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METHOD OF RECOVERING FILM SCRAP

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This invention relates to the reclamation of cellulose ester sheeting which contains a thin layer of cellulose nitrate thereon, such as met with in photographic film scrap.

In the manufacture of photographic film in which a lower fatty acid ester of cellulose, such as cellulose acetate, cellulose acetate propionate, or cellulose acetate butyrate, is employed as the film base, it is ordinarily necessary to employ a subbing layer to cause the photosensitive gelatin emulsion to adhere thereto. One of the most commonly employed subbing layers is a thin layer of cellulose nitrate and/or gelatin or other water-soluble material. In making photographic film the production of more or less waste is often unavoidable. To process this waste film for salvage purposes requires the removal of the nitrate subbing layer from the film base. Also, used film which is no longer of value and has been discarded, in order to be employed for some useful purpose must be treated to separate the gelatin and the nitrate subbing layers therefrom.

One object of my invention is to provide a method of removing the nitrate subbing layer from sheeting of an organic acid ester of cellulose without deleteriously affecting the organic acid ester of cellulose which will be referred to herein, for purposes of illustration, as cellulose acetate. Other objects of my invention will appear herein.

My invention involves the treatment of the scrap material at an elevated temperature with a dilute solution of an amine having trivalent nitrogen until the thin nitrate layer thereon is completely removed therefrom without contamination from the presence of any cellulose nitrate.

The cellulose ester material may, for instance, be treated with an aqueous solution of an amine of $\frac{1}{2}\%$ concentration at 145° F. for twenty hours' time. Although concentrations of not more than 1% have been found to satisfactorily remove the nitrate, higher concentrations can be used (limiting the concentration being only for economical reasons) but with no better results and, therefore, concentrations of not over 1%, such as $\frac{1}{4}\%$ to $\frac{3}{4}\%$, are most desirable. Also, the time of treatment is not fixed but depends to a great extent upon the temperature employed in treating the cellulose ester material. For example, temperatures of 140 – 160° , and a processing time of fifteen–twenty hours may be required. With higher temperatures shorter times are satisfactory. For instance, with a temperature of 180° F. the processing time may be reduced to from one to three hours. With temperatures above 180° F. a time of not more than one hour is ordinarily sufficient, the use of pressure bringing the time down still more. The time of treatment should be that which is sufficient to completely remove the subbing layer from the cellulose ester sheeting, and the time will be governed by the accomplishment of this purpose. With a

lower temperature such as 125° , much longer times are necessary than given, hence this is about the minimum temperature which one would care to use. In cases where films have backing dyes, such as carried by a backing layer or applied as a coating on the back of the film, it may be desirable to continue the treatment for a longer time to diminish or completely remove the dye, which is present, therefrom. In cases of film in which the dyes are also present in the emulsion layers, such as with Kodachrome or other colored films, it is desirable that the treatment for removal of the gelatin from the film contains some adsorbing material, such as activated carbon, to take up the color during that treatment.

The amines which may be employed for treating scrap material in accordance with my invention are of various types, all of which have been found to be effective, although in some cases, some of these amines form colored compounds which may stain the sheeting proper, and consequently some compounds of this type are more desirable than others. The amines which are useful in my invention may be conveniently divided into the following classes:

1. Alkylolamines—among the amines of this type which have been found satisfactory for this purpose are ethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, and butyl amino ethanol.

2. Alkylamines—the lower alkyl amines, such as methyl- and ethylamines are effective, but because of their low boiling point and high volatility they are less well adapted to this process than the higher alkylamines such as dibutylamine, diamylamine, octylamine, and the like, which are not driven off so easily under elevated temperature conditions. Any of these amines which are not sufficiently soluble in water may be combined with acids which facilitate water solutions, such as lactic acid or acetic acid.

3. Arylamines—benzylamine and benzyldiethanolamine have been found to be very effective for the purposes of my invention. With the arylamines, however, it is desirable that too high a temperature or too high a concentration of the amine be avoided, particularly with compounds such as aniline, p-toluidine, dimethyl aniline, or the like, due to their color-forming tendencies.

4. Cyclic tertiary amines—amines of this nature have been found to be quite suitable for use in accordance with my invention. Ethyl morpholine and methyl morpholine are representative of the types of compounds which are satisfactory for removing the nitrate subbing layer from cellulose acetate base films.

5. Heterocyclic compounds—some of the amines under this designation are less active than other types of compounds. For instance, pyridine exhibits a slow action and, also, is not

preferred for use in this connection because of its volatility. Quinoline also requires a longer processing time than is necessary with other amines. Compounds, however, of the nature of methylated pyridines, such as collidine or hexyl pyridine, have been found to be quite effective and avoid the disadvantages of pyridine and quinoline.

As has been pointed out, it is desirable that the amine which is employed for reclaiming cellulose esters in accordance with my invention have a rather high boiling point and low volatility as obviously, under the circumstances of use encountered in my invention, highly volatile materials introduce problems which may be avoided by the proper selection of the amines to be employed for this purpose.

