Aug. 8, 1939. G. F. NADEAU 2,169,004

LOW DYE RETENTION SUB FOR PHOTOGRAPHIC FILM

Filed Oct. 21, 1938

Fig. 1.

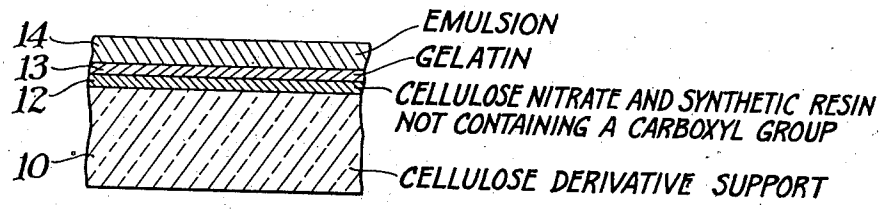


Fig. 2.

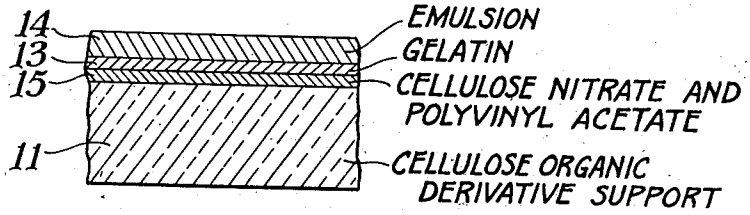
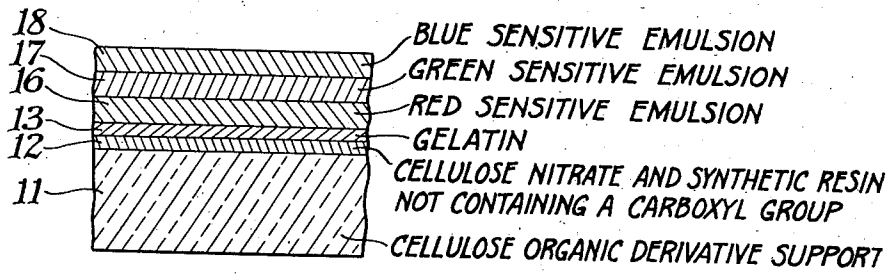


Fig. 3.



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LOW DYE RETENTION SUB FOR PHOTOGRAPHIC FILM

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12 Claims. (Cl. 95—2)

This invention relates to a method for subbing photographic film and particularly to a sub for film designed to receive a colored photographic image.

The problem of producing a photographic safety film base possessing satisfactory stripping and brittleness qualities has been an extremely difficult one. In order to cause photographic emulsion layers to adhere to cellulose organic acid ester supports, it is necessary to use intervening layers of such character that the several layers do not strip from the support when the film is used or when it is passed through processing baths and also of such character that the layers do not adhere with such firmness that the film becomes brittle. One successful way of making a photographic film having satisfactory stripping and brittleness properties is to use a synthetic resinous material as a sub or undercoat, as described in my prior application Serial No. 1547.

In the case of photographic film having an emulsion layer or several emulsion layers designed to receive colored photographic images, the subbing or undercoat layers must possess additional qualities. The dye or other coloring material used in the emulsion layers is likely to stain the sub or undercoat if it is not properly constructed and the sub or undercoat may also cause fading of the dye in the emulsion layer of the film next to the sub, when the film is incubated or stored after processing.

It is, therefore, an object of the present invention to provide a sub or undercoat for a photographic safety film having an emulsion layer or layers designed to receive colored images, which does not retain a dye stain caused by the colored image. A further object is to provide a subbing layer which does not cause the dye in an overcoat emulsion layer to fade or bleach during storage of the finished film. A still further object is to provide a safety film having satisfactory stripping and brittleness characteristics. Other objects will appear from the following description of my invention.

These objects are accomplished according to my invention by providing a subbing layer of a mixture of cellulose nitrate and a synthetic resin not containing a carboxyl group. The layer is coated directly on a cellulose organic acid ester film base and other suitable layers are coated over it.

In the accompanying drawing Figs. 1, 2 and 3 are sectional views of a photographic film having subbing layers thereon according to my invention.

