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MANUFACTURE OF PHOTOGRAPHIC FILMS

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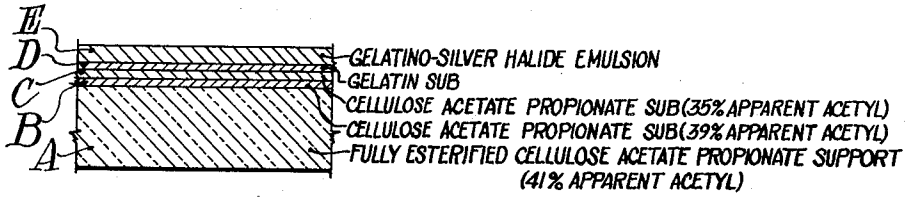

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MANUFACTURE OF PHOTOGRAPHIC FILMS

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10 Claims. (Cl. 95—9)

This invention relates to photographic materials and, more particularly to an improved type of photographic film comprising a cellulose organic ester support which has been especially treated to adapt it for the application of the light-sensitive emulsion.

As is well known, photographic emulsions (which are light-sensitive colloidal solutions or dispersions of gelatin in aqueous media) cannot be made to stick to the surface of a film support composed of a cellulose derivative material unless the support has been coated or subbed with gelatin or some other substance to which the emulsion can be made to adhere. In order to obtain adherence of the gelatin to a cellulose derivative surface it must be deposited from a solution which has a solvent or at least a softening or swelling action with respect to the cellulose derivative, that is, the solution must "bite into" the cellulose derivative material to a certain extent in order to anchor the deposited gelatin thereto. Experience has shown that, in general, the stronger the solvent action of the subbing solution, the greater will be the adherence; also that the greater the adherence, the less will be the flexibility, that is, the greater will be the brittleness of the resulting film. Gelatin and other subbing solutions are, accordingly, classified as strong or weak, depending on their solvent action with respect to the film support to which they are applied.

The manufacture of cellulose nitrate films has presented few difficulties because of the fact that a satisfactory degree of adherence may be attained, without a substantial loss of flexibility, by the use of relatively weak gelatin subbing solutions. Cellulose organic ester films of the safety type, on the other hand, require much stronger solvents in the subbing solution with a resulting increase in adherence of the deposited gelatin layer or layers and, therefore, in the brittleness of the finished product. In order to get around this difficulty, it has been proposed to first apply to the cellulose organic derivative material a thin undercoat of cellulose nitrate to which the gel sub may be applied, as previously indicated, from weak solutions, but this has the disadvantage that it introduces cellulose nitrate into the product and makes it difficult to meet the underwriters' specifications for safety film.

This invention has as an object to provide a light-sensitive photographic film having satisfactory flexibility and emulsion adherence characteristics and including a base or support composed of a cellulose organic ester. Another object is to provide a photographic film base composed of a mixed cellulose organic ester, such as cellulose acetate-propionate, which is adapted for the application of gelatin subs or undercoats without the use of solvents which induce brittlenes in the finished product. A further object is to provide a photographic film having satisfactory flexibility and emulsion adherence characteristics which may be gel-coated and emulsion-coated without the use of undercoats of cellulose nitrate. Other objects will hereinafter appear.

These objects are accomplished by the following invention which, in its broader aspects, comprises depositing upon a cellulose acetate-propionate support, for example, a series of progressively hydrolyzed layers of cellulose acetate-propionate, each of which is compatible with both the underlying and overlying layers and in each of which the hydrolysis of the ester has been carried to a greater extent than in the preceding layer.

In the following examples and description, I have set forth several of the preferred embodiments of my invention, but they are included merely for purposes of illustration and not as a limitation thereof.

In carrying out my invention I prepare a film support composed of cellulose acetate-propionate by coating an appropriate dope onto a film-forming surface by a known technique. Such a dope may, for example, be composed of 19% by weight of a fully esterified cellulose acetate-propionate containing 30% acetyl and 16% propionyl (apparent acetyl 41%), 4.75% of tri-phenyl phosphate, and 76.25% of ethylene dichloride. The conditions of coating are so controlled that, after evaporation of solvents and curing of the film by subjecting it to appropriate temperatures, a sheet or film of cellulose acetate-propionate approximately .008 inch in thickness is obtained.

I then deposit on the film support produced as described in the preceding paragraph a series of extremely thin layers of cellulose acetate-propionate, each layer composed of a cellulose acetate-propionate which is compatible, both with the material upon which it is applied and with the succeeding layer which is deposited on it. These layers may be deposited from appropriate solutions by a variety of methods well known to those skilled in the art, such as by immersion, beading, or the like, the support being passed through or in contact with the solution at such a rate that a layer of the desired thickness will be laid down on the material.

In general, these layers are extremely thin and possibly not more than a few millionths of an inch in thickness. After each application of the subbing solution, the support is subjected to an appropriate drying operation at a temperature sufficient to evaporate solvents and to set the deposited cellulose ester on the surface of the support. The concentration of the ester for any given subbing solution may be varied within rather wide limits, depending upon the thickness of layer which is desired and upon the speed of coating.