As my invention is adapted primarily to the recovery of photographic film scrap, it will be particularly described with reference thereto. The film scrap is preferably first chopped up into small particles and subjected to the action of water, preferably having a temperature of 90–120° F., either with or without a digestive enzyme, such as pancreatin, to remove the gelatin emulsion therefrom. If colored film or super-sensitive film is being processed it is also desirable to incorporate in the warm water used to remove the gelatin emulsion an adsorbent such as activated carbon, silica gel, alumina, or absorbent earth in the mass so that the dye, particularly if of a water-soluble type, is adsorbed thereby rather than being allowed to bleed into the cellulose ester material. This treatment is carried out for some time at a temperature between 90° F. and 120° F. until the gelatin is completely removed from the cellulose ester sheet. After removing the gelatin the material is washed and then treated with the hot aqueous solution of an amine at an elevated temperature for a sufficient time to remove the nitrate subbing layer from the film. Ordinarily the proportion of scrap to liquid is 1:20, or in other words, sufficient of the solution is employed to completely immerse the material being treated.

The following examples illustrate my invention:

Example I

50 parts of scrap film having a cellulose acetate base and containing a cellulose nitrate subbing layer, such as is described and claimed in U. S. patent No. 2,014,547 of G. S. Babcock, were immersed in a mixture of 1000 parts of water and 2.5 parts of 2:4:6 trimethyl pyridine. The mass was maintained at a temperature of 180° F. for a period of about three hours. The material was then washed and dried and was found to be suitable for solution in solvents for cellulose acetate in which cellulose nitrate does not dissolve in appreciable amounts. The resulting solutions are practically colorless (that is, no more color is present than is visible in the original solution from which the base was first formed) and upon spreading the solution or dope upon a film-forming surface there is obtained transparent sheeting free from grain and haze.

Example II

50 parts of a cellulose acetate film subbed with cellulose nitrate and from which the gelatin had been removed, were immersed in a solution consisting of 1000 parts of water and 2 parts of dimethyl ethanolamine. The mass was agitated at a temperature of 145° F. for twenty-four

hours. The material was washed and dried and was found to be suitable for solution in solvents for cellulose acetate in which cellulose nitrate does not dissolve in appreciable amounts. The resulting solutions are practically colorless (that is, no more color is present than is visible in the original solution from which the base was first formed) and upon spreading the solution or dope upon a film-forming surface there is obtained transparent sheeting free from grain and haze.

Example III

The details of Example I were followed except that 2 parts of stearyl dimethylamine were employed instead of trimethylpyridine. Similar results were obtained.

I claim:

1. A process of recovering a lower fatty acid ester of cellulose from sheeting comprising a base of the cellulose ester and an overcoating of cellulose nitrate thereon, which comprises subjecting the sheeting to the action of a dilute aqueous solution of an amine selected from the group consisting of alkylolamines, alkylamines, arylamines and cyclic tertiary amines at a temperature of at least 125° F. for a sufficient time to substantially completely remove the cellulose nitrate therefrom.
2. A process of recovering a lower fatty acid ester of cellulose from sheeting comprising a base of the cellulose ester and an overcoating of cellulose nitrate thereon, which comprises subjecting the sheeting to the action of water containing ¼–1% of an amine selected from the group consisting of alkylolamines, alkylamines, arylamines and cyclic tertiary amines at a temperature of at least 125° F. for a sufficient time to substantially completely remove the cellulose nitrate therefrom.
3. A process of recovering a lower fatty acid ester of cellulose from sheeting comprising a base of the cellulose ester and an overcoating of cellulose nitrate thereon, which comprises subjecting the sheeting to the action of a dilute aqueous solution of an amine selected from the group consisting of alkylolamines, alkylamines, arylamines and cyclic tertiary amines, at 180–212° F. for one hour.
4. A process of recovering a lower fatty acid ester of cellulose from sheeting comprising a base of the cellulose ester and an overcoating of cellulose nitrate thereon, which comprises subjecting the sheeting to the action of a dilute aqueous solution of an alkylolamine at a temperature of at least 140° F. for a sufficient time to substantially completely remove the cellulose nitrate therefrom.
5. A process of recovering a lower fatty acid ester of cellulose from sheeting comprising a base of the cellulose ester and an overcoating of cellulose nitrate thereon, which comprises subjecting the sheeting to the reaction of water containing ¼–1% of an alkylolamine at a temperature of 180–212° F. for approximately one hour.
6. A process of recovering a lower fatty acid ester of cellulose from sheeting comprising a base of the cellulose ester and an overcoating of cellulose nitrate thereon, which comprises subjecting the sheeting to the reaction of water containing ¼–1% of a dimethylethanolamine at a temperature of 180–212° F. for approximately one hour.

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