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CELLULOSE ESTERS OF FATTY ACIDS AND PROCESS OF MAKING THE SAME.

No Drawing.

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This invention relates to cellulose esters of fatty acids and processes of making the same.

One object of the invention is to provide fatty acid esters of cellulose in which approximately one molecular proportion of acid (especially one having more than one carbon atom) is combined with an amount of cellulose corresponding to twenty-four carbon atoms. Another object is to provide an inexpensive, stable, fatty acid ester of cellulose which is very susceptible to further esterification. Still another object is to provide such an ester in a purified condition. A further object is to provide an inexpensive and simple process for producing such esters. Another object is to provide a process for producing such esters in which no anhydrid is used, the fatty acid being the sole acylating agent. A still further object is to provide a process of making fatty acid cellulose esters in one stage of which esterification is carried on without the aid of a fatty acid anhydrid, and in a subsequent stage of which further esterification is effected with the aid of such an anhydrid but in only economical amounts. Other objects will hereinafter appear.

We have found that hitherto undescribed fatty acid esters of cellulose can be prepared in which approximately one molecular proportion of acid, containing less than eight carbon atoms, is combined with an amount of cellulose corresponding to twenty-four carbon atoms. Aside from the scientific bearing of this fact upon the theory of the structure of the cellulose molecule, these esters have properties of technical importance. They are relatively inexpensive, can be obtained in a sufficiently pure state and are very susceptible to further esterification. Moreover, those derived from fatty acids having more than one and less than eight carbon atoms are very stable, as indicated, for example, by their resistance to hydrolysis under prolonged treatment with boiling water. As a rule, the new compounds are superficially indistinguishable from the cellulose from which they have been prepared; for example, esters prepared from cotton cellulose still have the appearance of cotton fibers.

We have likewise found that the process

of producing these esters is very simple and inexpensive, and can be carried out without the aid of anhydrids of the fatty acids, which are relatively expensive. It is merely necessary to heat the cellulose with the fatty acid until the percentage of acyl group in the product becomes substantially constant. We have found that at this point the esters contain one acyl group to each twenty-four carbon atoms of the cellulose. While we prefer to carry out the esterification, with the acid as the sole acylating agent, to the point where the above mentioned ester is obtained, useful practical results are effected by esterifying to the point where at least 4% of acyl group is present in the compound.

We have also found that when these "one in twenty-four" esters are further esterified, say by using anhydrids or acyl chlorides in the ways previously described for the acylation of cellulose itself, technically useful economies in anhydrid or acyl chloride can be obtained. Savings of 10% to 25% of the amount of anhydrid used have been noted in this work.

Broadly speaking, our invention is concerned with esters of the fatty acids having more than one and less than eight carbon atoms, such as acetic, propionic, butyric, valeric, caproic, heptylic, etc. But since the rate of esterification falls off rapidly upon ascending the above cited homologous series, we have found that economy of time is obtained best when using fatty acids having more than one and less than eight carbon atoms. Of course, acetic acid, propionic acid and butyric acid are preferred, because of their relatively greater commercial availability and their greater speed of reaction.

Our process can utilize cellulose from any of the sources customarily used in the manufacture of esters, such, for instance, as sulfite wood pulp (preferably bleached), cotton, surgical cotton wool, tissue paper especially prepared from cotton, etc. It is an advantage that our process can utilize relatively impurer cellulose than is often employed in this art, because the heating with the fatty acid tends to separate any impurities from the cellulose, as is evidenced by the whiteness of our product. While we have mentioned bleached sulfite pulp above, it is not

essential that it be employed, because of the whitening tendency of our process when applied to the unbleached or partially bleached pulp. It will be seen that the above list relates to cellulose and does not include hydrocellulose or hydracellulose.

The process may be conducted over a considerable temperature range. We have found that the production of "one in twenty-four" esters takes place rapidly with the lower members of the fatty acid series at 117° C., but the working temperatures can range up to the point where the cellulose or the products suffer from degradation. We find it inadvisable, as a general proposition, to use temperatures above 170° C. Within the working range the temperature will vary with the particular acid or mixture of acids which is employed and with the pressure under which the process is carried out. For instance, working at atmospheric pressure and employing acids which boil below 170° C. at such pressure, we find it useful to conduct the process by boiling the cellulose in the acid, preferably in a considerable excess of acid over the amount which will enter into the ester. But the time can be very considerably shortened by using a superatmospheric pressure, provided the corresponding temperature does not reach the point where the product is degraded.

