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3,738,924

PROCESS FOR THE SOLVENT CASTING OF CELLULOSE FILMS USING RADIATION, AND PRODUCTS THEREOF

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15 Claims

ABSTRACT OF THE DISCLOSURE

Significantly increased processing rates can be obtained when cellulose ester dopes used in solvent casting processes for manufacturing cellulose ester film products (for photographic film base, for example) are modified with one or more compatible monomeric materials capable of undergoing free radical polymerization, and the resulting cast (modified) dopes are irradiated with high-energy radiation to polymerize the compatible monomer portion of the dope before the cast layer is stripped from the casting web. The resulting film products have properties equal to or better than conventional cellulose ester films in spite of the degradation of the cellulose ester material by the high-energy radiation that might have been expected.

The present invention relates to improved processes for manufacturing film materials containing, as a major component, at least one lower fatty acid ester of cellulose. More particularly, this invention relates to a method for significantly increasing the maximum rates at which film materials containing such cellulose esters can be manufactured via the so-called "solvent casting" method or procedure.

It is well known that in order to manufacture highest quality films (having very little color or haze, for example) of lower fatty acid esters of cellulose (such as cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, and the like, wherein the lower fatty acid portion contains 2-4 carbon atoms and the ester materials have intrinsic viscosities in 90/10 methylene chloride/methanol of at least about 1, it is necessary to (a) initially form an appropriate "dope" of the ester(s) dissolved in an appropriate blend of organic solvents having relatively low boiling points; (b) cast the dope upon a web having a smooth surface such as a stainless steel belt or a casting wheel (or a specially coated surface thereof) of relatively large circumference; (c) evaporate part of the solvent system from the dope to thereby cause the cellulose ester to "set up" and form a film material having enough internal strength to retain its form when it is removed or "stripped" from the web upon which it was cast; and (d) then removing still more of the solvent(s) from the film as it is passed through a drying (curing) zone. Such processes are described in detail in U.S. Pat. 2,492,977, for example.

Conventional "solvent casting" procedures such as just described are inherently limited with respect to the speed at which high quality cellulosic films can be manufactured. Thus, speed limitations appear, for example, at the point at which the partially "dried" film is removed from the casting web because of the inherent limitation that exists upon the rates of evaporation of the various solvents in the dope, since a fairly large proportion of such solvents must ordinarily be evaporated from the layer "as cast" before the layer develops sufficient integral strength to be removed from the web. Still another problem that necessitates a relatively long initial evaporation step (prior to the time the film is introduced into the curing zone) relates to the relative "stickiness" of the cast layer to the

2

casting web. Thus, if the partially dried film is removed too soon from the web, some of the film remains stuck to the web. This problem is recognized in the art as the web "pick-off" problem. Then, too, the drying or "curing" zone must conventionally be fairly long because of the necessity to remove from the film a very large proportion (i.e., generally about 90 percent or more) of the total amount of organic volatile solvents that had originally been present in the dope solution.

Typically, conventional cellulose ester film manufacture via such solvent casting techniques requires about 20-25 minutes (from initial solvent cast to final removal of the film from the "curing" or drying oven). Although many attempts have been made heretofore to significantly shorten this time interval (by, for example, using higher temperatures in the "drying" steps, or by using different volatile solvents, or by performing the solvent removal steps under vacuum conditions), such attempts have not been more than marginally successful for various reasons, both economical and practical.

It has now been discovered that solvent casting processes for manufacturing films composed mainly of cellulose lower fatty acid esters (preferably cellulose acetate) can be markedly shortened in an economical way by (a) incorporating into the solvent portion of the dope an effective amount of a compatible organic monomer (which not only can serve as a solvent or co-solvent for the cellulose ester film former in the dope, but also can be polymerized via a free radical procedure) and (b) subjecting the layer of cast dope, while it remains on the coating web and before it has developed sufficient integral strength to be satisfactorily stripable, to a sufficient amount of ionizing radiation to cause the free radical polymerization of the monomer(s) in the cast layer, said amount of ionizing radiation being less than that which causes the cellulose ester in the cast layer to degrade excessively. This "amount" of ionizing radiation will preferably be from about 0.3 to about 10 megarads. Still further preferred dosage, in the presence of sensitizers, for example, is from about 0.5 to about 3 megarads. By this improved technique, a substantial proportion of the monomer portion of the dope solution is caused to polymerize practically instantly upon exposure to the ionizing radiation, thereby causing the cast layer to develop almost immediately sufficient integral strength for the layer to be satisfactorily stripable (from the casting web) in a fraction of the time heretofore required by conventional "drying" techniques. An additional advantage that can result from practicing the present improved processes is that relatively smaller amounts of organic solvent(s) need be recovered from the "drying" and "curing" steps, thereby resulting in less total demand upon solvent collection and purification equipment (which presently represent a large necessary investment in conjunction with the conventional film solvent casting equipment described above).

