Patented Sept. 27, 1932

1,880,067

UNITED STATES PATENT OFFICE

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MANUFACTURE OF CELLULOSE ACETATE

No Drawing. Application filed April 3, 1930. Serial No. 441,428.

The object of the present invention is an improvement in the procedure for acetylating cellulose described in my United States Patent No. 1,668,484, issued May 1, 1928.

It is well known that the different industries that use cellulose acetate require that this material should have different properties according to the use to which it is to be put. Cellulose acetate is ordinarily used as a solution in suitable solvents, such as acetone, alcohol-chloroform, etc. The different qualities and properties of these cellulose acetates, according to the use to which they are to be put are indicated by measurements of the different viscosities when in a suitable solution. The viscosities of these solutions have been measured heretofore by noting the time in seconds that it takes a steel ball of $\frac{7}{32}''$ diameter to fall a distance of 10 centimeters through a 25% solution of the cellulose acetate in acetone, at a temperature of 25° C.

The usual industrial uses require that this viscosity vary between the limits of 30 seconds and 1500 seconds of time, measured by means of the above described steel ball. For example, cellulose acetate is used for the manufacture of aeroplane dope. For this particular use, its viscosity is usually of the order of 20 to 50 seconds. For the dry spinning of artificial yarns, the viscosity generally required is between the limits of 100 and 300 seconds. For the manufacture of moving picture and photographic film, the viscosity is of the order of 300 seconds up.

I have discovered and stated in my above mentioned United States Patent No. 1,668,484 that it was possible to obtain high grade industrial cellulose acetate through a process of acetylation that consists in subdividing the usual single bath acetylation method into a series of partial and consecutive acetylations, finally giving the required result. I explained in that patent that this method had as its main advantage the procedure of building up progressively the number of acetyl groups fixed on the cellulose molecule, and that because of this progressive action, the process was subject to close control.

Acetylation processes set free a certain total amount of heat produced by the chemical reactions. This heat is apt to be destructive and will damage and lower considerably the viscosity of the final acetate of cellulose produced. By splitting the acetylation up into a series of small successive acetylations, the heat set free is also developed in small amounts, and this heat can be eliminated without the use of severe refrigeration methods, such as cold brine circulation. I am therefore able to maintain an exact control of the temperature conditions at the interior of the mass under acetylation, and having this temperature regulation perfectly in hand, I can control absolutely the finished physical properties of the resulting cellulose acetate.

It is well known that a suitable catalytic agent such as sulfuric acid in small proportions must be used in the acetylation bath to obtain the desired chemical reaction. The action of the catalyst and of the evolved heat may cause the production of low quality cellulose acetate.

By my present invention the total acetylation process is carried out by means of at least four or five partial acetylation baths, similar to the method described in my prior patent, but including the following modifications:

(A). The strong acid that is used as the catalyst is employed only during the first two or three acetylation baths. These first acetylations are carried out by means of baths consisting of mixtures of acetic acid, acetic anhydride titrating about 12 to 18% of acetic anhydride, and a certain amount of strong acid catalyst. The composition of the baths is so calculated as to give a partial acetylation of the cellulose, this partial acetylation being sufficient to add a 10 to 15% proportion of acetyl groups to the cellulose molecule, the acetyl groups being calculated as acetic acid.

(B). After this point has been reached, the succeeding acetylation baths are carried out by means of mixtures of acetic acid and acetic anhydride titrating about 75 to 85% of acetic anhydride. I introduce, in one of these lat-

ter acetylation baths, preferably the first, a certain amount of a chemical reagent capable of retarding the catalytic action of the strong acid. The presence of this chemical reagent retards chemical action according to the proportion of chemical reagents used. In this way the length of time to complete the reaction may be made whatever is desired.

I have found that the following reagents are capable of slowing up the catalytic action of the sulfuric acid. These retarding reagents are the salts formed by a feeble acid and a strong base, such as sodium acetate, potassium acetate, sodium lactate, sodium benzoate, as well as the neutral sulfates of sodium and potassium. These salts are added to the acetylation bath in solution or in fine suspension in acetic acid and in quantities that can be accurately determined by calculation or tests.