In subbing film according to my invention a cellulose derivative support of any composition is coated with the subbing or undercoat layer of cellulose nitrate and the synthetic resin. The support may consist of cellulose nitrate or other inorganic acid ester of cellulose, but a cellulose organic acid ester will ordinarily be used with a sub of this type. The cellulose organic derivative support may be a simple ester, such as cellulose acetate or a mixed ester, such as cellulose acetate propionate or cellulose acetate butyrate.

The subbing layer first applied consists of a uniform mixture of a high alcohol soluble, low viscosity cellulose nitrate and a synthetic resin not containing a carboxyl group. I have found that the resins containing carboxyl groups are not suitable for subbing according to my invention since they tend to stain and, therefore, render the film unfit for use as color film. Among the synthetic resins which may be used are the following. The polyvinyl esters, such as polymerized vinyl acetate which is known, for example, under the trade name "Gelva," the preparation of which is described in the U. S. Patent Nos. 1,241,738; 1,586,803 and 1,710,825. A further type of resin which may be used is the polyvinyl acetal type. These resins are condensation products of partially or completely hydrolyzed polyvinyl acetate and an aldehyde, such as formaldehyde, acetaldehyde, or butyraldehyde and are known as polyvinyl acetals. They are sold under various trade names such as "Formvar" and "Alvar," the preparation of which is described in British Patent No. 351,082 and in U. S. Patents Nos. 1,955,068 and 1,990,399. A still further type of resin is the group known as the "Santolites" which are condensation products of formaldehyde with aromatic sulfonamides. I may also use the polyacrylic esters, such as the methyl or butyl esters of polyacrylic acid.

After drying, the layer of cellulose nitrate and synthetic resin may be coated with a cellulose nitrate layer or other layer or a gelatin layer may be coated directly on it. The gelatin layer is followed by a coating of one or more emulsion layers designed to record a colored photographic image.

My invention will now be described by particular reference to the accompanying drawing. As shown therein a support 10 of any suitable material such as cellulose nitrate or cellulose acetate is coated with a layer 12 of cellulose nitrate and a synthetic resin not containing a carboxyl group. On this layer there is coated a gelatin layer 13 and a gelatino-silver halide emulsion layer 14.

According to the modification shown in Fig.

2 a support 11 of an organic acid ester derivative of cellulose, such as cellulose acetate or cellulose acetate propionate, is coated with a layer 15 of cellulose nitrate and polyvinyl acetate. This layer is then coated with the gelatin subbing layer 13 and emulsion layer 14.

Fig. 3 shows a film designed for multi-color photography in which the support 11 is coated with the subbing layer 12 of cellulose nitrate and a synthetic resin not containing a carboxyl group, and this is followed by the gelatin layer 13. On the gelatin layer 13 are coated in succession a red sensitive silver halide emulsion layer 16, a green sensitive silver halide emulsion layer 17, and a blue sensitive silver halide emulsion layer 18. It is understood that this film may contain other layers, such as intermediate filter layers, which may be necessary to prevent the action of light of any spectral color on any of the layers of the film.

As stated above, the subbing layer applied directly to the film base consists of a mixture of cellulose nitrate and a synthetic resin not containing a carboxyl group. The cellulose nitrate is of the high alcohol soluble, low viscosity type which may have the following composition:

	Range
Alcohol solubility ---------- per cent --	30–100
Viscosity (dropping ball) -------- sec --	2–5
Nitrogen ----------	11.0–12.0

The synthetic resin may consist of any resin not containing a carboxyl group, or at least not containing an appreciable amount of carboxyl. The ratio of resin to nitrate in this undercoat may vary from about 1 part resin to 9 parts nitrate, to about an equal mixture of resin and nitrate. The preferred ratio is about 3 parts resin to 7 parts nitrate.

The resin and nitrate undercoat is coated on the film base from a suitable solvent or solvent mixture, such as acetone, acetone and methanol, acetone and methyl alcohol, ethylene dichloride with methyl alcohol or ethyl alcohol, and various combinations of these solvents together with methyl Cellosolve. A suitable solvent mixture consists of 40 parts acetone and 60 parts of methyl alcohol.