The "compatible monomers" referred to above are those well-known organic compounds;

- (a) having at least one "double bond" of unsaturation in their molecules,
- (b) having molecular weights of at most about 300,
- (c) soluble in the dope composition to at least the minimum extent required, and
- (d) having the ability to form clear films when they are blended, in a "compatibility" test, at a level of 25 parts monomer, to 100 parts of cellulose acetate containing about 40 percent acetyl and having an intrinsic viscosity of about 2.4 in a 90/10 blend of methylene chloride/methanol, cast into a thin 10 mil layer, exposed to a high energy electron beam at a dosage level of 1.5 Megarads, and then warmed at 60° C. for 3 minutes (to remove most remaining solvents).

Typical non-limiting examples of such "compatible monomers" are the lower alkyl acrylics such as methyl methacrylate, ethyl acrylate, ethyl methacrylate, acrylonitrile, butylene dimethacrylates, ethylene glycol dimethacrylate, and the like, as well as other "unsaturated" monomers such as acrylic acid, acrylamide, diacetone acrylamide, diallyl phthalates, styrene, vinyl acetate, vinyl butyrate, and the like.

It is believed surprising that the polymeric products that result from practicing the processes of this invention are apparently copolymeric in nature, (rather than a simple admixture of cellulose ester and polymerized monomers, as would be expected), involving the apparent multiple grafting of polymerized monomer to the cellulosic material. Thus, the products that result from practicing the present processes have unique and unexpected properties. For example, practically none of the "polystyrene" portion can be extracted from the film product from Example I, below even after prolonged treatment in boiling toluene. In addition, although the casting of a dope composition containing 14% cellulose acetate and 2.1% polystyrene (in an attempt to otherwise simulate Example I, without the use of monomers and ionizing radiation) results in a very hazy film product (having 100% haze) after the solvent is removed, the product resulting from the present process in Example I is of excellent clarity, having less than 2% haze. Thus, films of acceptable photographic quality can be made via the present processes utilizing starting compositions that (based upon conventional solvent casting process results) would be expected to yield hazy, unacceptable film products. Also, whereas one would expect ionizing radiation to attack and degrade the cellulose ester portion of the dopes of this invention (and indeed, such degradation has been measured to be as much as 30% in 4 mil conventional cellulose ester films when they are exposed to 2.5 megarads), for some reason the physical properties of the films made in accordance with the present preferred practice are not only satisfactory, but are sometimes enhanced, depending upon the particular monomer(s), the amounts thereof that are used in the practice of this invention, and the radiation level utilized.

In the practice of the present invention, the "compatible monomer(s)" that are used in the formulation of the various cellulose ester dopes should generally be present in the solvent fraction of the dopes (i.e., that portion that can be evaporated from the dopes in a circulating air oven at a temperature of 105° C. and at atmospheric pressure) in an amount equal to at least about 5 weight percent and will preferably represent from about 15 to about 80 weight percent of said volatile solvent fraction. Also, the "compatible monomers" should be used in amounts equal to at least about 10 weight percent of the cellulose esters in these compositions, but should not be used in amounts higher than twice the amount of cellulose ester(s) in the present dope compositions. In the preferred practice of this invention, the ratio of total "compatible monomers" to total cellulose ester(s) in the dope should be at most about 1 to 1, respectively, by weight. The remainder of the solvent fraction can contain any desired volatile, non-polymerizable organic solvent or blend of volatile non-polymerizable organic solvents that have conventionally been employed in cellulose ester dopes heretofore. This includes, but is not limited to methanol, ethanol, isopropanol, n-propanol, butanol, methylene chloride, cyclohexane, ethylene dichloride, chloroform, and the like. As is well known in the art, sometimes blends of such solvents are more desirable in certain formulations to yield completely clear dopes.

