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PROCESS FOR RECLAIMING CELLULOSE ESTER MATERIAL

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This invention relates to the separation of a thin layer of a hydrolyzed cellulose ester from a thicker cellulose ester layer to which it adheres, the thin layer being of a lower acyl content than the thicker layer, by treating with a dilute aqueous solution of an alkali metal permanganate and a strong mineral acid at a temperature of at least 150° F.

Ordinarily, photographic film consists of a base of a cellulose ester, one or more subbing layers, and a photosensitive emulsion thereon. Our invention relates to photographic film in which the base is an organic acid ester of cellulose. One or more subbing layers are applied thereover, followed by a gelatin coating or coatings, at least one of which contains photosensitive material. In the recovery of film scrap, the gelatin material is removed first, usually by means of hot water which softens or dissolves the gelatin and thereby loosens it from the cellulose ester material. The resulting material will then ordinarily consist of a base of a lower fatty acid ester of cellulose and one or more subbing layers of a lower fatty acid ester of cellulose which has been hydrolyzed to a greater extent than the film base ester. Our process is particularly applicable to cellulose ester materials primarily composed of a lower fatty acid ester of cellulose and having on one or both surfaces a thin layer of a similar type of cellulose ester but containing, at least, 5 per cent less acyl than the film base.

Heretofore, permanganates such as potassium permanganate have been employed in film scrap recovery processes, but usually those processes were merely concerned with removing the color or dye from the film. In those cases, the permanganate served as an oxidizing agent and could well be replaced by some other oxidizing agent such as hydrogen peroxide or some kind of a chlorine compound.

One object of our invention is to provide a process of recovering film base cellulose esters in which the use of chlorine compounds is unnecessary. Another object of our invention is to provide an inexpensive, but effective, method of removing cellulose ester subbing layers from cellulose ester sheeting. Other objects will appear herein.

We have found that cellulose ester sheeting made up of a thin and a thick layer of cellulose esters, the latter being less hydrolyzed than the former when treated after being chopped into small particles with a dilute solution of acidified permanganate in water at a temperature of at least 150° F., effectively loosens or removes the thin cellulose ester layer from the cellulose ester sheeting which is to be recovered.

Our process involves the treatment of cellulose esters such as cellulose acetate, cellulose acetate propionate, or cellulose acetate butyrate, or simple esters of the lower fatty acids in which a thin layer of one or a mixture of these esters is present therein; the acyl content of the ester of the thin layer being at least 5 per cent less than that of the base of the sheeting. Ordinarily there would be employed esters of not more than 10 per cent difference in acyl between the thin layer and the film base, or thick layer, because of the difficulty of otherwise obtaining adhesion. To illustrate, if the film base is composed of a cellulose acetate having an acetyl content of 40 per cent, it is usually desirable that the subbing layer have an acetyl content of more than 30 per cent. If however good adhesion should be attained between esters having more than 10% difference in acetyl, our process would also be applicable to reclaiming the scrap of the product obtained. Any thin layer of cellulose acetate or some other lower fatty acid ester of cellulose, for that matter, which has a more than 35 per cent acyl content cannot be satisfactorily treated by our invention, when the film base ester has an acyl content of no more than 40% or in other words there should be a span of at least 5% in acetyl contents.

The treating liquor is an aqueous solution of potassium (or other alkali metal) permanganate, and for economy's sake, contains between .25 and 2 per cent of permanganate. Obviously, if economy is not a consideration, a concentration of permanganate up to 5 per cent, or even more, can very well be employed. It is preferable that the amount of acid which is employed to acidify the treating liquor be at least twice that of the permanganate, figured in terms of molecular equivalents. It is only necessary that sufficient acid be employed to give a strong acid solution. The acid which is employed should be an inert strong acid, preferably mineral. Some of the acids which are useful are sulfuric acid, phosphoric acid, nitric acid, benzene sulfonic acid, or the like. As sulfuric acid has been found to be the best and the cheapest for this purpose, it is preferable to use sulfuric acid when removing subbing layers in accordance with our invention. As the presence of chlorides is usually undesirable, avoidance of the use of chlorine-containing acids is recommended.