The reaction temperature limits are maintained between 18° and 26° C. during the preparation of the acetyl cellulose titrating 10 to 15% as combined acetic acid. It is preferable after the addition of the catalyst retarding reagent to maintain the temperature of reaction between 25° and 40° C. over the time of preparation of acetyl cellulose titrating between 15 and 45% in combined acetic acid, and it is advisable to operate between 40° and 50° C. during the preparation of the cellulose acetate titrating between 45 and 60% in combined acetic acid.

I have found that in employing an acetylator composed of a hollow cylindrical water-jacketed body, which has an axis of rotation perpendicular to the axis of symmetry of the body, an effectiveness of mixing can be obtained at least as good as, if not superior to that which is obtained with the acetylator described in my Patent No. 1,668,484.

Purely as an example, and not as a limiting statement, I will now describe an example of acetylation in accordance with this invention.

Example:—110 kilograms of cotton which has previously been thoroughly purified and bleached, are charged into the acetylator and are put through a softening process of vaporizing through the mass of cotton 110 kilograms of glacial acetic acid fed from an auxiliary tank into the acetylation apparatus without interruption of the mechanical movement of the said apparatus in accordance with the treatment described in Patent No. 1,668,484. The temperature is brought to 18° C. by means of the water jacket through which water at about 16° C. is being circulated.

First acetylation

After the softening process has been completed the first acetylation bath is introduced on to the cellulosic material. It is composed of 130 liters of a mixture of acetic acid and acetic anhydride, this mixture being such as to titrate from 12 to 15% in anhydride content and into which there have previously been introduced 130 cc. of sulfuric acid of 66° Baumé with, if desired, the addition of 20 cc. of bromine. The first acetylation is completed in about an hour and a half. It is characterized—

(*a*) By an elevation of temperature, this temperature reaching a maximum of 21° C., notwithstanding the circulation of 16° C. cooling jacket water.

(*b*) By the analysis showing combined acetic acid of from 0.7% to 2% when chemical equilibrium is attained.

Second acetylation

There is then added a second acetylation bath composed of 140 liters of a mixture of acetic acid and acetic anhydride titrating 12 to 15% in anhydride content, and to which 140 cc. of sulfuric acid of 66° Baumé have been added, either with or without about 20 cc. of bromine. This second acetylation is completed in about two hours and is characterized—

(*a*) By an increased rise in temperature, the temperature reaching 23° C.

(*b*) By the production of an acetyl cellulose showing on analysis combined acetic acid of between 2 and 5% at the time the temperature has returned to its initial value.

Third acetylation

There is then added a third acetylation bath composed of 200 liters of a mixture of acetic acid and acetic anhydride titrating from 8 to 15% in acetic anhydride, and to which about 1500 cc. of sulphuric acid at 66° Baumé have been added. This third acetylation is completed in about three or four hours and is characterized—

(*a*) By a rise in temperature, which reaches 24 to 25° C. despite the external jacket cooling.

(*b*) When equilibrium has been attained, the acetyl cellulose formed presents a homogeneous appearance and is optically homogeneous when examined by means of polarized light.

(*c*) Its analysis shows combined acetic acid of between 13% and 15%.

The amount of sulphuric acid used in the first three acetylations may be considerably increased so that the total may be as high as about 5% by weight of the cellulose treated.

Fourth Acetylation
(with catalyst retardation)

A bath is then added, composed of 115 liters of a mixture of acetic acid and acetic anhydride, titrating 83 to 85% in acetic anhydride, and to which 7 liters of a 10% solution of sodium acetate in glacial acetic acid have been added, this solution carrying out the desired

effect of anti-catalyst, or retarder of catalytic action, as described in the early portion of this specification. An hour after this bath has been added, the temperature of the water jacket is raised to 35° or 37° C. for about 30 minutes, so as to accelerate the start of the reaction, which reaction reaches this same temperature within about an hour. The heat produced by the reaction is then absorbed by jacket water of 16° C. until the temperature has been brought down to between 25° and 30° C., which requires about an hour and a half. The acetyl cellulose fibers are at this time greatly swollen but have not passed into solution. The analysis shows combined acetic acid of this acetyl cellulose to be between 35 and 45%; that is, the tetra-acetate of cellulose stage has been nearly reached.

