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METHOD OF STABILIZING MIXED FATTY
ACID ESTERS OF CELLULOSE OF THE TRI-
ESTER TYPE

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This invention relates to the stabilizing of mixed fatty acid esters of cellulose of the triester type in which dilute acetic acid containing an alkaline salt in an amount which will not completely neutralize the catalyst is added to the esterification mass after the preparation of the ester and the mass is maintained at a temperature of at least 110° F. for a short time after the anhydride present has all been converted to acid.

Formerly in the stabilizing of cellulose esters the use of a high temperature was thought to be necessary such as by heating the ester with water in an autoclave. Also it was thought that complete neutralization of the catalyst in the cellulose esterification bath was desirable to diminish the percentage of combined mineral acid in the cellulose ester.

One object of our invention is to provide a method for stabilizing mixed fatty acid esters of cellulose of the triester type in which a moderate temperature only is necessary and in which no lowering of viscosity and substantially no hydrolysis of the cellulose ester occurs. Other objects of our invention will appear herein.

In the manufacture of cellulose organic acid esters the cellulose ester is hydrolyzed usually immediately after its preparation, which action not only removes fatty acid groups from the cellulose ester but, also, any combined sulphuric acid is removed from the product. However, in the preparation of substantially fully esterified esters, ordinarily termed triesters, no hydrolysis occurs and, consequently, some other means must be found to remove the combined mineral acid. In the case of the cellulose esters in which substantially all of the acyl is acetyl the removal of the combined mineral acid has been performed simply and easily. However, with the mixed esters of cellulose containing a substantial proportion of propionyl or butyryl, the combined mineral acid seems to be held more tenaciously and, hence, more difficulty is encountered in stabilizing esters of that type.

We have found that a mixed fatty acid ester of cellulose such as cellulose acetate propionate or cellulose acetate butyrate which has been prepared by means of a fatty acid anhydride and a sulphuric acid catalyst, may be readily stabilized and still remain of the triester type if at the end of the esterification a dilute fatty acid, particularly acetic acid, is added thereto, which acid also should contain an amount of an alkaline salt insufficient to neutralize the free sulphuric acid catalyst which is present, so that the residual anhydride in the batch is converted to acid, a por-

tion of the sulphuric acid is neutralized and the mass is then maintained at a temperature of at least 110° F. for a short period such as 20 or 40 minutes. By proceeding in this manner esters which have heretofore been very difficult to stabilize may be stabilized without any substantial change in the composition of the ester from substantially a triester. This method of stabilizing has been found to be particularly effective for stabilizing cellulose acetate butyrate of the triester or substantially fully esterified type, which esters contain an amount of butyryl between 15% and 19%. We have found that by our method of stabilizing, substantially all of the combined sulphur-containing groups present in the ester may be removed.

A convenient method of converting the acetic anhydride is to add to the cellulose esterification mixture, after completion of the esterification, hot dilute acetic acid slowly to the mass. This dilute acetic acid should contain also a small amount of an alkaline salt which will not completely neutralize the sulphuric acid present in the mass. The primary purpose for adding the dilute acetic acid is to convert the residual anhydride which may be present to the corresponding acid. However, by adding the dilute acid while hot the temperature of the batch will be raised to a point greater than 110° F. due both to the heat of the dilute acid and to the heat of reaction when the residual anhydride present combines with the water in the dilute acid. When the hydrous point is reached the mass is held at a temperature of at least 110° F. and preferably between 110° F. and 120° F. for about 20 to 40 minutes. If, however, the hot dilute acid does not raise the temperature to at least 110° F. it is desirable to apply external heating such as by means of a water jacket so that at least a temperature of 110° F. may be reached, at which the mass is maintained for a short time. The ester is then precipitated, such as in a precipitating amount of dilute acid or in water, and is then washed to form a very stable product.

The amount of dilute fatty acid which is added to the mass should only be such that an amount of water is added which will kill the anhydride, but without causing any precipitation therein. Obviously plain water could be added if extreme care were exercised, but the difficulty in adding water rather than dilute acid is too great to ordinarily justify the use of that method.

