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ALIEN PROPERTY CUSTODIAN

PROCESS FOR STABILIZING CELLULOSE ESTERS

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Our invention relates to cellulose esters and more especially to the stabilization of solid organic acid esters of cellulose in accordance with our copending application for patent Serial No. 64,793, of which the present application is a continuation-in-part.

As is well known, cellulose esters as prepared from cellulose and organic acids or acid anhydrids in the presence of catalysts and solvents or agents preventing solution, are subject to decomposition and not stable. More especially the sulfuric acid, which is the most widely used catalyst and which combines with the cellulose, forming mixed cellulose sulfate esters, is known to greatly impair the stability of the organic cellulose esters, such as the acetates, propionates and butyrates, from which films and other photographic materials are prepared.

A great many suggestions have been made regarding stabilization of such esters, but none of them has been found altogether satisfactory. More especially washing of the esters with water and dilute acids at normal or increased pressure has been found useless because at ordinary temperature these washing agents remain substantially ineffective for the purpose in view, while at elevated temperature they exert a saponifying action on the cellulose esters whereby these latter are impaired. Treatment with aliphatic acids or alkyl esters of such acids at elevated temperature has been found to also injure the cellulose esters. Methyl alcohol as such or mixtures of this alcohol with water, mineral oil products, benzol or carbon tetrachloride, when contacted with cellulose esters at ordinary temperature have not been found capable of imparting to cellulose esters the stability required to render them fit for use in the manufacture of photographic materials.

We have now found that all esterified organic esters of cellulose and quite especially cellulose triacetate, however also mixed esters, can be stabilized in a highly satisfactory manner by treating them at an elevated temperature, preferably above 50°C and better still at temperatures in the neighbourhood or above 100°C, however preferably not beyond 140°C, with an organic liquid and more especially with an aliphatic and/or aromatic hydrocarbon, an alcohol, a ketone, a derivative of such a compound or a mixture of two such compounds, which at these temperatures does not suffer decomposition with the liberation of an acid or alkali, is inert with respect to and does not dissolve the organic cellulose ester, such as for instance cellulose triacetate and renders the liberated acid, for instance sulfuric acid, innocuous by entering into chemical combination with it.

We may also employ low boiling organic liquids, provided that under a pressure above normal they remain liquid, stable and inert with respect to the cellulose esters under treatment.

Benzol, toluene, xylene, methylalcohol, ethylalcohol, propylalcohol, butylalcohol, amylalcohol, benzylalcohol, glycol, glycerine, methylethylketone, diacetonealcohol, methylcyclohexanone and commercial benzine have been tested and found useful as stabilizing agents at temperatures ranging between about 50° and 140°C, under and above normal pressure, the cellulose ester, such as cellulose triacetate, if treated for a sufficient period of time, on being heated one hour to 230°C, substantially retaining its color.

We have found that the treatment according to this invention is not by any means a mere washing process. For while free sulfuric acid can be extracted by washing, the mixed cellulose sulfate esters formed during esterification of cellulose in the presence of sulfuric acid cannot be washed out. We feel certain that it is the elevated temperature which is responsible for the stabilizing effect obtained by our treatment, in that the mixed cellulose sulfate ester is decomposed at this temperature and the sulfuric acid is set free so that it can be bound by chemical reaction and removed by washing.

We have further found that the absolute temperature at which this stabilizing treatment is carried out, plays an important rôle in that it determines the duration of this treatment. Thus, when using methylalcohol which under normal pressure boils already at 60°C, five hours boiling was required to render cellulose triacetate practically stable. With ethylalcohol, boiling at 80°C, a four hours treatment is required, while propylalcohol, boiling at about 110°C, will stabilize the ester after three hours.

