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PROCESS OF ESTERIFYING HYDRATED CELLULOSE WITH LOWER FATTY ACIDS.

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This invention relates to processes of esterifying hydrated cellulose with lower fatty acids, preferably those containing more than 1 and less than 8 carbon atoms.

One object of our invention is to provide an inexpensive and simple process of producing cellulose esters of the lower fatty acids without the aid of anhydrids or catalysts. Another object of the invention is to provide a process of making cellulose esters of the lower fatty acids in a plurality of stages, certain of the acid groups being combined into the ester during the first stage without use of anhydrids and catalysts, and the remainder of the acid groups being combined in the ester by the subsequent treatment of the esters formed in the first stage, thus effecting an economy in expensive ingredients, such as the anhydrids of the acids. Another object of the invention is to provide a process in which the first-stage esterification is performed in the absence of any material more hydrolytic than the fatty acids themselves, thus leaving the cellulosic material essentially unchanged in its physical appearance by the first stage of the process. Other objects will hereinafter appear.

In our application, Serial No. 122,028, filed July 12th, 1926, for "cellulose esters of fatty acids and processes of making the same" we have shown that unmodified or undegraded cellulose can be esterified, under proper conditions, by the lower fatty acids without the use of catalysts or expensive anhydrids and the like. In the case of each of the lower fatty acids, approximately one molecular proportion of acid is combined with an amount of cellulose corresponding to 24 carbon atoms. This first-stage ester is then esterified further by the usual process, but with notable economies in the use of anhydrids and with mild catalysts to avoid molecular degradation.

We have now found that cellulose esters of the lower fatty acids may be prepared in which approximately 4 molecular proportions of acid are combined with an amount of cellulose corresponding to 24 carbon atoms and without the use of anhydrids or catalysts,—in fact without modifying the physical appearance of the treated cellulosic material. We are able to bring about this result by using hydrated cellulose as the raw material to be heated with the acid as the sole acylating agent. These first-stage esters prepared by simple heating of the hydrated cellulose with the acids as the sole acylating agents are very stable, as indicated by their resistance to hydrolysis by prolonged boiling in water. In general the fibers of the new compounds are superficially indistinguishable from the hydrated cellulose forms, such as rayon fibers, from which they are prepared.

It is a useful fact that these esters are more readily esterified than plain cellulose. The practical effect is that when these "four in twenty-four" esters are further esterified by using anhydrids, or even acyl chlorids, in the ways previously described for the acylation of cellulose itself, savings of from 25% to 40% of the amount of anhydrid or chlorid may be obtained.

Our invention is concerned with the esters of the fatty acids having more than 1 and less than 8 carbon atoms, such as acetic, propionic, butyric, valeric, caprylic, heptylic, etc. The rate of esterification falls off rapidly with the higher members of this series of acids. Consequently acetic acid, propionic acid and butyric acid are those which are preferred, because of their relatively greater commercial availability and their greater speed of reaction. Acetic acid is commercially the most important at present, because of its lower cost.

We preferably use hydrated cellulose which has not been so degraded by hydrolysis or oxidation as to yield esters that form brittle films. We have found, for example, that reverted cellulose, in the form of viscose rayon fibers or cuprammonium rayon fibers, answers such requirements and responds readily to our treatment. So do rayon fibers of denitrated nitrocellulose. The fibrous state is not indispensable and any equivalent form, such as flakes, grains or powder is also convenient.

The first-stage esterification may be conducted over a considerable temperature

range. In general we prefer to operate above 100° C. in order to insure reasonably rapid action and we do not advise the use of temperatures above 170° C., because of the danger of further molecularly degrading the cellulose and the products produced from it. Within this preferred range the temperatures vary with the boiling points of the different acids. For example, those acids which boil below 170° C. can be used at atmospheric pressure, a considerable excess of acid over the amount which will enter the ester being used. But we find that the time can be very considerably shortened by using a superatmospheric pressure, say in an autoclave, provided the corresponding temperature does not reach the point where the product is degraded. While we use the acids as the sole acylating agents and prefer to employ them without admixture with other liquids, nevertheless, the esterification can be effected, when the acids are mixed with non-acylating liquids, such as chloroform, carbon tetrachloride, benzene, toluene, xylene, chloro-benzene, etc. But these produce no marked advantage, other than facilitating removal of water.

During the first-stage acylation it is desirable to keep the amount of water present very low. The total water present, including the water in the original ingredients, plus the water formed during the esterification, should never be allowed to reach the point where it prevents the introduction of more than 6% of the acyl group. We aim to maintain the conditions during the reaction such that the water is removed or diminished in quantity. The use of a fractionating column is one way of obtaining this result, the water vapor being allowed to pass out while the fatty acids are condensed and flow back to the bath. This is possible because all of the fatty acids having more than 1 and less than 8 carbon atoms boil considerably above the boiling point of water. The use of a reflux condenser, while useful with all of the acids, can be dispensed with more readily with the lower members of the series, such as acetic and propionic acids. It is especially advisable with the higher members of the series.

In the first stage of esterification the hydrated cellulose is heated in the acid until the "four in twenty-four" ester is formed. For example, we may boil 1 part of hydrated cellulose in 30 parts by weight of acetic acid, the operation being carried out at atmospheric pressure. The acid is initially substantially free from water, say of 99 to 100% strength. The boiling point of the reaction bath is thus kept at 117° C. or slightly above. Of course, any suitable precautions are taken to prevent the loss of acids through its vapors being carried away, the same being condensed and returned to the bath by the use of any of the expedients familiar to chemists.