The dilute acid which is added to kill anhydride should also contain an alkali metal salt in an amount which will only neutralize some of the

catalyst which is present so that some of the catalyst is still present, either as acid or as an acid salt. Our theory as to the operation of the stabilizing method is that the hot mass which contains a very slight amount of water and some mineral acid or acid salt of some mineral acid selectively hydrolyzes off the combined mineral acid without any appreciable hydrolysis of the fatty acid groups which are present. Therefore, the ester which remains is of substantially the tri-ester type, but yet the combined sulphuric acid is completely eliminated. As 20 to 40 minutes is usually sufficient and in any case no more than one hour is ordinarily necessary, the treatment should be limited to a time of not over one hour and preferably between 20 and 40 minutes. The treatment of the cellulose ester, in accordance with our invention, causes little, if any, lowering of the viscosity of the cellulose ester formed, or breaking of linkages in the cellulose structure of the ester. The amount of hydroxyl which is present in the ester stabilized in accordance with our invention is on the order of 0.1 hydroxyl group per glucose unit ordinarily, but this depends to some extent upon the percentage of combined sulphuric acid in the ester which is stabilized, and the conditions of hydrousness of the dope and the heating interval required to effect stabilization.

In some cases it may be desirable to stabilize the cellulose ester by adding dilute fatty acid to the mass, in which dilute acid there is sufficient neutralizing agent to neutralize all of the catalyst. However, by adopting the procedure of completely killing the anhydride when only a portion of the dilute acid is added and then slowly adding the remainder of the dilute acid, a condition is present in which the anhydride is completely destroyed but yet the catalyst present is only partially neutralized. Another procedure which may be employed is to add rapidly only enough of the dilute acid to destroy the anhydride and then heat the batch for about 30 minutes to one hour over a temperature range of 100° to 120°, which is followed by the addition of the remainder of the final. Various other methods of procedure in which the cellulose ester is neutralized in accordance with my invention will become apparent to those who are skilled in the cellulose ester art. The following examples illustrate processes of preparing cellulose esters in which stabilization is accomplished in accordance with our invention.

Example I

30 pounds of refined cotton linters were pre-soaked with 60 pounds of acetic acid for 4 hours at a temperature of approximately 105° F. 160 pounds of butyric acid were added thereto and the mass was cooled to a temperature of approximately 50° F. 42 pounds of acetic anhydride which had been cooled to 40° F. were added, followed by the addition of a mixture of 134 cc. of sulphuric acid and 435 cc. of acetic acid. After about ½ hour 33 pounds of acetic anhydride, which had been cooled to 42° F. were added, followed by the addition of a mixture of 342 cc. of sulphuric acid and 870 cc. of acetic acid. The reaction was allowed to proceed to a maximum temperature of approximately 95° F. 3½ hours after the last addition of sulphuric acid 3 pounds of acetic anhydride were added. The reaction was continued until the cellulose was completely dissolved, whereupon a mixture of 20 pounds

of water, 20 pounds of acetic acid, and 360 grams of sodium carbonate at a temperature of 120° F. was added slowly and the mass was heated to a temperature of approximately 120° F., which temperature was maintained for 20 or 30 minutes. The batch was then cooled and the ester was separated therefrom by precipitating and washing in the customary manner. A nicely stable cellulose acetate butyrate having a butyryl content of approximately 16% was obtained.

Example II

30 pounds of refined cotton linters were pre-soaked with 46 pounds of acetic acid for 4 hours at a temperature of approximately 105° F. 176 pounds of butyric acid were added thereto and the mass was cooled to approximately 50° F. at which point 39 pounds of acetic anhydride having a temperature of 40° F. were added, followed by the addition of a mixture of 134 cc. of sulphuric acid and 435 cc. of acetic acid. About ½ hour later 36 pounds of acetic anhydride, having a temperature of approximately 40° F., were added, followed immediately by the addition of a mixture of 343 cc. of sulphuric acid and 870 cc. of acetic acid. The reaction was allowed to proceed until it reached a maximum of 95° F. 5¼ hours after the last addition of sulphuric acid 3 pounds of acetic anhydride were added. The mass was maintained at the maximum reached until complete esterification had resulted. A mixture was prepared of 18 pounds of water, 20 pounds of acetic acid, and 350 grams of sodium carbonate. 6 pounds of this mixture with a temperature of 120° F. were slowly added and the mass was heated until it reached a temperature of 120° F. at which it was maintained for about ½ hour. The remainder of the mixture was then slowly added and the mass was cooled and precipitated in the customary manner. A cellulose acetate butyrate was obtained having a butyryl content of approximately 18%. This example illustrates the manner in which the anhydride is destroyed but yet the acid catalyst is not completely neutralized at that time and complete neutralization occurs with the addition of a subsequent portion of aqueous acid containing an alkaline salt.

