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RECOVERY OF CELLULOSE ESTERS FROM SCRAP

Carl J. Malm and Gustave B. Bachman, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

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This application relates to the recovery of an organic acid ester of cellulose, which has been used as the base for photographic film, from film scrap by means of an organic leaching liquid containing a small amount of a wetting agent.

Photographic film is composed of a photo-sensitive gelatin emulsion supported by a re-enforcing layer commonly referred to as the film base. Ordinarily the film base essentially consists of an organic acid ester of cellulose. A film base is usually overcoated or supported with a layer of material to promote the adhesion of a photo-sensitive emulsion thereto. Also, color or tinting is employed to prevent halation. When photographic film is scrapped, it is desirable to recover the organic acid ester of cellulose which is used as the base of the film. To do this requires the removal of the photo-sensitive emulsion and of the subbing layer and the coloring matter which is employed therewith. The present invention relates to the recovery of scrap film to which dye or color had been applied to prevent halation. The use of a combination of bleaching and washing has been suggested to remove the color from film; however, by this process impurities may be introduced into the cellulose ester or the bleaching agent may deleteriously affect the organic acid ester of cellulose. The use of leaching solvents for the removal of subbing layers has been suggested and some of the tinting material is removed thereby. By this treatment, the removal of color is far from completed, so that up to the time of our invention, subsequent bleaching has been necessary.

One object of our invention is to provide a method for recovering cellulose esters from film scrap in which the color and/or the subbing layers may be completely removed in one operation. Another object of our invention is to provide a method for film scrap recovery requiring less time and a less number of changes of leaching liquid than have been necessary heretofore. Another object of our invention is to provide a process in which less solvent is necessary to accomplish a satisfactory leaching than has been previously necessary.

We have found that, if the film scrap, after the emulsion has been removed therefrom, is treated with a leaching liquid, which will dissolve the subbing layers and remove the color but which will not deleteriously affect the film base, containing a small amount of wetting agent, the resulting product is free of color so that a subsequent bleaching treatment is unnecessary. We have found that, by incorporating a wetting agent, which is soluble in the leaching solvent, the leaching solvent is much more effective to accomplish the desired purpose, as evidenced by the decreased number of changes of solvent which are necessary and by the lessening of the time required to complete the leaching operation. By employing a wetting agent with the leaching solvent, a film scrap can be satisfactorily leached in as little as five minutes, although a longer time is preferred.

Only a small amount of wetting agent need be employed in the leaching solvent, although the presence of large amounts is not objectionable. As little as .025% of wetting agent has been employed and resulted in a satisfactory product; smaller amounts can be used, such as .016%, however, with too small an amount of wetting agent, the results are not as satisfactory. If .016% wetting agent is incorporated in the leaching solvent, a satisfactory product is obtained. Whereas, the film scrap, treated in accordance with our invention with only one leaching operation, comes out nearly colorless and has a clean shiny surface when dried, the same material, which is treated in like manner in the absence of a wetting agent, exhibits appreciable coloration and upon drying has an opaque surface.

To prepare the film scrap for treatment in accordance with our invention, the photographic gelatin emulsion is ordinarily removed, such as by treating with hot water. After this treatment, the film scrap is subjected to the leaching treatment in which a small amount of wetting agent is present. It is preferred that the film scrap be first dried after the removal of the emulsion layer, as the amount of moisture present in the leaching solvent is thereby kept low. After the film scrap has been agitated in the leaching solvent containing a small amount of wetting agent, the scrap is separated from the liquid and, if the leaching liquid is water miscible, it may be washed with water and dried. Often in the washing with water, considerable foaming occurs. In that case it is preferred that the film scrap be given a washing with leaching solvent alone subsequent to the treatment with leaching solvent and wetting agent and prior to the washing with water. In this way the foaming in the water is prevented. In this procedure the leaching solvent employed for the second washing can, after use, be mixed with a small amount of wetting agent and be employed for the first treatment of another batch of film scrap. This second leaching solvent may be used

until its effectiveness for preventing foaming is destroyed whereupon it may be either used for the first leaching or, separated from the impurities therein and re-employed for the foam preventing step.

The wetting agents, which are miscible with the leaching solvent and inert to the film base, may be employed in our invention. Some of the wetting agents, which may be used, are as follows:

1. Aliphatic or cyclo-aliphatic sulphonates or sulfates. A hydrocarbon radical in these compounds should contain ten or more carbon atoms. Other groups, which are not opposed to the conditions of operation, may be also present. These compounds are usually obtainable either in the form of their inorganic or organic salts.