While we have found it practical to carry out the process by heating the cellulose in the acid or mixtures of acids, as the sole treating bath, nevertheless, useful amounts of the acyl group may be introduced, say well above 4%, for example, when the acids are mixed with non-acylating liquids, such as chloroform, carbon tetrachloride or benzene.

The amount of water present during the reaction is important because it has a depressing effect upon the total percentage of acyl group which can be introduced. Taking into account both the initial water in the reagents and the water formed during the esterification, it should never be allowed to reach the point where it prevents the introduction of more than 4% of the acyl group. We prefer, in fact, to maintain the conditions during the reaction such that water tends to be removed or diminished in quantity rather than increased in amount. The use of a reflux condenser, which will condense and return to the bath the vapors of the fatty acids without condensing the water vapor, is one way of effecting this result. Such a reflux condenser action is not always essential, especially when working with the lower members of the above recited series, provided the acid and cellulose are sufficiently low in moisture. With the higher members of the series it is best to eliminate the water during the reaction.

We shall now describe various embodi-

ments of our process by way of illustration, but it will be understood that the invention is not limited to such details except as indicated in the appended claims.

One part of cellulose, say cotton fibers, is boiled in an excess of acetic acid, say 30 parts by weight, the operation being carried out at atmospheric pressure. The acid is initially substantially free from water, say of 99 to 100% strength. Consequently the boiling point of the reaction mass is 117° C. or slightly above. Of course, any suitable precautions are taken to prevent the loss of acid through its vapors being carried away, the same being condensed and returned to the bath in any of the ways well known to those skilled in the art.

As the boiling continues, in this example, the esterification gradually takes place and eventually the percentage of acetyl group in the ester reaches the point where it is not materially increased by further boiling, say about 6%. This time varies somewhat with the type and condition of cellulose employed, representative times, for example, being 160 to 200 hours. But a distinctly useful product is obtained after a much shorter time, say about 48 hours, for instance. At that time the amount of acetyl group is very considerably above 4% and the ester is eminently suited for rapid and economical acetylation in which acetic anhydrid is used. As indicated above, the maximum amount of acetyl group, which can be introduced by prolonged boiling, is substantially one molecular proportion of the fatty acid combined with an amount of cellulose corresponding to twenty-four carbon atoms. It is convenient to note that the percentage of acyl group in a given ester corresponds 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 example, 4% of acetyl group means 5.58% of combined acetic acid.

After the esterification has reached the desired point, the excess of acid is removed if the ester is to be further esterified by treatment with an anhydrid and a catalyst. Enough of the acid can be left with the "one in twenty-four" ester to properly function as a diluent or solvent along with the anhydrid and catalyst, as is customary in the acetylation of plain cellulose. But where the lower ester is desired by itself, the excess of acid is completely wrung and washed out of it and the latter then dried. Acetyl cellulose, thus obtained, has substantially the superficial appearance of the cellulose from which it was prepared,—in other words, it looks like cotton when it is prepared from cotton fibers, as in the above example. Moreover, such an ester is remarkably stable and withstands rather prolonged

boiling in water without loss of the acetyl group. Of course, in the above and in the following examples, the cotton fibers can be replaced by the other kinds of cellulose which have been proposed in this art.

Instead of boiling one part of cellulose with 30 parts by weight of very pure acetic acid, the latter may contain up to about 10% of water. But in this case it requires a very much longer time before the proportion of acetyl group rises above 4%. It is, therefore, highly preferable to keep the water content lower than 10% and preferably below 1%.

In a further example, one part of cellulose, say cotton fibers of the usual purified form, is boiled under atmospheric pressure with 30 parts by weight of propionic acid, provision being made for the removal of the water during the boiling, say by a suitable reflux condenser. In general the percentage of propionyl group rises to about 6% after 48 hours and reaches a maximum of about 8% after between 100 and 200 hours boiling.

In another example one part by weight of cellulose, say cotton fibers somewhat purified, is boiled at atmospheric pressure with 30 parts by weight of butyric acid. After 48 hours boiling the product contains in the neighborhood of 5% of butyryl group and after 200 hours has well above 10% of this acyl group present.

In another example one part of cellulose, such as purified cotton fibers, say surgical cotton wool, is heated with 30 parts by weight of heptylic acid, the materials during the reaction being kept between the temperatures of 145° and 165° C. This is below the boiling point of the acid, but a notable esterification, nevertheless, takes place. By observing these temperature precautions the tendency to degrade the product is lessened.

