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PROCESS FOR STABILIZING CELLULOSE ESTERS

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This invention relates to the removal of small concentrations of volatile acids after the preliminary spray or countercurrent washing of cellulose esters and to the stabilizing of cellulose esters by treating the esters with a dilute solution of a weakly alkaline neutralizing agent, dewatering the mass and then heating to its vapor temperature, followed by the condensing of steam thereon and heating to further drive off any weak volatile acid which may be present.

The commonest cause of instability in the lower fatty acid esters of cellulose is combined sulfuric acid remaining from an esterification reaction in which sulfuric acid is employed as the catalyst. Various methods of stabilizing those cellulose esters have been suggested such as boiling in water or weak acid followed by washing or by neutralizing or both, or washing, using as the last wash water, an aqueous solution of an alkaline carbonate of low concentration. These methods have been fairly satisfactory with the cellulose esters which are hydrophilic.

Recently, however, interest has increased in the lower fatty acid esters of cellulose in which propionyl or butyryl rather than acetyl predominates. With increased ratios of the higher acyl to acetyl, the products obtained tend to become more impervious and more hydrophobic as cellulose esters of this nature offer considerable resistance to the washing out of the free organic acids or neutralizing of the combined sulfuric acid which remains therein. Therefore, the stabilizing of the hydrophobic cellulose esters has created a problem which was not met with in the case of cellulose acetate.

The procedure which is generally used for processing a cellulose ester after completion of the initial esterification reaction is as follows:

1. Hydrolysis, in "dope" solution.
2. Precipitation, separating the ester from the solvent in which it is dissolved.
3. Spray-washing or counter-current washing of the ester to recover economically the bulk of the organic acids retained in the wet precipitated ester, such washing usually reducing the acidity to approximately 0.1% acid.
4. Washing with successive soakings and drainings in fresh water until the ester is acid-free, usually 10–30 times.
5. Boiling before, during, or after step #4 to stabilize the ester, such boiling being carried out for 1–24 hours, in some cases with changes of water one or more times during the boiling operation.
6. Drying.

An object of this invention is to provide a method of eliminating the extensive washing step and at the same time stabilizing organic acid esters of cellulose the acyl of which is predominately fatty acid groups of 2–4 carbon atoms, particularly when those esters have a propionyl or butyryl content of at least 25%. Another object of this invention is to provide a method of refining and stabilizing those esters when they are in a physical form which is unfavorable to satisfactory stabilizing treatment. A further object of this invention is to provide a more economical means of processing, after the usual counter-current wash, to remove free organic acids. When the cost of wash water is high, such as when using specially processed, color-free water to obtain a low color cellulose ester product, our process becomes applicable with considerable savings in processing costs and time. Other objects of this invention will appear herein.

We have found that lower fatty acid esters of cellulose are readily stabilized by soaking the esters in dilute aqueous solutions of weakly alkaline neutralizing agents such as the alkali salts of the weak volatile acids followed by the rapid removal of the free volatile acids formed thereby. This removal is accomplished readily and quickly by controlled heating of the cellulose ester to or slightly above the boiling point of the weak acid which is formed. In this manner a product is obtained which is free of organic acids and of unstable sulfo-esters or combined sulfuric acid in any form. We have found that by steam treating cellulose esters in accordance with this invention, the time required for the final processing and drying of the cellulose ester is considerably reduced and the resulting product is more uniform than it is possible to obtain in using other treatment methods, particularly with celluose esters having a physical form which resists refining and stabilizing.

We have found that such a treatment can be carried out successfully on partially washed cellulose esters, our process being applied immediately after the precipitated ester has been spray-washed or counter-current washed to remove the bulk of the acid (when such washing is necessary for reasons of economy). In this manner, we accomplish both a stabilization and a reduction in processing costs and operation since by our process the customary extensive washing usually performed after spray-washing is eliminated. However, it is to be emphasized that our process is not liimted in its application to cellulose esters at this particular stage of the customary processing but may be applied even after the usual extensive washing process has been applied to remove all the free acid from the product. We have found, however, that with the combination of refining steps, as described herein, the usual extensive washing process can be dispensed with in favor of a more simple washing treatment.

This invention, in its broadest aspects, comprises the steps of,

1. Treating the cellulose ester with a water

solution of a suitable neutralizing agent, such as herein described, the solution having a concentration usually between 0.01 and 0.5%, this concentration depending roughly on the combined sulfuric acid in the celluose ester.

2. Removal from the ester of a considerable amount of the liquid, preferably as much as possible, such as by draining and centrifuging or screw pressing.

3. Heating the cellulose ester mass to the vapor temperature of the liquid components of the mass but well below that at which decomposition of the cellulose ester is likely to occur.

