ROCHESTER, NEW YORK, ASSIGNORS TO EASTMAN KODAK COMPANY, OF ROCHESTER, NEW YORK, A CORPORATION OF NEW YORK

PROCESS FOR MAKING CELLULOSE NITRO-ACETATE

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This invention relates to processes of esterifying cellulose with the lower fatty acids, and particularly the treatment of cellulose, which has been pre-treated with nitric acid, with fatty acids containing not more than eight carbon atoms.

Cellulose acetate is generally manufactured at the present time by the interaction of cellulose with acetic anhydride acetic acid and a catalyst. The most expensive ingredient of this reaction is the acetic anhydride and it is therefore of advantage to the manufacturer to cut down to the smallest amount possible the quantity of this material used. In the U. S. patent of Clarke and Malm Number 1,668,945 there is disclosed a process for esterifying cellulose by heating it in a boiling solution of acetic acid. By this treatment the cellulose is partially acetylated. In the subsequent esterification of such a cellulose ester, to the triacetate, a much smaller amount of acetic anhydride is required than would be necessary if this chemical were used to impel all of the acetyl into the cellulose. In a co-pending application of Staud and Webber Serial Number 334,349 there is described a process for pre-treating cellulose with concentrated nitric acid prior to boiling this pre-treated cellulose in a bath of concentrated acetic acid. By this process, which is an improvement over the Clarke and Malm process, the initial acetylation of the cellulose is carried out in a considerably shorter time, but at the boiling point of the acetic acid.

An object of the present invention is to provide a method of esterification which is an improvement over the above described processes. Another object of this invention is to provide the pre-acetylation of cellulose without the necessity of treating it in boiling acetic acid. A further object of this invention is to provide a process for the pre-treatment of cellulose in such a manner that it may be acetylated in the presence of a fatty acid and a catalyst. Other objects will hereinafter appear.

We have found that when cellulose is treated with concentrated nitric acid for a certain period of time and subsequently partially esterified with a fatty acid in the presence of a catalyst, a fairly high percentage of the acyl radical will combine with the cellulose. For example, a certain amount of acetyl will be combined with cellulose upon the treatment of an unpretreated cellulosic material such as cotton with glacial acetic acid and a catalyst at a temperature of approximately 50° centigrade; no more than 6% combined acetyl, however, will be obtained even after treatment for a period of as much as 240 hours under these conditions. If the cellulose, on the other hand, be pre-treated with a strong nitric acid solution prior to acetylation in the presence of acetic acid and a catalyst, 6% of combined acetyl will result in as short a time as 24 hours even under the same identical conditions of acetylation while as much as 15–16% acetyl will combine in a matter of 240 hours.

Cellulose in the form of cotton linters, paper, wood pulp, or similar cellulosic materials,—but we generally prefer to employ cotton linters,—is preferably treated for a period of from 2 to 8 hours at approximately room temperature with a concentrated nitric acid solution say of 68%. If the temperature of the treatment is much above room temperature, the time of the treatment will be considerably shortened, while on the other hand if the pre-treatment with the nitric acid is conducted at temperatures much below room temperature a considerably longer time will be advisable in order to obtain the same results.

Cellulose pre-treated as described above is in condition after washing and drying for the esterifying step of the reaction. According to the above cited patents and applications, this reaction is effected at the boiling point of the fatty acid used. By our process, however, the nitric acid pre-treated cellulose is placed in a mixture containing the fatty acid together with an efficient catalyst. This solution is maintained at a temperature in the neighborhood of 53° C. and in accord with the type of fatty acid employed the maximum acyl content of the cellulose will be reached generally in less than 240 hours of such treatment. It is not necessary to boil

the acetic acid. If boiling is resorted to, however, an even greater percentage of acetyl can be combined with the cellulose, but this is accompanied by rapid degradation.

While acetic acid is the acid which would be most generally used at the present time, due to the fact that cellulose acetate has more commercial uses than the other organic esters of cellulose, nevertheless, our invention is concerned not with cellulose acetate alone, but with the esters of the fatty acids having more than 1 and less than 8 carbon atoms, such as acetic, propionic, butyric, valeric, caproic, heptoic, etc. The rate of esterification falls off rapidly with the higher members of this series of acids. Consequently acetic acid, propionic acid, butyric acid, are those which are generally preferred, because of their relatively greater commercial availability and their greater speed of reaction.

After the esterification of the pre-treated cellulose with the fatty acid and a catalyst, it may be treated further in an ordinary esterifying bath, for example, if cellulose is being acetylated, by treating the pre-acetylated cellulose in an acetylating bath containing acetic anhydride, acetic acid and a suitable catalyst. The commercial advantage of our process is herein realized in that a saving of from 25 to 40% of the amount of anhydride is realized if a pre-acetylated cellulose is employed as starting material rather than an untreated cellulose.

An example showing one method of conducting our process and by which we shall not be restricted except as this process is restricted by the claims appended hereto will show those skilled in the art the manner of conducting this pre-acetylating process.