The alkaline salts which may be employed for the partial neutralization of the mineral acid catalyst are those in which a base is joined to a relatively weak negative ion such as sodium carbonate, sodium acetate, or the like. Although our stabilization process may be performed at temperatures generally of at least 110° F., ordinarily the temperatures between 110° F. and 120° F. are sufficient for all practical purposes. Therefore, operation within this range is preferred. The only criterion of the maximum temperature which may be employed for stabilizing in accordance with our invention is that the temperature of treatment is not so high as to cause chemical degradation of the cellulose ester which is being stabilized.

Ordinarily an acetic acid dilution with water of approximately 50% will destroy the anhydride present without too greatly diluting the mass. It is to be understood, however, that the concentration of acetic acid employed is not critical. This concentration might be as much as 80% or 90%, but use of a concentrated acetic acid would ordinarily be wasteful as the acetic acid content of the bath would be too greatly increased merely to supply sufficient water to kill the anhydride present. On the other hand

a very dilute acetic acid requires considerable care in its addition to avoid the formation of localized precipitating areas in the mass. However, very dilute acetic acid, or even water, can be employed if sufficient care is exercised to avoid precipitation action therefrom. As the acetic acid merely acts to facilitate the addition of the water it is apparent that other lower fatty acids, such as propionic or even butyric acid, might be employed for this purpose instead of acetic acid. It is preferred, however, to employ acetic acid both for reasons of economy and for its value in facilitating the precipitation of the cellulose ester from the reaction mixture.

Our invention depends primarily on the complete conversion of the acid anhydride present into the corresponding acid with water, together with the addition of a small amount of further water to render the mass slightly hydrous, for example, 2-6% of water together with only a partial neutralization of the mineral acid catalyst which is present. By applying the elevated temperature for a short time under slightly hydrous conditions and but a small proportion of mineral acid, stabilization of the cellulose ester prepared is effected without any appreciable change in its acyl content.

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

1. A method of stabilizing a mixed fatty acid ester of cellulose of the triester type the acyl of which essentially consists of fatty acid radicals of 2-4 carbon atoms while in solution in the reaction mixture in which it was prepared, which mixture contains sulfuric acid catalyst, which comprises adding to the mass sufficient aqueous lower fatty acid to destroy the anhydride present without throwing the ester out of solution, which acid contains an alkaline alkali metal salt in an amount sufficient to only partially neutralize the mineral acid catalyst present, and maintaining the mass at a temperature of at least 110° F. but insufficient to cause chemical degradation of the cellulose ester for approximately 20 minutes to 1 hour so as to remove the combined mineral acid from the cellulose ester.

2. A method of stabilizing a mixed fatty acid ester of cellulose of the triester type the acyl of which essentially consists of fatty acid radicals of 2-4 carbon atoms while in solution in the reaction mixture in which it was prepared, which mixture contains sulfuric acid catalyst, which comprises adding to the mass sufficient aqueous acetic acid to destroy the anhydride present without throwing the ester out of solution, which acid contains an alkaline alkali metal salt in an amount sufficient to only partially neutralize the mineral acid catalyst present, and maintaining the mass at a temperature of at least 110° F. but insufficient to cause chemical degradation of the cellulose ester for approximately 20 minutes to 1 hour so as to remove the combined mineral acid from the cellulose ester.

3. A method of stabilizing a cellulose acetate butyrate of the triester type the acyl of which essentially consists of fatty acid radicals of 2-4 carbon atoms which contains a butyryl content of 15%-19% while in solution in the reaction mixture in which it was prepared, which mixture contains sulfuric acid catalyst, which comprises adding to the mass sufficient aqueous lower fatty acid to destroy the anhydride present without throwing the ester out of solution, which acid contains an alkaline alkali metal salt in an amount sufficient to only partially neutralize the

mineral acid catalyst present and maintaining the mass at a temperature of at least 110° F. but insufficient to cause chemical degradation of the cellulose ester for approximately 20 minutes to 1 hour so as to remove the combined mineral acid from the cellulose ester.