We have found that ordinarily the subbing layer

can be removed from the film base to which it is attached in one hour at a temperature between 180 and 212° F. in accordance with our invention. If a temperature between 170 and 180° F. is employed, ordinarily two hours is desirable. For temperatures from 170 down to 150° F. times between two and six hours are ordinarily desirable, the time employed depending on not only the temperature used, but also on the ease with which the subbing layer is loosened from the cellulose ester sheeting to which it is attached. For instance, a cellulose acetate having an acetyl content of 30 per cent is more susceptible to penetration by the treating liquid and hence is more easily removed in accordance with our invention than a cellulose acetate having an acetyl content of 35 per cent. It is preferable that a temperature be employed which will bring about the removal of the subbing layer from the film base in at least one hour and preferably less. Although it is desirable to operate at a temperature between 150° F. and the boiling point of water, the temperature may be raised above this range without detrimentally affecting the operation of the process. Obviously, if the temperature is above the boiling point of the water, it is desirable either to operate in an enclosed vessel or under conditions whereby the liquid, after boiling off, is returned to the vessel or is replaced by a fresh addition of water. No advantage has been found, however, in operating under pressure. After the subbing layer has been treated until it becomes water soluble or, at least, water susceptible, the scrap is washed to remove this material leaving only the film base which ordinarily consists of the cellulose ester and plasticizer. The film base so recovered when dissolved in a solvent forms a clear solution which is suitable for reuse in making sheeting for the production of film base or any other purpose.

Ordinarily, in treating the film scrap with the permanganate solution, especially with the lower concentrations of permanganate, the disappearance of the purple color signifies the end of the treatment. It is preferred to then wash the scrap with hot acid sodium sulfite solution, thereby removing the manganese dioxide which is formed by the process. Although there is no critical limitation of the amount of treating liquid to be employed with a given amount of film scrap, we have found that 20 parts of liquid to one part of scrap gives a satisfactory condition of treatment and allows thorough mixing of the scrap, especially in finely chopped condition, with the permanganate solution.

The following examples illustrate the usefulness of our process.

Example I

40 grams of chopped safety film scrap containing blue dye and from which the gelatin emulsion has been removed was stirred and heated to a temperature between 180° and 212° F. in about 800 cc. of an aqueous solution containing 1 per cent $KMnO_4$ and 2 per cent of HNO_3. The base from which the film was made was cellulose acetate butyrate having approximately 30 per cent acetyl and 17 per cent butyryl content. The subbing layer thereon was a cellulose acetate propionate containing about 24 per cent acetyl and 15.5 per cent propionyl. The elevated temperature was maintained until the purple permanganate color was discharged. The liquid was drained off and the mass was stirred a short time with 800 cc. of a hot acidic 1 per cent solution of sodium acid sulfite in water. The sulfite liquid was drained off and this operation was repeated. The scrap was then rinsed by stirring it in several changes of hot water, treating for one-half hour with each change. The cellulose ester material was then dried, and it was found that when the recovered film base was dissolved in a 1:1 mixture of propylene and ethylene chlorides, it gave a clear, substantially colorless, grain-free solution, as compared with a similar solution of the untreated film scrap, which was incompletely dissolved, and deep blue in color.

A practical test to determine whether or not the thin cellulose ester layer has been completely removed is to prepare a viscous solution of the material in a solvent or solvent mixture which will readily dissolve the heavy film but is not a solvent for the thin coating. The untreated films, or those in which the thin layer has not been completely removed, give, under this test, solutions containing numerous particles of undissolved material, while products from which the thin coatings have been properly removed give entirely uniform solutions.

Example II

40 grams of chopped safety film support such as is employed in the preceding example except that it contained no dye as in the first example was stirred and heated to 180–212° F. in about 800 cc. of a solution of 0.25 per cent $KMnO_4$ and 0.5 per cent H_2SO_4 in water. The treatment was continued until the permanganate color was gone. The MnO_2 was removed by stirring with two warm acidified aqueous solutions of sodium acid sulfite of 2.5 per cent concentration in water. The scrap was then rinsed and dried as in the preceding example. The product when dissolved in the solvent mixture used in Example I gave a solution which was clear, colorless, and free of grain.

It may be seen from the above examples that under the conditions described the potassium permanganate in the treating liquor need be only about ¼ per cent concentration unless there is some reason why the permanganate will be used up. For instance, in the first example using a colored film, permanganate was necessary to oxidize the color present therein. The amount of permanganate may be selected by the individual operator for the conditions employed. For instance, with some kinds of dye a 1 per cent concentration of potassium permanganate is sufficient while with other kinds of dye even the use of a treating liquor having a 2 per cent permanganate concentration may not be sufficient to completely discharge the color. In some kinds of photographic film more than one type of dye may be employed or a heavier coating of dye material may be used. In those cases the amount of potassium permanganate employed would obviously be adjusted to provide for removal of the dye as well as the subbing layers.