A typical example of the influence of the temperature on the result of this treatment is the following: A cellulose triacetate, after two hours boiling in xylene at 60°C, on being heated one hour to 200°C, showed an appreciable brown coloration, while, when treated with xylene two hours at 130°C, one hour's heating to 200°C did not in any way change the pure white color of the ester. This shows clearly that it is the heat that is the principal factor, which fully agrees with the theory advanced by us that stabilization will be obtained only if the mixed ester which contains the radical of the catalyst acid, such as the organic cellulose sulfate ester, is decomposed and the catalyst acid, such as sulfuric acid, set free so that it can be bound by chemical reaction and removed by washing.

The upper temperature limit is determined by the temperature up to which the material to be stabilized may be heated without being affected detrimentally.

Our findings also account for the fact that with the liquids mentioned above, for instance with methylalcohol, when applied at normal temperature, no adequate degree of stability is obtained even if they are allowed to act on the cellulose ester several days. If cellulose triacetate is treated with methylalcohol at 70°C, adequate stability is obtained only after 6 hours, whereas at 120° C the same degree of stability is reached already after some minutes.

This interrelation between the temperature and the length of time required for stabilization enables use to adapt our process to the particular nature of the material to be treated. Cellulose esters which are injured when exposed to a high temperature, are stabilized at a correspondingly low temperature in a correspondingly longer period of time, while others which are less sensitive to heat, may be stabilized at a higher temperature and in a correspondingly shorter period of time.

In every case the results obtained are the better and more reliable, the higher the temperature of treatment and it is therefore advisable to operate at as high a temperature as possible in each individual case. However, when stabilizing cellulose triacetate, the temperature should not substantially exceed 130°C, since at 140°C decomposition would set in.

We have found benzol and ethylalcohol to be particularly suitable as stabilizing liquids, since these substances are available at low cost and do not in any way affect cellulose esters at temperatures such as may be used in our process.

If it should be desired to use low boiling liquids, for instance in order to enable the stabilized product to be dried rapidly at low temperature, the stabilizing treatment should be carried through in a closed vessel, i. e. under pressure above normal and consequently at a higher temperature.

The stabilizing liquid may be recovered by distillation with steam.

Examples

1. 100 parts by weight cotton cellulose are treated with a mixture of 400 parts acetic anhydrid, 200 parts acetic acid and 5 parts sulfuric acid. After acetylation some water is added, whereafter a maturing period of several hours is interposed, followed by precipitation and washing with water. The diacetate obtained is then introduced, for the purpose of stabilization, into about eight times is quantity of ethylalcohol, and left therein for six hours at a temperature of 70°C. This is followed by centrifuging and drying. The diacetate thus treated is of excellent stability. A sample of the acetate, when heated one hour at 200°C, does not show any brown discoloration.

2. 100 parts cotton cellulose are treated with a mixture of 600 parts acetic anhydrid, 1000 parts benzol and 2 parts sulfuric acid. Acetylation is followed by centrifuging and washing out with benzol. The product is cellulose triacetate in fibrous state. The still unstable product is placed in a container and 1200 parts benzol are added. The container is then closed hermetically and heated to about 120°C, the internal pressure being thereby raised to about 3 atms. After two hours the liquid is drained off and the traces of benzol expelled from the triacetate with steam. The triacetate now possesses the same stability as the product obtained in accordance with example 1.

3. 100 parts triacetate obtained in accordance with example 2 are heated with 900 parts methylalcohol to about 110°C in a closed vessel, the internal pressure rising to about 4.5 atmospheres. After a 3 hours treatment the liquid is run off and the adhering methylalcohol centrifuged and washed out with water. This product when subjected to the stability test by being heated to about 200° C, does not turn brown even after an hour.

4. 100 parts cotton cellulose are treated with a mixture of 400 parts acetic anhydrid, 200 parts butyric acid, 3 parts sulfuric acid and 1000 parts toluene. The esterification-product, a mixed ester in fibrous state is treated, after centrifuging and washing out with toluene, four hours with 1000 parts toluene at 90°C. The product thus obtained, when heated one hour to 200°C, retains its white color.

Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

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