As the boiling in acetic acid is continued under these conditions the esterification progressively takes place and the acetyl groups in the ester reach the point where their proportion is not materially increased by further boiling. Roughly the proportion of acetyl is 21% of the weight of ester. This full esterification may be obtained after different lengths of time with different samples of cellulose. Some of them reach approximately this percentage after 200 hours of treatment. But a useful product is obtained after a much shorter time. For instance, the percentage of acetyl in the ester reaches 13% before 96 hours in practically every instance. This 13% ester has the property of being readily esterified further in the usual baths but with economy in acetic anhydrid. It should be noted that in the above discussion, as well as in the claims, we have referred to the percentage of the acyl group, such as the acetyl group. The percentages thus given, correspond in each instance to a still higher percentage of "combined acid," the relation being in the proportion of the molecular weight of the acyl group to the molecular weight of the acid. For instance, 14% of the acetyl group means about 19.5% of combined acetic acid.

One typical example of the acetylation of a reverted cellulose, such as cuprammonium silk, is given in the following table:

I Hours.	II Per cent of acetyl group.
24	8.2
48	10.8
96	13.2
200	19.2
300	20.9
400	22.0
500	22.2
600	22.4

The first column gives the hours of treating of the sample with acetic acid boiling at atmospheric pressure. The second column gives the corresponding percentages of acetyl group in the product.

After this first-stage etherification, the excess of acid is removed if the ester is to be further esterified in a bath containing an anhydrid and a catalyst. Part of the acid can, however, be left with the "four in twenty-four" ester to function as a diluent or a solvent during the second-stage acylation, as is usual in the ordinary acetylation of plain cellulose. If the acetylated fibers, from the first stage, are desired to be used in that condition, they are, of course, thoroughly washed in water and dried, in which event they look like the hydrated fibers from which they were derived. Instead of the 30 parts of acetic acid in the above example,

we may employ 30 parts by weight of propionic or butyric acid and employ, preferably, a reflux condenser through which the water vapors may pass, while retaining the acid vapors. The time of boiling is conveniently about 200 hours.

When 30 parts of heptylic acid are used with 1 part by weight of hydrated cellulose, the temperature should be kept below 165° C. and preferably above 145° C. This is under the boiling point of the acid, but sufficient to obtain a useful esterification without too serious degradation.

When it is desired to work at superatmospheric pressures, 1 part of hydrated cellulose may be heated, for example, with 30 parts of acetic acid by weight of 99 to 100% strength at a temperature between 140 and 160° C., say in a vessel of the autoclave type. The time of esterification is enormously shortened under these conditions, being generally less than 20 hours.

The esterification may even be carried out with the vapors of the acids. For example, the hydrated material may be placed in an acid-resisting tube heated by any suitable means, such as an oil bath, and the vapor of acetic acid conducted through the tube. This operation may be conducted either at atmospheric pressure or subatmospheric pressure, provided the temperatures do not go above 170° C. The excess of acid vapor may be repassed or recirculated, preferably after slightly reheating, through the tube. This enables a rapid acetylation to take place. The subsequent esterification of the first-stage ester can take place in any of the usual esterifying baths, but with the amount of anhydrid diminished by from 25 to 40%. Moreover, the increased susceptibility of our "four in twenty-four" esters to further esterification enables us to carry out the latter operation without the use of strong catalysts, thus avoiding the danger of degradation when such catalysts as sulfuric acid are employed. We can operate with a milder and safer one, such as zinc chlorid or magnesium perchlorate trihydrate. As such esterification methods have been previously described, it is unnecessary to go over them in detail here.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

1. In the process of making a cellulose ester of a fatty acid, heating together hydrated cellulose and a fatty acid having more than 1 and less than 8 carbon atoms without a catalyst at a temperature between 100° and 170° C. inclusive until substantially 4 molecular proportions of said fatty acid combine with an amount of cellulose corresponding to 24 carbon atoms, said acid being the sole acylating agent.

2. In the process of making cellulose acetate, heating together hydrated cellulose and substantially anhydrous acetic acid without a catalyst above 100° C. and below 170° C. inclusive until the acetyl group in the ester thus produced reaches at least 6%, said acetic acid being the sole acetylating agent.

3. In the process of making a fatty acid cellulose ester, partially esterifying hydrated cellulose by heating it with a fatty acid having more than 1 and less than 8 carbon atoms, in the absence of any anhydrid and catalyst, the action being stopped while the ester, thus produced, still has substantially the same appearance as the original hydrated cellulose, and thereafter esterifying it further with the aid of an anhydrid of a fatty acid and a catalyst.

4. In the process of making a fatty acid cellulose ester, heating hydrated cellulose between 100° and 170° C. with a fatty acid having more than 1 and less than 8 carbon atoms without any catalyst until substantially 4 molecular proportions of said fatty acid combine with an amount of cellulose corresponding to 24 carbon atoms, said acid being the sole acylating agent, and thereafter further esterifying it with the aid of an anhydrid of a fatty acid and a catalyst.

5. In the process of making cellulose acetate heating hydrated cellulose in an excess of acetic acid at a temperature between 100° and 170° C. in the absence of a catalyst, the acid being the sole acetylating agent, until the acetyl group in the ester reaches at least 6%, and thereafter further acetylating the ester thus produced in the presence of acetic anhydrid and a milder catalyst than sulfuric acid.

Signed at Rochester, New York, this 7th day of January, 1927.

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