Some examples of this type of wetting agent are:

Sodium diamyl sulfosuccinate
Sodium lauryl sulfate
Sodium lauryl sulfonate
Sodium n-oleyl-n-methyl taurate

2. Non-ionic wetting agents. Examples of compounds of this type are glycerin mono-oleate, diglycol oleate and glyceryl mono-stearate. As a matter of fact, a wetting agent of this type might be prepared by taking natural fat and adding glycerin thereto.

3. Cation-active wetting agents. These are compounds in which the positive ion is large. They are usually substituted ammonium salts, such as cetyl ammonium chloride, dimethyl benzyl ammonium chloride, lauryl pyridinium p-toluene sulfonate and dimethyl benzyl cetyl ammonium chloride. Although only compounds containing nitrogen have been listed under this item, compounds having similar atoms instead of nitrogen, such as arsenic or phosphorus, in like chemical structures are suitable in this connection. Compounds of this type which are suitable in my invention, where compatible with the leaching solvent are disclosed in U. S. Patent No. 2,125,031 of Polak and Weeldenburg.

4. Alkyl-substituted aromatic sulphonic acids. The compounds under this group, which are suitable for use as wetting agents in our process, may be represented by the following structural formula:

$$R''—\underset{\displaystyle (R')_n}{Ar}—SO_2—OX$$

where Ar is an aromatic hydrocarbon nucleus, R′ is an aliphatic hydrocarbon radical, X is hydrogen or an alkali metal, R″ is hydrogen, OH, or OR‴, R‴ being an aliphatic or aromatic hydrocarbon radical, n is 1, 2, 3 or 4, and the total number of carbon atoms in the unit $—Ar—(R')_n$ is at least 11. When n is 2, 3 or 4, the aliphatic hydrocarbon radicals represented by R′ may be the same or different. The total number of carbon atoms in the unit $—Ar—(R')_n$ is preferably about 18 to 24.

Examples of wetting agents of this nature are keryl benzene sulfonic acid (keryl representing the mixture of hydrocarbon radicals derived from kerosene) the sodium salt of which is known as Nacconol NR; keryl phenol sulfonic acid, the sodium salt of which is known as Nacconol AX; cetyl phenol sulfonic acid and p-tertiary-amyl phenol sulfonic acid. Compounds of this type, which are useful in our invention, are mentioned in Staud and Bachman application Serial No. 231,916, filed September 27, 1938.

5. Salts of aliphatic carboxylic acids having a large number of carbon atoms such as found in ordinary soaps. Examples are: sodium palmitate, sodium stearate, triethanol ammonium laurate and diethyl ethanol ammonium oleate.

In some cases in our process the addition to or presence of water in the leaching solvent cuts down the efficiency. If the dyes, which are to be removed from the film scrap, are not water soluble or water susceptible, the presence of water renders the dyes less susceptible to the action of the leaching solvent; therefore, as a rule, the presence of water is to be avoided.

The leaching solvent, which may be employed, is any organic solvent which will remove the dye and also preferably the subbing layer, without any bad effect on the film base itself. The leaching solvent to be employed will be governed to some extent by the subbing layer which is to be removed. It is also preferred, but not necessary, that the leaching liquid be water miscible, as this contributes to the facility with which the film scrap can be washed after the leaching. The solvent may be a mixture of methyl alcohol or some other lower aliphatic alcohol mixed with a small amount of acetone or it may be the alcohol without dilution, particularly if the alcohol is suitable for this purpose without any further addition.

The following examples illustrate processes embodying our invention:

Example I

200 parts of methyl alcohol-acetone, consisting of 4 parts of alcohol and 1 part of acetone, containing 1.6% of a Nacconol NR extractant, was agitated for 30 minutes with 50 parts of film scrap from which the photographic emulsion had been removed. The methyl alcohol-acetone was then drained off and the scrap was thoroughly washed. Whereas the scrap prior to this treatment was blue, after the treatment it was colorless and had a clean shiny surface when dried. The used solvent, containing wetting agent, was added to a fresh 50 gram sample of scrap and agitated for 30 minutes. The scrap was then washed thoroughly and found to be substantially colorless, although it did not have as good appearance as the film scrap obtained in the initial treatment.