In all of the above examples the operations are conducted at atmospheric pressure. The reaction may be considerably hastened by carrying out the action under pressure, say in a suitable acid-resisting autoclave. For example, one part of any suitable kind of cellulose is heated with 30 part of acetic acid of 99 to 100% strength at a temperature of 140° to 160° C., and under a corresponding superatmospheric pressure. Under such circumstances upwards of 5% of acetyl group will be found combined in about 2 hours, thus enormously shortening the time of the operation.

The esterification may be conducted with the acid in the vapor phase. For example, cotton fibers, may be placed in a glass tube, heated by any suitable means, such as an oil bath, and vapor of acetic acid conducted through the tube. It is convenient to operate at atmospheric pressure with the

vapor from boiling acetic acid, but super-atmospheric pressure can be used, say one corresponding to 140° C. The temperature of the reaction tube is between 117° and 170° C., say 140° C., for instance. The action is continued until the desired esterification takes place. The excess of acid vapor may be repassed or recirculated through the tube. The action is comparatively rapid and, with the tube at 140° C., we have obtained an ester with well over 4% acetyl content in 12 hours, and a full 6% in 20 hours.

It will be noted that no catalysts are used in any of the hereinabove described examples; and consequently there can be no degradation from that source, even upon prolonged heating.

It is a remarkable fact that all of the esters of low esterification produced in the above examples are especially susceptible to further esterification, say by the methods customarily employed in esterifying cellulose itself. Moreover, the acyl group, which is further introduced by the conventional methods, employing anhydrides and catalysts, need not be the same acyl group as that originally present in the lower or "one in twenty-four" ester. Thus, for example, the cellulose propionate, described above, may be acetylated and the final product will contain both propionyl and acetyl groups. Obviously a wide combination of mixed esters may be obtained in this manner.

It is a characteristic of our new esters that further esterification can be carried out with economy in expensive ingredients. For example, we have in some instances carried out a further acetylation with an economy in acetic anhydrid ranging between 10 and 25%. Because of the susceptibility of our low esters to further esterification, the latter operation can be conducted with milder catalysts, such as zinc chloride, thus avoiding any danger of degradation of the product through careless or incorrect use of sulfuric acid as the condensing agent. As these methods of esterification with anhydrid and a weak catalyst are well known to those skilled in the art, it is unnecessary to describe them in detail here as they can be used in their original form but with a useful lowering of the amount of acetic anhydrid.

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

1. A fatty acid ester of cellulose having substantially one molecular proportion of fatty acid combined with an amount of substantially unhydrolyzed cellulose corresponding to twenty-four carbon atoms, said fatty acid having more than one and less than eight carbon atoms.

2. Substantially unhydrolyzed cellulose acetate having the appearance of cellulose

and being stable to boiling water at atmospheric pressure, the proportion of the acetyl group therein being between 4% and 6.5%.

3. In the process of making a cellulose ester of a fatty acid, heating together cellulose and a fatty acid having more than one and less than eight carbon atoms at a temperature between 117° and 170° C. inclusive until substantially one molecular proportion of said fatty acid combines with an amount of cellulose corresponding to twenty-four carbon atoms, said acid being the sole acylating agent.

4. In the process of making a cellulose ester of a fatty acid, heating together substantially unhydrolyzed cellulose and a fatty acid having more than one and less than eight carbon atoms, said acid being the sole acylating agent, the temperature during the reaction being kept below the decomposition points of the ingredients and product, and the proportion of water in the reaction mass permitting the acyl group in the ester to reach at least 4%.

5. In the process of making a cellulose ester of a fatty acid, heating together cellulose and an excess of a fatty acid having more than one and less than eight carbon atoms, said acid being the sole acylating agent, the reaction being conducted at a pressure above atmospheric but the tem-

perature being maintained below the decomposition points of the ingredients and product.

6. In the process of making cellulose acetate, heating cellulose in the absence of a catalyst in an excess of acetic acid, the latter being the sole acetylating agent, until the acetyl group in the ester reaches at least 4%.

7. In the process of making a fatty acid cellulose ester, partially esterifying cellulose with a fatty acid having more than one and less than eight carbon atoms in the absence both of an anhydrid and a catalyst, and thereafter esterifying it further with the aid of an anhydrid of a fatty acid.

8. In the process of making a fatty acid cellulose ester, heating cellulose, together with a fatty acid having more than one and less than eight carbon atoms until substantially one molecular proportion of said fatty acid combines with an amount of cellulose corresponding to twenty-four carbon atoms, said acid being the sole acylating agent, and thereafter further esterifying it with the aid of an anhydrid of a fatty acid.

Signed at Rochester, New York, this 21st day of June 1926.

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