4. A method of stabilizing a mixed fatty acid ester of cellulose of the triester type the acyl of which essentially consists of fatty acid radicals of 2-4 carbon atoms while in solution in the reaction mixture in which it was prepared, which mixture contains sulfuric acid catalyst, which comprises adding to the mass sufficient aqueous acetic acid of 50% strength to destroy the anhydride present without throwing the ester out of solution, which acid contains an alkaline alkali metal salt in an amount sufficient to only partially neutralize the mineral acid catalyst present, and maintaining the mass at a temperature of at least 110° F. but insufficient to cause chemical degradation of the cellulose ester for approximately 20 minutes to 1 hour so as to remove the combined mineral acid from the cellulose ester.

5. A method of stabilizing a mixed fatty acid ester of cellulose of the triester type the acyl of which essentially consists of fatty acid radicals of 2-4 carbon atoms while in solution in the reaction mixture in which it was prepared, which mixture contains sulfuric acid catalyst, which comprises adding to the mass sufficient aqueous acetic acid to destroy the anhydride present without throwing the ester out of solution, which acid contains an alkaline alkali metal salt in an amount sufficient to only partially neutralize the mineral acid catalyst present, and maintaining the mass at a temperature of at least 110° F. but insufficient to cause chemical degradation of the cellulose ester for approximately 20 minutes to 1 hour so as to remove the combined mineral acid from the cellulose ester.

6. A method of stabilizing a mixed fatty acid ester of cellulose of the triester type the acyl of which essentially consists of fatty acid radicals of 2-4 carbon atoms while in solution in the reaction mixture in which it was prepared, which mixture contains sulfuric acid catalyst, which comprises adding to the mass sufficient aqueous acetic acid to destroy the anhydride present without throwing the ester out of solution, which acid contains sodium carbonate in an amount sufficient to only partially neutralize the mineral acid catalyst present, and maintaining the mass at a temperature of at least 110° F. but insufficient to cause chemical degradation of the cellulose ester for approximately 20 minutes to 1 hour so as to remove the combined mineral acid from the cellulose ester.

7. A method of stabilizing a mixed fatty acid ester of cellulose of the triester type the acyl of which essentially consists of fatty acid radicals of 2-4 carbon atoms while in solution in the reaction mixture in which it was prepared, which mixture contains sulfuric acid catalyst, which comprises adding to the mass sufficient hot aqueous acetic acid to destroy the anhydride present without throwing the ester out of solution, which acid contains an alkaline alkali metal salt in an amount sufficient to only partially neutralize the mineral acid catalyst present, and maintaining the mass at a temperature of at least 110° F. but insufficient to cause chemical degradation of the cellulose ester for approximately 20 minutes to 1 hour so as to remove the combined mineral acid from the cellulose ester.

8. A method of stabilizing a mixed fatty acid

ester of cellulose of the triester type the acyl of which essentially consists of fatty acid radicals of 2-4 carbon atoms while in solution in the reaction mixture in which it was prepared, which mixture contains sulfuric acid catalyst, which comprises adding to the mass sufficient hot aqueous acetic acid of 50% strength to destroy the anhydride present without throwing the ester out of solution, which acid contains an alkaline salt in an amount sufficient to only partially neutralize the mineral acid catalyst present, and maintaining the mass at a temperature of at least 110° F. but insufficient to cause chemical degradation of the cellulose ester for approximately 20 minutes to 1 hour so as to remove the combined mineral acid from the cellulose ester.

9. A method of stabilizing a cellulose acetate butyrate of the triester type, which ester con-

tains 15%-19% butyryl, while in solution in the reaction mixture in which it was prepared, which mixture contains sulfuric acid catalyst, which comprises adding to the mass sufficient hot aqueous acetic acid of 50% strength to destroy the anhydride present without throwing the ester out of solution, which acid contains an alkaline alkali metal salt in an amount sufficient to only partially neutralize the mineral acid catalyst present, and maintaining the mass at a temperature of at least 110° F. but insufficient to cause chemical degradation of the cellulose ester for approximately 20 minutes to 1 hour so as to remove the combined mineral acid from the cellulose ester.

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