

[54] CELLULOSE ESTER DOPE SOLUTION
CONTAINING INORGANIC CHROMIUM
SALTS

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[57] ABSTRACT

The addition of certain soluble metallic salts to dopes of cellulose esters having at most about 3.3 percent hydroxyl results in improved stripping performance of the resulting films after the dopes have been cast and partially dried on a smooth metallic sheet casting surface.

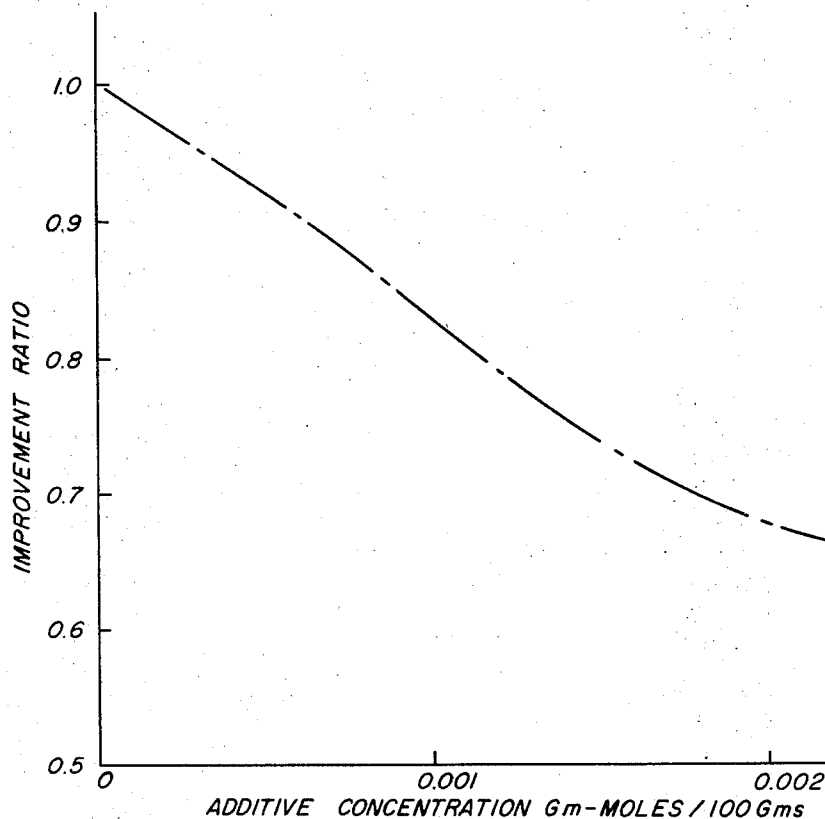
[52] U.S. Cl. 106/194, 106/196
[51] Int. Cl. C08b 27/02, C09j 3/04
[58] Field of Search 106/194, 196; 117/6

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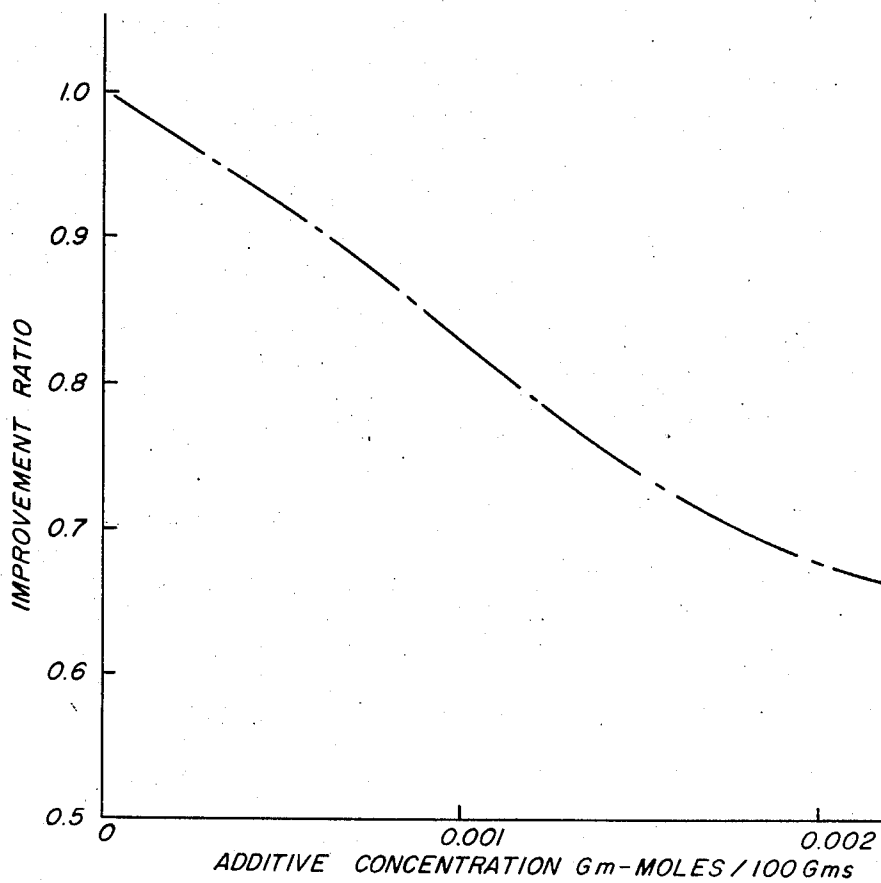
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1 Claim, 1 Drawing Figure