The dissolved (non-volatile at 105° C.) fraction of the initial dope compositions of the present invention should consist essentially of one or more of the film-forming lower fatty acid cellulose esters described heretofore, and can also contain a relatively smaller amount [up to about 25 weight percent, based on the combined weights of

5 plasticizer(s) and cellulose ester(s) in the dope of one (or a blend) of those materials that are known to plasticize the cellulose ester film], as well as colorants such as dyes, anti-oxidants, and stabilizers. Typical, non-limiting examples of plasticizers for cellulose ester films are triphenylphosphate, methoxyethyl phthalate, diallyl phthalate (a polymerizable plasticizer), and the like. This dissolved fraction represents at least about 10 weight percent of the present dope compositions, but preferably 10 should represent from about 15 to about 35 weight percent of the dope compositions.

15 Typical examples of the types of ionizing radiation that can be used in the successful practice of this invention include high energy electrons (see "Industrial Radiation Cured Coatings Speed Product Finishing" by John A. Mock, Material Engineering, October 1970, pp. 56 through 59), beta particles, gamma rays, X-rays, positive ions such as alpha particles, and ionizing radiation from decomposing radioactive materials such as radioactive cobalt, for example. The particular physical manner whereby the 20 ionizing radiation is applied to the dope layers in the practice of this invention is not critical. The radiation should be of sufficient intensity or strength to penetrate through the entire thickness of the cast dope layer. Thus, it is preferred that at least half of the ionizing radiation 25 be strong enough to pass completely through the cast dope layer.

30 The particular source of the ionizing radiation that causes the polymerization of a substantial proportion of the "compatible monomer" in the dope compositions of this invention is not critical, so long as the dosage level at the cast dope layer is at least about 0.3 megarads. The ionizing radiation must be directed onto the cast dope layer while the layer remains on the initial casting web. 35 Thus, if the dope is cast onto a slowly turning stainless steel wheel, for example, a high energy electron beam can be directed onto the dope layer shortly, or practically immediately, after the dope layer is cast, thereby causing an immediate, very large increase in the integral strength 40 of the layer and enabling the partially cured layer to be stripped successfully from the wheel in a much shorter time than would otherwise be possible without undesirable "pickoff." Thus, in the preferred (but not essential), 45 practice of this invention, the ionizing radiation should be applied to the "wet" dope layer within about three minutes of the time the layer is cast into the web.

In the following examples, all parts are by weight unless otherwise specified:

EXAMPLE 1

50 Ten parts of cellulose acetate (containing 43.5% acetyl and having an intrinsic viscosity of 2.40 at 25° C. in a 90:10 blend of methylene chloride and methanol, respectively) are dissolved in 50 parts of a 90:10 blend of methylene chloride and methanol. Twenty parts of a solution containing equal amounts of styrene monomer and the same solvent blend are then mixed with the solution of cellulose ester. The resulting dope contains equal amounts of cellulose acetate and styrene monomer. This 55 dope is then coated at room temperature on a glass plate to a thickness of 7 mils. It is almost immediately thereafter radiated at a dosage level of 2 megarads by a conventional high energy electron 300 kv. accelerator having a 25 milliamp beam current. Almost immediately thereafter (about 10 seconds from the time the layer was cast) the film is stripped from the glass plate as an integral film. The film is then subjected to 30 seconds of drying/curing (to remove most of the volatile organic solvents 60 remaining in the film) in a forced draft oven at 60° C. The film is clear and of excellent photographic film base quality.

65 By comparison, a cast layer of the same dope without the radiation treatment cannot be stripped until 150 seconds had passed at room temperature. A comparison of

several physical properties of these films, after the drying/curing treatment is tabulated below:

Test	Irradiated	Not irradiated
Tensile (10 ³ p.s.i.)	15.4	16.8
Percent elongation	9.4	11.1
Modulus (10 ⁵ p.s.i.)	7.0	5.0
Tear (grams)	11	8

Infrared analysis of these films indicated that a large amount of polystyrene is present in the irradiated film, but none is present in the film that was not irradiated. The "irradiated" film product has properties which are considered definitely acceptable for use as a base for photographic film.