For the treatment of film scrap by our invention, the removal of any gelatin layers such as of emulsion is ordinarily desirable. This may be accomplished by thoroughly washing the scrap with hot water before subjecting it to the permanganate treatment.

We claim:

1. A method of separating a thin layer of a lower fatty acid ester of cellulose from a thicker layer of a lower fatty acid ester of cellulose to which it adheres in which the cellulose ester which comprises the thin layer has an acyl content of at least 5 per cent less than the cellu-

lose ester of the thicker layer which comprises treating the material at a temperature of at least 150° F. but not more than the boiling temperature of the liquid employed under conditions of operation with an aqueous solution of an alkali metal permanganate and an inert strong acid in sufficient amount to remove the thin layer from the thicker layer.

2. A method of separating a thin layer of a lower fatty acid ester of cellulose from a thicker layer of a lower fatty acid ester of cellulose to which it adheres in which the cellulose ester which comprises the thin layer has an acyl content of at least 5 per cent less than the cellulose ester of the thicker layer which comprises treating the material at a temperature of at least 150° F. but not more than the boiling temperature of the liquid employed under conditions of operation with an aqueous solution of potassium permanganate and an inert strong acid in sufficient amount to remove the thin layer from the thicker layer.

3. A method of recovering cellulose organic ester film base material from photographic film scrap containing it which comprises first washing the scrap with hot water to remove gelatinous material therefrom, treating the so-washed material at a temperature of at least 150° F. but not more than the boiling temperature of the liquid employed under conditions of operation with an aqueous solution of an alkali metal permanganate and an inert strong acid for a sufficient time to remove subbing or other layers which are present upon the film base.

4. A method of separating a thin layer of a lower fatty acid ester of cellulose from a thicker layer of a lower fatty acid ester of cellulose to which it adheres in which the cellulose ester which comprises the thin layer has an acyl content of at least 5% less than the cellulose ester of the thicker layer, which comprises treating the material at a temperature of at least 150° F. but not more than the boiling temperature of the liquid employed under conditions of operation with an aqueous solution of an alkali metal permanganate and sulfuric acid, the permanganate being present in sufficient amount to remove the thin layer from the thicker layer.

5. A method of recovering the film base from photographic film scrap having a base of a lower fatty acid ester of cellulose and a subbing layer thereon of a farther hydrolyzed lower fatty acid ester of cellulose which comprises first washing the film scrap with hot water to remove the gelatinous material therefrom and treating the so-washed material with an aqueous solution of an alkali metal permanganate and sulfuric acid at a temperature of at least 150° F. but not more than the boiling temperature of the liquid employed under conditions of operation, the permanganate being present in sufficient amount to remove the thin layer from the thicker layer.

6. A method of separating a thin layer of a lower fatty acid ester of cellulose from a thicker layer of a lower fatty acid ester of cellulose to which it adheres in which the cellulose ester, which comprises the thin layer, has an acyl content of at least 5% less than the cellulose ester of the thicker layer, which comprises treating the material at a temperature of 180–212° F. with an aqueous solution of an alkali metal permanganate and an inert strong acid in a sufficient amount to remove the thin layer from the thicker layer.

7. A method of separating a thin layer of a lower fatty acid ester of cellulose from a thicker layer of a lower fatty acid ester of cellulose to which it adheres in which the cellulose ester, which comprises the thin layer, has an acyl content of at least 5% less than the cellulose ester of the thicker layer, which comprises treating the material at a temperature of 180–212° F. with an aqueous solution of potassium permanganate and sulfuric acid, the permanganate being present in sufficient amount to remove the thin layer from the thicker layer.

8. A method of recovering the film base ester from photographic film scrap in which the base of the film comprises a cellulose acetate butyrate having an acetyl content of 30% and a butyryl content of 17% and the subbing layer thereon comprises a cellulose acetate propionate containing about 24% acetyl and 15.5% propionyl, which comprises washing the film scrap in hot water to remove the gelatinous material therefrom and subsequently treating the scrap at a temperature of 180–212° F. with an aqueous solution of potassium permanganate and a strong mineral acid, the permanganate being present in sufficient amount to remove the subbing layer from the film base.

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