The concentration of the subbing solution is adjusted to the speed of coating and may vary from about 2% to about 6% or more of nitrate and resin in the solution. The sub is coated at a linear speed of from 3 to 10 feet per minute and a layer which may vary in thickness from 0.00006 inch to 0.00015 inch is thereby obtained.

The gelatin sub coated over the nitrate-resin layer may have the following composition:

	Per cent
Gelatin ----------	1.2
Acetic acid ----------	2
Water ----------	12
Methyl alcohol ----------	84.8

The emulsion layer coated over the gelatin sub may consist of an ordinary gelatino silver halide emulsion or it may be sensitized to record various regions of the spectrum. In the case of multi-layer film, the successive emulsion layers applied to the gelatin sub may be differentially sensitized and may or may not contain dyes or color forming compounds designed to produce a colored photographic image or images in the layers. The film may also have other layers, such as filters, overcoating layers, or anti-halation layers applied thereto.

My invention will be further understood by reference to the following specific examples which are understood to be illustrative only.

Example I

A photographic film base of cellulose acetate containing about 40.5% acetyl was coated with the following subbing solution:

	Grams
Polyvinyl acetate ----------	1.2
Cellulose nitrate ----------	1.2
Acetone ----------	38.8
Methanol ----------	58.8

This solution was coated at a linear speed of 6 feet per minute and was dried after coating. A gelatin subbing layer having the following composition was then applied:

	Per cent
Gelatin ----------	1.2
Acetic acid ----------	2
Water ----------	12
Methyl alcohol ----------	84.8

Over the gelatin layer there was then coated a gelatino silver halide emulsion layer. The film produced in this way was found to have satisfactory stripping and brittleness properties and when a colored image was formed in the sensitive emulsion layer, the dye was not retained by the subbing layer.

Example II

A photographic film base of cellulose acetate propionate containing 16% propionyl and 29% acetyl was coated with a subbing solution having the following composition:

	Grams
Polymethyl acrylate ----------	2
Cellulose nitrate ----------	4.6
Acetone ----------	93.4

After drying, there was coated on this layer a solution of gelatin having the same composition as that in Example I and successive layers of red sensitive emulsion, green sensitive emulsion, and blue sensitive emulsion were coated on the gelatin layer. A filter layer of gelatin containing a yellow coloring material was coated between the green sensitive layer and the red sensitive layer.

I have referred to "satisfactory stripping and brittleness properties" throughout the specification. It is to be understood that this term, although not susceptible of precise definition, nevertheless has a definitely accepted meaning in the photographic art, and that film can be tested to determine whether it is commercially satisfactory with respect to stripping and brittleness. Tests to which the film may be subjected for this purpose are outlined in my prior U. S. Patent No. 2,096,616, granted October 19, 1937.

I have also referred above to the "dropping ball method" for determining the viscosity of cellulose nitrate. The "dropping ball method" for determining viscosity of cellulose nitrate is as follows:

10 grams of dry nitro cellulose is dissolved in 100 cc. of a mixture comprising 50% by volume of methyl alcohol and 50% by volume of acetone at 25° C. Viscosity is measured by the time in seconds it takes for a steel ball having a diameter of 1/8 of an inch and weighing .1320 to .1340 gram to fall 15 centimeters through the nitro cellulose solution at 25° C. in a tube having a diameter of 1.7±.05 centimeters.

The subbing method used according to my invention has a number of important advantages.

In addition to the fact that the sub does not retain any dye which is used in the emulsion layers to form color photographic images and does not cause fading of the dye contained in these layers, my subbing method also has other advantages. For example, the mixture of resin and nitrate can be conveniently handled in coating machines as it is not tacky and does not adhere to the machine parts. The resulting film is not brittle although the emulsion adheres well to the base. The wearing qualities of motion picture film made in this way are very good and film was found to be in good condition after having been passed through a projector a number of times.

I have referred in the present description of my invention, to subbing safety film support, that is, cellulose organic acid ester film support, as constituting the preferred embodiment of my invention. However, although the problem of subbing cellulose inorganic acid ester supports is usually not so difficult as in the case of cellulose organic acid esters, the matter of staining the support in color processes must be considered. I have found that the use of subs according to my invention, prevents dye staining of cellulose nitrate supports as well as supports of cellulose organic acid esters.