Example II

50 parts of film scrap, from which the emulsion had been removed, was leached with 200 parts of 4:1 alcohol-acetone containing 0.1% of N-oleyl-N-methyl taurate. As in Example I, the leaching liquid was drained from the scrap and it was then rinsed twice with 200 parts of the solvent containing no wetting agent. The scrap was then washed with water. No foaming occurred in washing of the scrap with water as in Example I the scrap was clean and free of color. If desired, this method can be performed countercurrently, such as by adding the detergent about half way through the leaching process. Thus the fresh solvent would remove any residual wetting agent from the film scrap before it entered the washed water.

Example III

The procedure of Example I was repeated except that the agitation took place for five minutes. The solvent was poured off and the sample was washed and dried. The product compared favorably in appearance with the sample obtained in Example I.

Example IV

The same conditions, described in Example I, were repeated except that 0.167% wetting agent was employed. The film scrap, after washing and drying, appeared to be as good as that obtained in Example I.

By using a wetting agent, various other treatments, such as bleaching, which were formerly thought necessary in the recovery of scrap film, have been eliminated so that the scrap is recovered in one operation in a form suitable for directly dissolving and coating out into sheeting. The resulting sheeting, if plasticized to the same degree, has substantially the same properties as that of the sheeting which was employed to prepare the film base. Various organic acid esters of cellulose, such as cellulose acetate, cellulose acetate propionate, cellulose acetate butyrate, cellulose propionate or cellulose butyrate, may be recovered from film scrap in which it has been employed in the film base in accordance with our invention.

Any organic solvent which does not dissolve the base of the film scrap but does dissolve the dye or backing to be removed is suitable in our process. Examples of the types of compounds which are suitable for use as organic solvents are:

Liquid aromatic hydrocarbons such as toluene
Ethers such as di-isopropyl ether and the cellosolves
Liquid esters such as ethyl acetate
Ketones such as methyl ethyl ketone
Lower aliphatic alcohols such as ethyl alcohol and isopropyl alcohol

Any liquids selected from these classes having the characteristics pointed out above may be employed for recovering photographic film scrap in accordance with our invention.

We claim:

1. A method for recovering photographic film scrap having a base of a lower fatty acid ester of cellulose which comprises treating scrap, which is free of gelatin emulsion, with an organic leaching solvent which will not dissolve or deteriorate the film base, the leaching solvent containing a small amount of a material to assist the leaching selected from the group consisting of the aliphatic and cyclo-aliphatic sulphonates and sulphates in which a hydrocarbon radical therein contains at least 10 carbon atoms, the glycols incompletely esterified with higher fatty acids, the glycerols incompletely esterified with higher fatty acids, the cation-active substituted ammonium salts, the alkyl-substituted aromatic sulphonic acids, the alkyl substituted aromatic unit containing at least 11 carbon atoms and the alkali metal and substituted ammonium salts of the higher fatty acids.

2. A method for recovering photographic film scrap having a base of a lower fatty acid ester of cellulose which comprises treating scrap, which is free of gelatin emulsion, with an organic leaching solvent essentially consisting of a lower aliphatic alcohol and acetone in proportions which will not dissolve the cellulose ester but which will effectively remove the color therefrom, the leaching solvent containing a small amount of a material to assist the leaching selected from the group consisting of the aliphatic and cyclo-aliphatic sulphonates and sulphates in which a hydrocarbon radical therein contains at least 10 carbon atoms, the glycols incompletely esterified with higher fatty acids, the glycerols incompletely esterified with higher fatty acids, the cation-active substituted ammonium salts, the alkyl-substituted aromatic sulphonic acids, the alkyl substituted aromatic unit containing at least 11 carbon atoms and the alkali metal and substituted ammonium salts of the higher fatty acids.

3. A method for recovering photographic film scrap having a base of a lower fatty acid ester of cellulose which comprises treating the scrap, which is free of gelatin emulsion, with a leaching solvent essentially consisting of a lower aliphatic alcohol and acetone in proportions which will not dissolve the cellulose ester, the leaching solvent containing the sodium salt of keryl benzene sulphonic acid to assist the leaching operation.

4. A method for recovering photographic film scrap having a base of a lower fatty acid ester of cellulose which comprises treating the scrap, which is free of gelatin emulsion, with a leaching solvent essentially consisting of a lower aliphatic alcohol and acetone in proportions which will not dissolve the cellulose ester, the leaching solvent containing sodium N-oleyl-N-methyl taurate.

CARL J. MALM.
GUSTAVE B. BACHMAN.