Cotton linters are treated for a period of four hours at a temperature of 20 to 25° C. with concentrated nitric acid of approximately 68%. After this preliminary treatment of the cellulose it is washed until neutral to brom-thymol-blue, then dried or dehydrated by the extraction of the water by an organic liquid preferably of low boiling point which is miscible with the water or by any suitable dehydrating process. Fifty grams of this pre-treated material may then be placed in a mixture of 300 cc. of glacial acetic acid containing 2 cc. of a mixed catalyst which is composed of 25% concentrated sulphuric acid and 75% concentrated phosphoric acid. After thoroughly mixing these ingredients they are held at a temperature of 50° C. until the desired acetyl content is attained. After 240 hours of such treatment the product contains from 15 to 16% acetyl.

The nitrogen content of the cotton after the pre-treatment with nitric acid reaches a maximum of 3.5%. This nitrogen is largely removed during the acetlyation with acetic acid and the catalyst, and the material after this pre-acetylation treatment generally contains in the neighborhood of 1% nitrogen. By adding 110 cc. of acetic anhydride of 85% concentration to the reaction mixture above-described and allowing the acetylation to continue at a temperature of 50° C. for a period of 15 to 24 hours, a cellulose acetate will be obtained. This ester may be hydrolyzed if desired.

The treatment of cellulose with concentrated nitric acid and subsequent acetylation by our process to an acetyl content in the neighborhood of 15 to 16% not only increases the reactivity of the cellulose partially acetylated to the regular acetylating bath containing acetic anhydride, acetic acid and a catalyst, but the cellulose acetate produced from such a solution is also very clear and transparent due to the bleaching resulting from the action of the nitric acid.

From a consideration of the above description, it will be realized that any process in which cellulosic materials are treated with a concentrated nitric acid solution and are subsequently placed in a bath containing a fatty acid and a catalyst, will come within the scope of this invention as well as the product obtained by completing the acylation of the cellulose by immersing the thus pre-acylated cellulose in a bath containing an anhydride of the organic acid, and the organic acid, with or without more catalyst.

What we claim as our invention and desire to be secured by Letters Patent of the United States is:

1. In the process of making a partially esterified cellulose, treating cellulose in the presence of concentrated nitric acid, and subsequent to such treatment, partially acylating the pre-treated cellulose in a bath containing as the sole acylating agent a fatty acid having more than 1 and less than 8 carbon atoms, and a catalyst.

2. In the process of making a partially acetylated and nitrated cellulose, treating cellulose in the presence of concentrated nitric acid, and subsequent to such treatment partially acetylating the pre-treated cellulose in a bath containing as the sole acetylating agent acetic acid, and a catalyst.

3. In the process of making a partially acetylated and nitrated cellulose, treating cellulose in the presence of concentrated nitric acid, and subsequent to such treatment partially acetylating the pre-treated cellulose in a bath containing as the sole acetylating agent acetic acid, and a mixed catalyst containing sulphuric acid and phosphoric acid.

4. In the process of making a partially esterified cellulose, treating cellulose in the presence of concentrated nitric acid, and subsequent to such treatment partially acylating the pre-treated cellulose in a bath containing as the sole acylating agent a fatty acid having more than 1 and less than 8 car-

bon atoms, and a catalyst at a temperature of approximately 50° centigrade.

5. In the process of making a partially acetylated and nitrated cellulose, treating cellulose in the presence of concentrated nitric acid, and subsequent to such treatment partially acetylating the pre-treated cellulose in a bath containing as the sole acetylating agent acetic acid, and a catalyst until the cellulose contains approximately 16% acetyl.

6. In the process of making a cellulose ester of a fatty acid, treating cellulose in the presence of concentrated nitric acid, and subsequent to such treatment partially acylating the pre-treated cellulose in a bath containing as the sole acylating agent a fatty acid having more than 1 and less than 8 carbon atoms, and a catalyst, and subsequent to this pre-acylating treatment, continuing the esterification of the cellulose in a bath containing an anhydride of the fatty acid employed.

7. In the process of making a cellulose acetate, treating cellulose in the presence of concentrated nitric acid, and subsequent to such treatment, partially acetylating the pre-treated cellulose in a bath containing as the sole acetylating agent acetic acid, and a catalyst, and further esterifying the pre-acetylated cellulose in a bath containing acetic anhydride until an acetone soluble cellulose acetate is obtained.

8. A process for bleaching and partially esterifying cellulose which comprises treating cellulose in the presence of concentrated nitric acid, and subsequently partially acylating the thus pre-treated cellulose in a bath containing as the sole acylating agent a fatty acid having more than 1 and less than 8 carbon atoms, and a catalyst.

9. A process for bleaching and partially acetylating and nitrating cellulose which comprises treating cellulose in the presence of concentrated nitric acid, and subsequently partially acetylating the thus pre-treated cellulose in a bath containing as the sole acetylating agent acetic acid, and a catalyst.

Signed at Rochester, New York, this 7th day of May, 1930.

CYRIL J. STAUD.
JAMES T. FUESS.