4. Condensing steam onto the cellulose ester and,

5. Then heating the mass again to the vapor temperature of the mass followed by washing, if necessary, and drying.

In carrying out our invention, it is preferred that the cellulose ester be treated with a neutralizing agent to neutralize free sulfuric acid in the reaction mixture before it is precipitated so that the only sulfuric material with which the applicants will have to deal is that which is present in combined form. After the catalyst has been neutralized, the cellulose ester should then be precipitated and counter-current washed to approximately 0.1% free acid. It is to the cellulose esters obtained after a washing treatment removing all except a low concentration (0.1% approximately) of free organic acids but leaving the combined sulfuric acid that this invention is applicable. The thoroughly washed cellulose ester is first soaked with an aqueous solution of a salt, such as aqueous sodium acetate, followed by removal of all of the liquid possible by a dewatering operation. The applicants have found that draining and centrifuging works satisfactorily for this purpose. The cellulose ester mass should be agitated in the next treatment and a satisfactory method of agitating has been a slow tumbling action. For instance, the material may be put through a horizontal heating tube having some kind of agitating equipment, such as a spiral agitator. The temperature is brought to, or slightly above, the boiling point of the weak volatile acid to drive off such residual acid as may be present. In this step it is also desirable to pass steam over or through the mass which acts as a flushing agent for removing the acid vapors from the system.

After this treatment, the ester is treated with steam, the mass being held at a temperature below 100° C. so as to cause the condensation of the steam on the cellulose ester. This condensation treatment is for the purpose of driving the salts, which may be present, into the cellulose ester so that thorough penetration is obtained. This brings the neutralizing agent into intimate contact uniformly throughout the individual particles with sulfuric acid which has been split off during the initial heating and steaming treatment as well as with any sulfo-ester groups which are not yet hydrolyzed off. (The concentration of salt in the original treatment is designed to give a slight excess of this agent.) After this penetration has been accomplished, the mass is again heated to a point at which weak volatile acid, formed by reaction of the salt with the hydrolyzed sulfuric acid, is driven off without damage to the cellulose ester. Ordinarily the cellulose ester is then dried first by subjecting it to a current of air in the same equipment. If, however, the amount of salts present in the ester is large, it will be necessary to include a washing step after the steaming operation but before drying. By this invention low color cellulose esters are obtained in addition to being exceptionally stable.

Although the stabilizing treatment of this invention is adapted for stabilizing lower fatty acid esters of cellulose generally, this process has been found to give stable products with the hydrophobic esters which ordinarily are difficult or sometimes heretofore have been impossible to stabilize.

The alkaline salts of weak acids, which acids have a sufficiently low boiling point that when formed they may be readily driven off, are used in this invention. As the carbonates and acetates are the most common and most representative compounds of this nature, it is salts of this type which will be employed to the greatest extent. Some salts, suitable in this connection, are sodium, magnesium and calcium acetates and sodium, magnesium and calcium carbonates and sodium bicarbonate. We have also found that weak bases, such as calcium or magnesium hydroxide, may be employed in this connection to give a satisfactory stabilized product.

After the cellulose ester from an esterification process, while still present in the reaction mixture, is subjected to neutralization of the free catalyst present and is precipitated and washed, the latter being preferably a counter-current washing, it is soaked with an aqueous solution of the weak alkali or the alkaline salt of a weak volatile acid. The concentration of this alkaline solution is ordinarily between .01 and 0.5% and is roughly governed by the amount of combined sulfuric acid which is present in the cellulose ester being treated, this in turn being a function of the sulfuric acid concentration during hydrolysis, or, if unhydrolyzed, during the reaction. Some of the neutralizing salts mentioned are of limited solubility in water and, therefore, may either be in the form of a suspension or if only a small proportion is used may be a solution or will be used auxiliary to other more soluble neutralizing agents. For instance, the normal calcium carbonate is only soluble to a limited extent in water and if a greater percentage is necessary than is soluble in water, it preferably should be employed in the form of the acid carbonate or some other neutralizing agent should also be employed therewith.

The percentage of the neutralizing salt employed in the soaking treatment is roughly governed by the combined sulfuric acid in the cellulose ester. This in turn is governed by the concentration of the sulfuric acid in the hydrolysis of the cellulose ester. If the cellulose ester, after precipitation and counter-current washing, is centrifuged, the ester will ordinarily retain approximately 60% moisture; that being the case, the following table shows the percentage of neutralizing agent to employ, depending upon the percentage of sulfuric acid in the hydrolysis:

Percent sulfuric acid in hydrolysis bath	Percent sodium acetate in treating solution
0.15	.01–0.05
0.30	0.10–0.15
0.60	0.30–0.50

The soaking is carried on for a sufficient time to thoroughly saturate the cellulose ester with the aqueous alkaline solution. Dewatering is then

applied so as to remove any excess liquid on the cellulose ester.