Fifth acetylation

140 liters of the bath are then added, composed of acetic acid and acetic anhydride, titrating 83 to 85% in acetic anhydride. The temperature begins to rise spontaneously and slowly. This rise of temperature may be accelerated, if necessary, by the circulation of jacket water at about 38° C. In about two hours the temperature reaches a point which is carefully limited between 40° and 50° C. whereupon the whole mass passes into a state of homogeneity. At this time, the rate at which the heat is carried away by the jacket water is limited, by bringing the temperature of the water in the jacket up to 35° to 39° C., so as to prevent too rapid cooling. The viscosity diminishes during this time, notwithstanding the fact that the temperature drop over this period does not exceed more than about 1° C. Viscosity measurments of the acetyl-cellulose formed are made at 5 minute intervals. The saponification bath is introduced, for example, in accordance with my Patent No. 1,668,484, as soon as the viscosity obtained on measurement corresponds exactly to the quality of cellulose acetate that it is desired to obtain.

In using the expression "cellulose" in the claims, it is not intended to restrict the invention to chemically pure cellulose, the exact composition of which is not known, the invention being applicable to materials referred to commercially as cellulose or its derivatives and recognized as being adapted for the production of cellulose acetate by the methods indicated in the specification as set forth in the claims.

I claim:—

1. A process of homogeneous acetylation of cellulose, which comprises carrying out the total acetylation by a series of acetylation baths containing acetic anhydride diluted with acetic acid, the first acetylation baths of the series containing sulphuric acid as catalytic agent, and a later bath containing a reagent capable of reducing the catalytic power of the sulphuric acid without totally destroying it.

2. A process of homogeneous acetylation of cellulose, which comprises carrying out the total acetylation by a series of acetylation baths containing acetic anhydride diluted with acetic acid, the first acetylation baths of the series containing sulphuric acid as catalytic agent, and a later bath containing a normal salt of a strong base and a weak organic acid.

3. A process of homogeneous acetylation of cellulose, which comprises carrying out the total acetylation by a series of acetylation baths, containing acetic anhydride diluted with acetic acid, the first baths of the series containing sulphuric acid as catalytic agent, and a later bath containing a salt.

4. A process of homogeneous acetylation of cellulose, which comprises carrying out the total acetylation by a series of acetylations, in the first three of which the temperature is kept between 18° C. and 26° C., during the fourth acetylation between 25° C. and 40° C., and the maximum temperature during the fifth acetylation being between 40° C. and 50° C.

5. A process of homogeneous acetylation of cellulose, which comprises carrying out the total acetylation by a series of at least four acetylation baths, containing acetic anhydride diluted with acetic acid, the first two acetylation baths containing sulphuric acid as a catalytic agent, and the fourth bath containing a reagent capable of reducing the catalytic power of the sulphuric acid without totally destroying it.

6. In the process of acetylation of cellulose, the steps which comprise carrying out partial acetylations using a catalyst and completing the acetylation with an anti-catalyst added.

7. In the process of acetylation of cellulose, the steps which comprise carrying out partial acetylations using an amount of sulphuric acid catalyst equal to about 2% to 5% of the weight of the cellulose and completing the acetylation with an anti-catalyst added.

8. In the process of acetylation of cellulose, the steps which comprise carrying out partial acetylations using an amount of sulphuric acid catalyst equal to about 2% to 5% of the weight of the cellulose and completing the acetylation with an anti-catalyst added, the maximum temperature during the last step being between 40° C. and 50° C.

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