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CELLULOSE ESTER DOPE SOLUTION CONTAINING INORGANIC CHROMIUM SALTS

This invention relates generally to solutions for, and an improved method of, forming cellulose ester films or sheets by the casting method. More particularly, the invention relates to the addition of certain specified non-photoactive ingredients to cellulose ester solutions, which ingredients facilitate to a large degree the stripping of the cellulose ester film from the casting surface upon which it is formed.

It is common practice in the manufacture of cellulose ester sheeting for photographic film base or other uses to cast a film of a solution of the desired cellulose ester in a volatile solvent upon a casting wheel or other surface, evaporate at least a portion of the volatile solvent and strip the sheeting from the casting wheel or surface. As is well known to those skilled in this art, the speed with which an apparatus such as the casting wheel used in such an operation can be successfully operated relates directly to how quickly the sheeting can be drawn from the casting surface, which in turn depends on how fast the film attains sufficient strength to be so stripped. The strength factor is required since during formation of the sheet from the cast film, some degree of adhesion between the sheet and the casting surface arises and the sheet, before removal, must be strong enough to withstand the force required to overcome this adhesion without damage. One possible source of a large portion of this adhesive force is explained below.

Thus, for many years means have been sought to reduce the amount of adhesion arising between the casting surface and the sheeting and hence the force required to remove the sheeting therefrom.

Initial attempts in this direction related to improvements in, and modifications of, the casting wheel. These attempts included the use of chromium or stainless steel coated surfaces. Subsequently, efforts turned to modification of the cellulose ester solution and although some progress has been made in this field no entirely satisfactory system has yet been devised, particularly in areas where the finished sheeting is to be used in photographic applications and the sheeting must not only achieve a high degree of physical perfection, but must also be absolutely free of photoactive materials.

It is therefore an object of the present invention to provide a method which facilitates stripping of the cellulose ester sheeting from the casting wheel or other surface and hence provide a valuable means for increasing the speed and production of casting operations and improving overall quality of the finished stripped film surfaces.

It is another object of the present invention to provide cellulose ester casting solutions containing additives which, although they greatly increase the ease with which cast cellulose ester film base or sheeting can be removed from the casting surface, produce no detrimental effects when such sheeting is subsequently used in photographic applications.

It has been discovered that the addition of soluble metallic salts of aluminum, copper, tin and chromium (which will hereinafter often be referred to as "stripping additives") to certain cellulose ester dopes before casting will greatly reduce the sheet-to-casting surface adhesion described above. Addition of such salts as indicated in the Examples set out below can lower the

required stripping force by as much as 90 percent and can lower the required minimum stripping time by as much as 70 percent.