The cellulose ester is then placed in a vessel, wherein it will be agitated, if not already present in such a vessel. The use of a slow tumbling action, such as obtained by a spiral agitator in a horizontal tube, is satisfactory in this connection. The tube is provided with a heating means, such as a jacket, and in this treatment the mass is heated up to a temperature between 100° and 155° C., preferably between 120 and 130° C., and the treatment lasts normally for 3–5 hours. The time is governed by that necessary to bring the cellulose ester uniformly to the desired temperature and depends upon the amount of heating surface, the agitation and the various other factors of design. There is no advantage in continuing the treatment at the prescribed temperature for longer than 4 or 5 hours and a longer time might cause some hydrolysis or lowering of viscosity which, in some cases, might be undesirable or cause lack of uniformity in the product. During this period of treatment, it is desirable to pass steam through the cellulose ester mass, which steam acts as a flushing agent to aid in removing volatile acid.

The next step in the stabilizing process is the condensing of steam on the cellulose ester mass to drive the neutralizing material into the cellulose ester and thus thoroughly penetrate it. This step may be accomplished in the same apparatus as used in the preceding step with the heat reduced below 100° C., preferably with a jacket temperature of 70–95° C. Also, this treatment is more effective if wet steam rather than dry steam is passed into the mass, although dry steam may be employed if a temperature in the lower part of the range specified is used. The temperature employed in this step depends upon the size of the charge and of the cooling surface, as it is desirable to bring the charge uniformly below 100° C. in a reasonable time and avoid overcooling any part of it to obtain the most economical conditions of operation. The following table gives approximately the time of the cooling period at the prescribed jacket temperature:

Jacket temperature, °C	Cooling period to 95° C.
	Hours
95	3 –5
85	1 –2
75	¼– ½

The steam is fed into the unit uniformly over the cooling period and it is preferable to use between 0.2 and 1.5 pounds of wet steam per pound of cellulose ester. The rate of entry of the steam can be widely varied without affecting the results.

After the condensation period, the temperature is again elevated to obtain a vapor pressure of the volatile acid equal to atmospheric. If an hydroxide was employed as the neutralizing agent, obviously this step may be omitted. When this vapor temperature is attained, the flow of steam may then be cut off or the treatment may be continued for the time desired by the individual operator.

If a large amount of neutralizing salt was used, it is preferable to subject the cellulose ester to a washing operation at this stage of the process. Ordinarily, however, this is unnecessary, as the amount of salt present is so small that its presence in the cellulose ester is not objectionable. The cellulose ester may then be dried, such as by subjecting it to a current of air.

Although the above steps are best performed at atmospheric pressure, the use of other pressures is permissible. For instance, if a lower vapor temperature is desired, a reduced pressure can be employed and vice versa. With the less stable esters which tend to color at higher temperatures, a lower temperature treatment for a longer time is recommended to avoid any possibility of discoloration while removing the sulfur from the cellulose ester.

The following examples illustrate this invention. These examples deal with the stabilizing of a high butyryl cellulose acetate butyrate which was precipitated in powder form, this material being most difficult to stabilize ordinarily.

Example I

A sample of powder precipitated cellulose acetate butyrate, having a butyryl content of 35–38%, was counter-currently washed in a system in which in the last wash 0.2% sodium acetate was added and the cellulose ester was soaked in that solution for one hour. The cellulose ester powder (containing 0.1% free organic acid) was then centrifuged and placed in a jacketed tube where it was subjected to a slow tumbling action. The temperature of the material was brought up to 208° F. by jacket heating the tube for 40 minutes while passing a current of steam through the tube over the ester. At the end of 40 minutes, the liquids were completely vaporized, as shown by the increasing temperature of the ester which rose quickly. The jacket temperature was then controlled so that the cellulose ester temperature was approximately 230° F. for 45 minutes. The flow of steam was stopped and a current of air was passed over the ester until dry. The product showed fair stability, freedom from acidity and good clarity.

Example II

A sample of a powder precipitated cellulose acetate butyrate, having a butyryl content of 35–38%, was treated for 24 hours in an aqueous sodium acetate solution of .5% concentration. The mass was then centrifuged and placed in a jacketed tube, as described in the preceding example. The temperature was brought up as before and after two hours, the vapor temperature was reached. The jacket heat was then reduced at the same time continuing the steam flow and the temperature of the mass dropped back to slightly below the boiling point for ½ hour. The heating was then resumed until the vapor temperature was again attained. The flow of steam through the cylinder was then shut off and the product was dried in a current of air. Analysis of the product, compared with a regular product of like type, was as follows:

	Steam treated sample	Regular plant processed sample
4:1 viscosity	36 sec.	35 sec.
Acetyl	13.1%	13.1%.
Propionyl	0	.8.
Butyryl	36.5%	35.7%.
Acidity	Neutral	Neutral.
160° C. heat test	No melting v. s'l't. brown	Melted spots.
Color (4:1 acetone)	300	150.
Haze (4:1 acetone)	125	135.
Melting point	210° C.	205° C.
Charring point	305° C.	297° C.