Many different layers of progressively hydrolyzed cellulose acetate-propionate may be deposited on the support as desired, a typical series of subbing solutions for coating a cellulose acetate-propionate film support of the above indicated composition (41% apparent acetyl) being indicated below:

A.	Percent by weight
Cellulose acetate-propionate (16% propionyl, 39% apparent acetyl)	3
Acetone	35
Methyl alcohol	62

B.	Percent by weight
Cellulose acetate-propionate (16% propionyl, 35% apparent acetyl	3
Acetone	35
Methyl alcohol	62

The above formulae are merely typical examples of appropriate solutions for depositing the cellulose acetate-propionate layer, and many changes therein may be made within the scope of my invention. As will be apparent, an almost infinite number of cellulose acetate-propionates hydrolyzed to different degrees may be employed, so long as a series of layers is deposited upon the support, each of which layer is compatible, both with the layer of cellulose acetate-propionate underlying it, and that overlying it. Various solvents or solvent combinations may be employed in the place of the acetone and methyl alcohol included in the above formulae, typical examples being mixtures of 85% ethylene dichloride and 15% methyl alcohol and 85% propylene dichloride and 15% methyl alcohol.

After deposition on the support of the final cellulose acetate-propionate coating, the support is subjected to appropriate drying, after which the usual gelatin sub-layer is applied, its application being carried out similarly to the deposition of the cellulose acetate-propionate layers, a typical solution for this purpose having the following composition:

	Percent by weight
Gelatin	1.2
Acetic acid	0.6
Water	5.0
Acetone	70.0
Ethyl alcohol	23.2

After drying, the film is coated with a light-sensitive gelatino-silver halide emulsion in known manner.

With respect to the preparation of a fully esterified cellulose acetate-propionate, this may be carried out in accordance with known technique, for example, that described in the patent to H. T. Clarke and C. J. Malm, No. 1,800,860. The various hydrolyzed forms of cellulose acetate-propionate adapted for use in accordance with my invention may be prepared as outlined in the copending application of W. O. Kenyon and R. H. Van Dyke, Serial No. 722,251, filed April 25, 1934, and the patent to C. J. Malm and C. F. Fletcher, 2,026,583, relating to the selective hydrolysis of mixed organic esters of cellulose.

My invention will be more fully understood by reference to the accompanying drawing in which A designates a film support composed of a fully esterified cellulose acetate-propionate (41% apparent acetyl), B designates a cellulose acetate-propionate sub-layer containing approximately 16% propionyl (39% apparent acetyl), C designates a second cellulose acetate-propionate sub-layer in which the ester contains about 16% propionyl (35% apparent acetyl), D is the usual gelatin sub-layer, while E represents the final gelatino-silver halide emulsion.

Although all of the layers of the above described film structure are strongly adherent to one another, the film as a whole has a high degree of flexibility and excellent emulsion adherence characteristics as determined by the usual tests for these properties.

One of the outstanding features of my invention is the fact that I can produce a highly satisfactory photographic film without the use of the usual cellulose nitrate undercoats and can obtain the desired degree of adherence of the emulsion to the base through the agency of the weaker types of gel-subbing solutions, thus avoiding objectionable brittleness in the finished product.

While I do not confine myself to any particular theory or explanation of the results obtained, it appears that the effectiveness of my invention is due to the fact that each of the successive layers of cellulose acetate-propionate is compatible, both with the underlying and overlying layers of material, and the further fact that as the degree of hydrolysis of the ester is increased, the weaker are the solvents required to stick the gel sub to the base. In other words, I am enabled to use substantially the same types of gel subs as are customarily used for nitrate film base without a sacrifice of adherence.

As indicated above, the particular cellulose-acetate-propionates employed may range anywhere from a fully esterified cellulose acetate-propionate, such as one containing 41% apparent acetyl, to an ester which has been hydrolyzed to 34.8%, or less, apparent acetyl. While I have chosen to illustrate my invention by reference to cellulose acetate-propionates in which the ratio of acetyl to propionyl has been maintained constant, my invention is equally applicable to the use of mixed esters in which the acetyl-propionyl ratio may vary. Likewise, other cellulose esters may be employed in the manner herein described, typical examples being cellulose acetate-butyrate, cellulose acetate-stearate, cellulose propionate-butyrate, and many others.

While I have found it convenient to illustrate my invention by reference to a support or sheet of cellulose acetate propionate having a plurality of superimposed layers of progressively more hydrolyzed cellulose acetate propionate on one surface, my invention is in no sense limited to this particular form of product as it may be equally well applied to the manufacture of products in which such layers are applied to both surfaces, as is the case in X-ray and portrait types of film.