I have also referred to the use of my subbing method in film designed to receive colored images. Film support may also be subbed according to my invention where the film is designed to record black-and-white silver images.

It is to be understood that the above examples, ranges, and methods of procedure are illustrative only and that my invention is to be taken as limited only by the scope of the appended claims.

Having thus described my invention, what I declare is new and desire to secure by Letters Patent of the United States is:

1. A photographic film for use in color photography having low dye retention subbing layers, comprising a cellulose ester support, an emulsion layer adapted to receive a colored image, and between said support and said emulsion layer, a subbing layer of a mixture of cellulose nitrate and a synthetic resin free of carboxyl groups.

2. A photographic film for use in color photography having low dye retention subbing layers, comprising a cellulose organic ester support, a subbing layer of a mixture of cellulose nitrate and a synthetic resin free of carboxyl groups directly attached to said support, a gelatin layer attached to said subbing layer, and an emulsion layer adapted to receive a colored image attached to said gelatin layer.

3. A photographic film for use in color photography having low dye retention subbing layers, comprising a cellulose organic acid ester support, and in order thereon, a subbing layer of a mixture of cellulose nitrate and a synthetic resin free of carboxyl groups, the resin in the sub being present in not greater amount than the cellulose nitrate, a gelatin layer, and an emulsion layer adapted to receive a colored image.

4. A photographic film for use in color photography having low dye retention subbing layers, comprising a cellulose organic acid ester support, and in order thereon, a subbing layer of a mixture of cellulose nitrate and a synthetic resin free of carboxyl groups, the resin and the nitrate being present in substantially equal amounts, a gellatin layer, and an emulsion layer adapted to receive a colored image.

5. A photographic film for use in color photography having low dye retention subbing layers, comprising a cellulose organic acid ester support, and in order thereon, a subbing layer of a mixture of cellulose nitrate and a synthetic resin free of carboxyl groups, a gelatin layer, and a plurality of differentially sensitized emulsion layers.

6. A photographic film for use in color photography having low dye retention subbing layers, comprising a cellulose organic acid ester support, and in order thereon, a subbing layer of a mixture of cellulose nitrate and a synthetic resin free of carboxyl groups, the resin and the nitrate being present in equal amounts, a gelatin layer, and a plurality of emulsion layers sensitized to record different regions of the spectrum.

7. A photographic film for use in color photography having low dye retention subbing layers, comprising a cellulose organic acid ester support, and in order thereon, a subbing layer of a mixture of cellulose nitrate and a polyvinyl acetate resin, a gelatin layer, and a plurality of emulsion layers sensitized to record different regions of the spectrum.

8. A photographic film for use in color photography having low dye retention subbing layers, comprising a cellulose organic acid ester support, and in order thereon, a subbing layer of a mixture of cellulose nitrate and a polyvinyl acetate resin, the resin being present in less amount than the cellulose nitrate, a gelatin layer, and a plurality of emulsion layers sensitized to record different regions of the spectrum.

9. A photographic film having satisfactory stripping and brittleness properties, comprising a cellulose organic acid ester film support and a sensitive emulsion layer, and between said support and said emulsion layer, successive layers of a mixture of cellulose nitrate and a synthetic resin free of carboxyl groups, and a gelatin layer.

10. A photographic film having satisfactory stripping and brittleness properties comprising a cellulose organic acid ester support, a subbing layer of a mixture of cellulose nitrate and a synthetic resin free of carboxyl groups coated directly on said support, said subbing layer having a thickness of from 0.00006 inch to 0.00015 inch, a gelatin layer attached directly to said subbing layer, and a sensitive emulsion layer attached directly to said gelatin layer.

11. A photographic film for use in color photography having low dye retention subbing layers, comprising a cellulose inorganic acid ester support, a subbing layer of a mixture of cellulose nitrate and a synthetic resin free of carboxyl groups directly attached to said support, a gelatin layer attached to said subbing layer, and an emulsion layer adapted to receive a colored image attached to said gelatin layer.

12. A photographic film for use in color photography having low dye retention subbing layers, comprising a cellulose nitrate support, and in order thereon, a subbing layer of a mixture of cellulose nitrate and a synthetic resin free of carboxyl groups, a gelatin layer, and a plurality of emulsion layers sensitized to record different regions of the spectrum.

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