As this invention is particularly applicable to cellulose esters which have been precipitated in powdered form due to their impervious nature, the following example is given to illustrate the preparation of a powder type of precipitate: A completed esterification mass having the following composition:

	Pounds
Cellulose acetate butyrate (37% Bu)	1,175
Butyric acid	2,150
Acetic acid	2,500
Water	250

was pumped to a vessel equipped with a suitable agitator. 6000 lbs. of glacial acetic acid was added and stirred in well. The first precipitating liquor, consisting of approximately 7000 lbs. of 40% acid figured as acetic acid, from a previous precipitation, was added over a period of 15–45 minutes with good agitation. This reduces the concentration of acid in the precipitator to approximately 60–64% and at this stage the ester has separated as a granular gel. The precipitation is completed by the addition of sufficient acid (10–15% weak acetic acid), to reduce the acid concentration in the precipitator to 40%. The precipitate can now be separated as a fine granular material by decantation or by draining on a screen. After separation the precipitate may be spray washed to recover the larger part of the retained acid, after which it is treated with dilute salt solution and steamed as described herein.

We claim:

1. A method of stabilizing a powder-precipitated cellulose acetate butyrate of 35–38% butyryl which comprises treating a thoroughly washed powder-precipitated cellulose ester of this type with an aqueous solution of the alkali metal salt of a weak volatile acid stable to moderate heat having a concentration of 0.01–0.5%, then removing liquid therefrom, agitating the cellulose ester while heating the wet mass to the vapor temperature of the liquid components of the mass, followed by lowering the temperature of the mass to 70–95° C., passing steam therethrough and condensing it on the cellulose ester.

2. A method of stabilizing a powder-precipitated cellulose acetate butyrate of 35–38% butyryl which comprises treating a thoroughly-washed powder-precipitated cellulose ester of this type with an aqueous solution of a weakly alkaline salt of acetic acid having a concentration of 0.01–0.5%, then removing liquid therefrom, agitating the cellulose ester while heating the wet mass in the liquid container to the vapor temperature of the liquid components of the mass, followed by lowering the temperature of the mass to 70–95° C., passing steam therethrough and condensing it on the cellulose ester.

3. A method of stabilizing a powder-precipitated cellulose acetate butyrate of 35–38% butyryl which comprises treating a thoroughly-washed powder-precipitated cellulose ester of this type with an aqueous solution of an alkaline metal salt of acetic acid having a concentration of 0.01–0.5%, then removing liquid therefrom, agitating the cellulose ester while heating the wet mass in the liquid container to the vapor temperature of the liquid components of the mass, followed by lowering the temperature of the mass to 70–95° C., passing steam therethrough and condensing it on the cellulose ester.

4. A method of stabilizing a powder-precipitated cellulose acetate butyrate of 35–38% butyryl which comprises treating a thoroughly-washed powder-precipitated cellulose ester of this type with an aqueous solution of sodium acetate having a concentration of 0.01–0.5%, then removing liquid therefrom, agitating the cellulose ester while heating the wet mass in the liquid container to the vapor temperature of the liquid components of the mass, followed by lowering the temperature of the mass to 70–95° C., passing steam therethrough and condensing it on the cellulose ester.

5. A method of stabilizing a powder-precipitated cellulose acetate butyrate of 35–38% butyryl which comprises treating a thoroughly-washed powder-precipitated cellulose ester of this type with an aqueous solution of alkaline metal carbonate having a cencentration of 0.01–0.5%, then removing liquid therefrom, agitating the cellulose ester while heating the wet mass in the liquid container to the vapor temperature of the liquid components of the mass, followed by lowering the temperature of the mass to 70–95° C., passing steam therethrough and condensing it on the cellulose ester.

6. A method of stabilizing a powder-precipitated cellulose acetate butyrate of 35–38% butyryl which comprises treating a thoroughly-washed cellulose ester of this type with an aqueous solution of sodium acetate having a concentration of 0.2%, then removing the liquid therefrom, agitating the cellulose ester while heating the wet mass to the vapor temperature of the liquid components of the mass, followed by lowering the temperature of the mass to 70–95° C., passing steam therethrough and condensing it on the cellulose ester.

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