What I claim is:

1. A photographic film support comprising a cellulose organic acid ester film base of substantial thickness having superimposed on and ad-

hesively joined thereto, a composite layer composed of a series of separate and distinct extremely thin layers of a cellulose organic acid ester material substantially identical with the material of the base, but each of said layers composed of material hydrolized to a greater degree than the material of the layer next underlying it and to a less degree than the layer next overlying it, each of said layers being compatible with the material of both the underlying and overlying layers and adhesively joined thereto.

2. A photographic film support comprising a cellulose acetate film base of substantial thickness having superimposed on and adhesively joined thereto, a composite layer composed of a series of separate and distinct extremely thin layers of a cellulose acetate material substantially identical with the material of the base, but each of said layers composed of material hydrolized to a greater degree than the material of the layer next underlying it and to a less degree than the layer next overlying it, each of said layers being compatible with the material of both the underlying and overlying layers and adhesively joined thereto.

3. A photographic film support comprising a mixed cellulose organic acid ester film base of substantial thickness having superimposed on and adhesively joined thereto, a composite layer composed of a series of separate and distinct extremely thin layers of a cellulose organic acid ester material substantially identical with the material of the base, but each of said layers composed of material hydrolized to a greater degree than the material of the layer next underlying it and to a less degree than the layer next overlying it, each of said layers being compatible with the material of both the underlying and overlying layers and adhesively joined thereto.

4. A photographic film support comprising a cellulose acetate propionate film base of substantial thickness having superimposed on and adhesively joined thereto, a composite layer composed of a series of separate and distinct extremely thin layers of a cellulose acetate propionate material substantially identical with the material of the base, but each of said layers composed of material hydrolized to a greater degree than the material of the layer next underlying it and to a less degree than the layer next overlying it, each of said layers being compatible with the material of both the underlying and overlying layers and adhesively joined thereto.

5. A photographic film support comprising a film base of substantial thickness composed of fully esterified cellulose acetate propionate having superimposed on and adhesively joined thereto a composite layer composed of a series of separate and distinct extremely thin layers of cellulose acetate propionate, the material of these layers, respectively, being hydrolized progressively within the range of 41% to 34.8% apparent acetyl, each of said layers being compatible with the material of both the underlying and overlying layers and adhesively joined thereto.

6. A photographic film of satisfactory flexibility and free from brittleness comprising a cellulose organic acid ester support and a photographically sensitive colloid layer adhesively joined to the support by a composite intervening layer comprising a series of separate and distinct extremely thin subs composed of a cellulose organic acid ester material substantially identical with the material of the base but each of said subs composed of material hydrolized to a greater degree than the material next underlying it and to a less degree than the material next overlying it, each of said subs being compatible with the material of both the underlying and overlying layers and adhesively joined thereto, and a gel sub adhesively joined to the most hydrolized sub and to the sensitive colloid layer.

7. A photographic film of satisfactory flexibility and free from brittleness comprising a cellulose acetate support and a photographically sensitive colloid layer adhesively joined to the support by a composite intervening layer comprising a series of separate and distinct extremely thin subs composed of cellulose acetate, each of said subs being hydrolized to a greater degree than the material next underlying it and to a less degree than the material next overlying it, each of said layers being compatible with the material of both the underlying and overlying layers and adhesively joined thereto, and a gel sub adhesively joined to the most hydrolized sub and to the sensitive colloid layer.

8. A photographic film of satisfactory flexibility and free from brittleness comprising a mixed cellulose organic acid ester support and a photographically sensitive colloid layer adhesively joined to the support by a composite intervening layer comprising a series of separate and distinct extremely thin subs composed of a material substantially identical with the material of the base, but each of said subs consisting of material hydrolized to a greater degree than the material next underlying it and to a less degree than the material next overlying it, each of said layers being compatible with the material of both the underlying and overlying layers and adhesively joined thereto, and a gel sub adhesively joined to the most hydrolized sub and to the sensitive colloid layer.

9. A photographic film of satisfactory flexibility and free from brittleness comprising a cellulose acetate propionate support and a photographically sensitive colloid layer adhesively joined to the support by a composite intervening layer composed of a series of separate and distinct extremely thin subs composed of cellulose acetate propionate, each sub consisting of material hydrolized to a greater degree than the material next underlying it and to a less degree than the material next overlying it, each of said subs being compatible with the material of both the underlying and overlying layers and adhesively joined thereto, and a gel sub adhesively joined to the most hydrolized sub and to the sensitive colloid layer.

10. A photographic film of satisfactory flexibility and free from brittleness comprising a fully esterified cellulose acetate propionate support and a photographically sensitive colloid layer adhesively joined to the support by a composite intervening layer comprising a series of separate and distinct extremely thin subs composed of cellulose acetate propionate, the material of each sub being respectively hydrolized progressively within the range of 41% to 34.8% apparent acetyl, each of said layers being compatible with the material of both the underlying and overlying layers and adhesively joined thereto, and a gel sub adhesively joined to the most hydrolized sub and to the sensitive colloid layer.

HARRY LE B. GRAY.