Although the actual reasons for the surprising benefits that can be obtained by practicing this invention are not known, one possible "mechanism" for these benefits is that the metallic stripping additive(s) in the dope somehow combines with adhesion promoting groups in the cellulose ester film, thereby inhibiting any bonding of the polymer to the casting surface which might result otherwise. Tests on samples such as those prepared in the Examples below, indicate that the addition of such agents produces no major detrimental effect upon either the physical properties of the finished sheet nor upon the photographic properties of film which might be subsequently manufactured therefrom. The metallic stripping additives which may be utilized in the successful practice of this invention generally include those materials, especially metal salts, which upon dissolution in the cellulose ester dope yield a chemically active cation which is able to "tie up" adhesion promoting groups (such as, for example, carboxylic acid groups in the ester thereby preventing the formation of any bonds between the polymer and the casting surface by the carboxylic acid groupings). It is interesting that some support for this theory can be found in the fact that, if the metallic stripping additive is dissolved in an alcohol such as methyl alcohol before it is incorporated into the dope solution, the stripping benefits described above apparently are not obtained. It has been found that only certain metallic salts can be used in the successful practice of the present invention. Also, apparently, the beneficial effects of these salts are produced only when the cellulose ester contains at most about 3.3 weight percent of hydroxyl. Useful metallic stripping additives include all inorganic chromium, aluminum, nickelous, ceric, lead, tin and cupric salts that are soluble at 25°C in a solution of 20 grams of cellulose acetate (having an intrinsic viscosity of 2.0, and acetyl content of 43 percent) dissolved in 68 grams of methylene dichloride to the extent of at least about 0.0005 gram moles/100 grams of dry cellulose acetate, and all organic aliphatic carboxylate and naphthenate, chromium, aluminum, tin and cupric salts that contain from 2 to 14 carbon atoms. Of course, the salt must also be photographically inactive at the use levels employed. These materials will often be referred to herein by use of the term "metallic stripping additives".

Cellulose ester dopes useful in the preparation of cellulose ester sheet or film base are well known in the art and need not be described in great detail here (see, for example, U.S. Pat. No. 2,607,704) except in the context that useful cellulose esters include cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, cellulose acetate propionate, and cellulose propionate butyrate, containing at most about 3.3 weight percent (preferably at most about 3 weight percent) of hydroxyl, and having intrinsic viscosities of from about 0.8 to about 5. They are generally used when dissolved at levels of at least about 20 weight percent in such volatile solvents as acetone, methyl alcohol, ethyl alcohol, methyl ethyl ketone, ethylene dichloride, hexane, cyclohexane, and the like and mixtures thereof.

The value of the present invention can be readily determined by experimentally casting a film on a clean smooth chromium plate and determining in a conven-

tional way (a) the amount of time necessary for the resulting film to "set up" with sufficient strength to be removable from the plate in a single piece (this being termed "green peel time" in the art), and (b) the amount of force needed to remove the green film from the plate after 180 seconds, and by comparing the resulting data with typical "green peel time" data (measured in the conventional manner) for comparable dopes containing no "metallic stripping additive". Table I below was prepared from such data. The figures for "improvement ratio" were obtained from the ratio:

$$\frac{[\text{green peel time (experimental dope)}]}{[\text{green peel time (control-no additive)}]}$$

The concentration of "additive" in these experimental dopes was 0.001 gram moles per 100 grams of cellulose acetate (dry basis).

TABLE I

Improvement Ratios From Green Peel Times For Some Additives		
Example No.	Additive	Improvement Ratio
	Control (No additive)	1.00
1	Aluminum nitrate	0.61
2	Cupric chloride	0.81
3	Stannic chloride	0.82
4	Nickelous chloride	0.83
5	Chromium naphthenate	0.74
6	Chromium nitrate	0.78
7	Chromium neodecanoate	0.80
8	Chromium carbonate	0.85
9	Chromium acetate	0.87
10	Stannous chloride	0.92
11	Chromium octoate	0.91
12	Chromium stearate	1.00
13	Chromium oleate	1.03
14	Sulfur	1.06
15	Cadmium nitrate	1.01
16	Cuprous iodide	1.01
17	Chromium chloride	0.83

From this table it is clear that the effective metallic stripping additives of this invention generally reduce the green peel time (G.P.T.) by at least about 10 percent at the indicated concentration.

The effect of varying the concentration of one of the preferred metallic stripping additives of this invention in a particular dope is demonstrated in the single FIGURE, which shows a measure of "improvement ratio" on the vertical axis measured against the concentration of chromium chloride additive in a cellulose triacetate dope similar to that used to obtain the data reported in Table I and Example 3, below. From this graph it is clear that at very low levels of additive, the relationship between the two variables is substantially linear, i.e., "green peel time" is reduced in almost a direct proportion as the concentration of the metallic stripping additive, in this case a metal salt, is increased. Testing indicates that this relationship exists up to levels of concentration of the additives described herein of about 0.0025 gm.-mole/100 grams of dry cellulose ester in the dope.