EXAMPLE 2

Example 1 is repeated, using methyl methacrylate monomer in place of the styrene monomer. The resulting dried/cured film has the following properties:

Tensile (10 ³ p.s.i.)	14.6
Percent elongation	7.5
Modulus (10 ⁵ p.s.i.)	5.9
Tear (grams)	11

EXAMPLE 3

Example 1 is repeated using vinyl acetate monomer. The resulting dried/cured film has the following properties:

Tensile (10 ³ p.s.i.)	10.7
Percent elongation	3.8
Modulus (10 ⁵ p.s.i.)	5.3
Tear (grams)	13

EXAMPLE 4

Example 1 is repeated using 1,3-butylene dimethacrylate as the monomer in place of the styrene monomer. The resulting dried/cured film has the following properties:

Tensile (10 ³ p.s.i.)	7.7
Percent elongation	1.5
Modulus (10 ⁵ p.s.i.)	5.5
Tear (grams)	Irregular

The use of mixtures of "compatible monomers" (in conjunction with the cellulose esters) yield similarly high quality films via such processes. All of the above films are clear and colorless, although colorants can be used in the dopes (and products) if desired. Similarly, all "dopes" used in the practice of the present invention should be substantially clear when they are cast initially (just prior to their being irradiated).

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.

What is claimed is:

1. In a process which comprises the steps of
 - (a) casting a cellulose ester dope in the form of a wet film onto a web; said dope consisting of a solvent fraction and a dissolved fraction; said dissolved fraction consisting essentially of a film-forming cellulose lower fatty acid ester and said solvent fraction consisting essentially of at least one volatile solvent for said dissolved fraction;
 - (b) evaporating a portion of said solvent fraction from said wet film to thereby cause said dope to set into the form of a partially dried film; and

5

6

- (c) thereafter stripping said partially dried film from said web and passing said partially dried film through a drying zone to thereby remove at least half of the organic solvent material remaining in said partially dried film;
- the improvement which comprises (i) incorporating into said solvent portion at least about 5 weight percent of a soluble, compatible unsaturated monomer, and (ii) subjecting said wet film to ionizing radiation in an amount equal to at least about 0.3 megarad prior to step (c); said compatible unsaturated monomer having a molecular weight of at most about 300 and being capable of free radical polymerization.
2. An improved process as in claim 1, wherein said cellulose lower fatty acid ester is selected from the group consisting of cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, and cellulose butyrate film formers having intrinsic viscosities of at least about 1.
- 15 3. An improved process as in claim 2, wherein the amount of said ionizing radiation is from about 0.5 to about 3 megarads, and said ionizing radiation has sufficient strength to penetrate said wet film.
- 20 4. An improved process as in claim 2, wherein said ionizing radiation is comprised of high energy electrons.
- 25 5. An improved process as in claim 4, wherein the amount of said ionizing radiation is from about 0.5 to about 3 megarads, and said ionizing radiation has sufficient strength to penetrate said wet film.
6. An improved process as in claim 5, wherein the amount of said monomer is from about 20 to about 80 weight percent of said solvent portion, said dope being clear at the time it is cast onto said web.
- 30 7. An improved process as in claim 6, wherein said monomer is styrene.
- 35 8. An improved process as in claim 7, wherein said monomer is methyl methacrylate.
9. An improved process as in claim 8, wherein said monomer is vinyl acetate.
- 40 10. An improved process as in claim 9, wherein said monomer is 1,3-butylene dimethacrylate.
11. A clear film product containing at least about 50 weight percent of lower fatty acid ester of cellulose and at least about 10 weight percent of polymerized compatible monomer unsaturated copolymerized therewith; said film product having been manufactured according to the process of claim 1.
- 45 12. A film product as in claim 11, wherein said polymerized compatible unsaturated monomer is polystyrene.
13. A film product as in claim 11, wherein said polymerized compatible unsaturated monomer is poly(methyl methacrylate).
- 50 14. A film product as in claim 11, wherein said polymerized compatible unsaturated monomer is poly(vinyl acetate).
- 55 15. An improved process as in claim 1, wherein the web is a moving web.

References Cited

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