For some as yet unexplained reason, the particular cellulose ester contained in dopes prepared and utilized in accordance with this invention is apparently a critical element thereof. Generally improved results in the form of a greater G.P.T. reduction are achieved when the cellulose ester treated is one having a fairly low level of hydroxyl, i.e., at most about 3.3 percent hydroxyl. Specifically preferred for such treatment are

dopes of cellulose esters containing at most about 3.0 percent hydroxyl. Other than this limitation, the make-up of the particular ester contained in the dope appears to have little or no impact on the improved stripping characteristics achieved with the subject method.

Similarly, the concentration of the ester in the solvent produces no apparent effect adverse or otherwise upon the improved stripping characteristics obtained when solutions of the types described herein are cast and stripped according to conventional techniques in greatly reduced periods of time.

The following examples illustrate the application of our invention and the stripping properties of casting dopes produced in accordance therewith.

EXAMPLE 1

Hydrated chromium nitrate is added to a cellulose triacetate dope at a level of 0.001 gm.-mole/100 grams of dry ester and mixed for 24 hours. The dope is then cast using experimental equipment to a cured thickness of 3.8 mil. The minimum stripping time is found to be 55 seconds. After curing on the casting surface for 180 seconds, 0.017 lbs./in. is required to strip the plastic sheet from the casting surface. A check solution containing no additive strips in 75 seconds at a thickness of 4.0 mil and requires 0.067 lb./in. of force to strip at 180 seconds.

EXAMPLE 2

Soluble chromium bromide is added to a cellulose triacetate dope at a level of 0.001 gm.-mole/100 grams of dry ester and mixed for 72 hours. Minimum stripping time when a film is cast from this solution as described in Example 1 is 65 seconds at a cured thickness of 5.4 mil. The force required to strip after 180 seconds is found to be 0.067 lbs./in. A check solution requires 112½ seconds to peel at a thickness of 4.9 mil and 0.10 lbs./in. to strip at 180 seconds.

EXAMPLE 3

25 grams of a cellulose acetate propionate ester comprising 30 percent acetyl, 14 percent propionyl and 1.7 percent hydroxyl, having an average molecular weight of about 80,000 and an intrinsic viscosity of 1.8 is dissolved in 100 grams of a solvent mixture comprising 85 grams of methylene dichloride, 10 grams of butyl alcohol and 5 grams of methyl alcohol, and containing as a plasticizer for the ester 2.0 grams of triphenyl phosphate. A check solution, and solutions containing (a) 0.001 gm.-mole/100 grams of dry ester of chromium nitrate and (b) 0.001 gm.-mole/100 grams of dry ester of aluminum nitrate are prepared. Five mil cured thickness films cast with each of these solutions produce the stripping results recorded at A of Table II.

EXAMPLE 4

25 grams of a cellulose acetate-butyrate ester comprising 29.5 percent acetyl, 17.5 percent butyryl and 1.3 percent hydroxyl, having an average molecular weight of about 60,000 and an intrinsic viscosity of 1.32 is dissolved in 100 grams of a solvent mixture containing 70 grams of methylene dichloride, 20 grams of cyclohexane and 10 grams of butyl alcohol and 2.0 grams of triphenyl phosphate as a plasticizer for the ester. A check solution and solutions containing (a) less than 0.001 gm.-mole/100 grams of dry ester of aluminum nitrate; and (b) 0.001 gm.-mole/100 grams of dry

ester of chromium nitrate are made therefrom. Five mil cured thickness films cast with each of these solutions produce the stripping results recorded at B of Table II.

EXAMPLE 5

20 grams of a cellulose triacetate ester comprising 43.3 percent of acetyl and 1.09 percent hydroxyl, having an average molecular weight of about 98,000 and an intrinsic viscosity of 2.8 is dissolved in 100 grams of a solvent mixture comprising 82 grams of methylene dichloride, 8 grams of cyclohexane, 10 grams of methyl alcohol and as a plasticizer for the ester, 3.0 grams of triphenyl phosphate. A check solution and solutions containing (a) 0.001 gm.-mole/100 grams of dry ester of aluminum nitrate; and (b) 0.001 gm.-mole/100 grams of dry ester of chromium nitrate are prepared. Five mil cured thickness films cast with each of these solutions produce the stripping results recorded at C in Table II.

EXAMPLE 6

17 grams of scrap (higher acetyl) cellulose ester are dissolved in 100 grams of a solvent mixture comprising 89 grams of methylene dichloride, and 10 grams of methyl alcohol and containing 2.8 grams of triphenyl phosphate as plasticizer for the ester. A check solution and solutions containing (a) 0.001 gm.-moles/100 grams of ester of chromium nitrate and (b) about 0.0005 gm.-moles/100 grams of ester of aluminum nitrate are prepared. Films having a cured thickness of 5 mils cast with each of these solutions produce the stripping results recorded at D in Table II.

EXAMPLE 7

25 grams of a cellulose acetate ester containing 40 percent acetyl and 3.4 percent hydroxyl, having an average molecular weight of about 51,000 and an intrinsic viscosity of 1.34 is dissolved in 100 grams of a solvent mixture comprising 90 grams of methylene dichloride and 10 grams of methyl alcohol and containing 3.7 grams of triphenyl phosphate and 3.7 grams of methoxymethylphthalate as plasticizers for the ester. A check solution and solutions containing (a) 0.001 gm.-moles/100 grams of ester of chromium nitrate are prepared. Five mil cured thickness films cast with each of these solutions produce the stripping results recorded at E of Table II.

TABLE II

	Additive	Corrected G.P.T. (Sec. 5 Mils)	Improvement Ratio
A	Check Sol.	75	—
	Aluminum Nitrate	30	.4
	Chromium Nitrate	16	.21
B	Check Sol.	24	—
	Aluminum Nitrate*	22	.92
	Chromium Nitrate*	25	1.04
C	Check Sol.	95	—
	Aluminum Nitrate	48	.51
	Chromium Nitrate	78	.82
D	Check Sol.	163	—
	Aluminum Nitrate*	125	.77
	Chromium Nitrate	97	.60
E	Check Sol.	90	—
	Chromium Nitrate	120	1.33

* Less than 0.001 gm.-mole/100 grams in solution due to solubility limitations.

In all of the above examples, no detrimental effect upon the properties of the dope or upon the photographic film products manufactured from the films cast with the various dopes has been observed. Thus, it can be concluded that the various complexing additives of this invention produce no detrimental effects.

From the above results, it is quite clear that the esters whose solutions produce the data recorded A, C and D (i.e., the fairly low hydroxyl content esters), demonstrate the most improved stripping characteristics while the higher hydroxyl content esters which yield the data recorded at B and E of Table II demonstrate smaller degrees of improvement or alternatively, none at all.

Thus, in summary, almost any agent which is soluble in a dope of a cellulose ester having a fairly low hydroxyl content and which is capable of forming an organic complex with the "foreign" carboxylic acid groups present in the polymeric ester is suitable for use in accordance with the present invention. The concentration of the complexing agent may range up to about 0.0025 gm.-mole/100 grams of dry ester or more, if desired, but preferably should range up to only about 0.0015 gm.-moles/lb. of dry ester.

The particular solvent utilized to form the ester dope is not critical, and almost any conventional solvent used for this purpose may be provided as the dissolving medium. Of course, care should be exercised to choose a solvent which will not produce a deleterious effect upon the ester or the finished film or result in a preferred usage of the additives by complexing or compounding of the complexing agent.

Varying the concentration of the ester in the volatile solvent produces no apparent effect upon the beneficial stripping properties achieved in the successful practice of the instant invention, and hence this parameter should not be considered as in any way critical to the successful practice thereof.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A cellulose ester dope solution comprising a cellulose ester selected from the group consisting of cellulose acetates, cellulose propionates, cellulose butyrates, cellulose acetate butyrates, cellulose acetate propionates and cellulose propionate butyrates, said ester having at most about 3.3 percent hydroxyl, at least one volatile organic solvent in which said ester is dissolved, said ester being present in an amount equal to at least about 20 weight percent of said dope solution, and at least about 0.0005 gram moles per 100 grams of said ester of a metallic stripping additive selected from the group consisting of: chromium acetate, chromium chloride, chromium carbonate and chromium nitrate, said salts being soluble at 25°C to the extent of at least about 0.0005 gram moles per 100 grams of cellulose acetate in a test solution of 20 parts by weight of cellulose acetate in 68 parts by weight of methylene dichloride, said cellulose acetate having an intrinsic viscosity of about 2 and an acetyl content of about 43 percent; said dope solution being adapted for casting a layer onto a smooth metallic casting surface and, to form a cellulose ester film thereupon by evaporating part of said volatile solvent from said layer, which film can then readily be stripped from said casting surface.

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