Nov. 8, 1938. G. F. NADEAU 2,135,524

SUBBING PHOTOGRAPHIC FILM

Filed Nov. 5, 1937

Fig. 1.

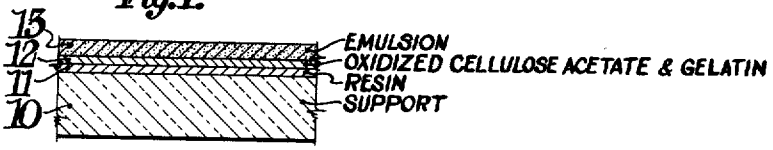


Fig. 2.

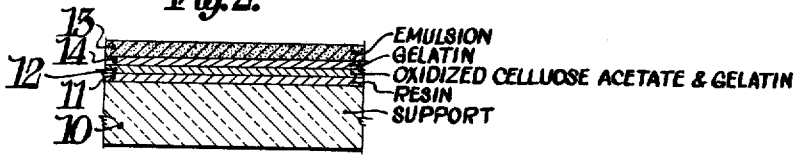


Fig. 3.

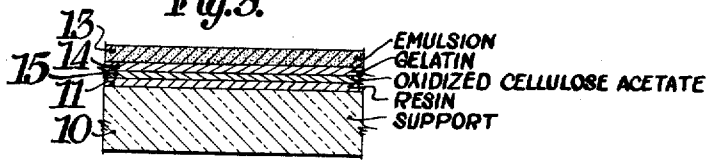
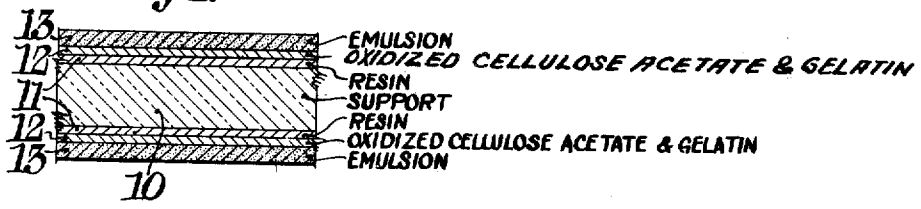


Fig. 4.



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UNITED STATES PATENT OFFICE

2,135,524

SUBBING PHOTOGRAPHIC FILM

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Application November 5, 1937, Serial No. 173,020

8 Claims. (Cl. 95—9)

This invention relates to photographic materials and more particularly to the subbing of photographic film.

In the manufacture of photographic safety film in which the film base is formed of a substantially non-inflammable derivative of cellulose such as cellulose acetate, the manner of securing the proper adhesion of the various layers to the film base constitutes a serious problem. The degree of adhesion of the layers to the base must be regulated so that neither brittleness nor stripping results. If the degree of adhesion is too great, the film is brittle and cracks when bent, on the other hand, if the degree of adhesion is too slight, the layers strip from the base or support when the film is treated in the processing baths.

A further requirement is that each layer of the film must adhere to the layer adjoining it. Adhesion may be brought about either by the natural compatibility of the materials or by the use of a solvent material which is a solvent for the material of the adjoining layer. For example, it is well-known that a water solution of gelatin will not wet a cellulose organic derivative film support such as cellulose acetate and, consequently, will not adhere to it. It has, therefore, been the practice in subbing a film base of this type to use a solution of gelatin in an organic solvent capable of swelling or dissolving the film base. The degree of adhesion of the layer to the film base is then regulated by varying the strength of the solvent. It has been found, however, that in order to secure the proper degree of adhesion when using the gelatin subbing solution, the solvent must be of such a strength that the resulting film is brittle.

In my prior application, Serial No. 1,547, filed January 12, 1935, I have described a method of subbing a cellulose organic derivative film base in which the resulting product has satisfactory stripping and brittleness properties. This method consists in applying directly over a cellulose organic derivative film base, a solution of a synthetic resin. This resin layer is followed by a protective layer of cellulose nitrate or acetate and on top of this there is a gelatin subbing layer followed by the emulsion layer. It has been found in practice that the resin layer applied to the film base does not dry readily and therefore tends to adhere to parts of the coating machine such as the driers or idle rolls. In order to overcome this tendency, a protective layer is applied over the resin layer before application of the gelatin and emulsion layers. This necessitates the use of an additional layer and if a cellulose nitrate protective layer is used for this purpose, the fire hazard is somewhat increased.

It is, accordingly, an object of the present invention to provide means for eliminating the protective coating layer in films of this type, thereby reducing the required number of layers. A further object is to provide a method for eliminating the nitrate from the film.

I have found that oxidized cellulose acetate is compatible with both synthetic resins and gelatin and may be used as a subbing material for photographic film, thereby reducing the required number of layers on the film base and also eliminating the nitrate from the film.

In the accompanying drawing, I have shown in enlarged sectional views a number of modifications of photographic film made according to my invention. In the drawing—

Fig. I is a sectional view of a film base in which a layer of oxidized cellulose acetate and gelatin is coated over a resin subbing layer;

Fig. II is a sectional view of a film in which the layer of oxidized cellulose acetate and gelatin is followed by a weak gelatin layer;

Fig. III is a sectional view of a film in which an oxidized cellulose acetate layer alone is coated over a resin subbing layer;

Fig. IV is a sectional view of a film having emulsion layers on both sides of the support, the resin subbing layer being coated in each case with a mixture of oxidized cellulose acetate and gelatin.

The application of the various layers to the film base may be carried out in any manner well-known to those skilled in the art. The film support may be of any of the usual cellulose organic derivative compositions such as cellulose acetate, cellulose acetate propionate, cellulose ethers, etc. For example, when coating a cellulose acetate base, the base is treated with a solution of a synthetic resin such as a polyvinyl acetal in a suitable solvent. This solvent may be ethyl alcohol or methyl alcohol or a mixture of acetone and methyl alcohol or methyl Cellosolve. Ethylene dichloride can also be used together with acetone and/or methyl alcohol to effect solution of the resin. The exact composition of the solvent to be used is determined by the nature of the cellulose ester or ether of which the support is made.

After the resin has been set or become somewhat firm, it is treated with the protective layer of oxidized cellulose acetate or mixed oxidized cellulose acetate and gelatin. The preparation

of this material is described below. The composition of this layer may vary in respect to total content of oxidized cellulose acetate or oxidized cellulose acetate and gelatin, with respect to the ratio of gelatin to oxidized cellulose acetate, or with respect to the composition or nature of the solvents. This protective layer is followed, in one form of my invention, by a gelatin layer deposited from a weak gel sub, and the emulsion layer, or the emulsion layer may be applied directly over the protective layer.

Other layers may be applied to the film base in the usual manner, for example, a gelatin coating may be applied to the reverse side of the support in order to counteract the tendency of the film to curl or a layer may be applied over the emulsion layer to resist abrasion.

Among the synthetic resins which may be used as subbing materials, any of the resins described in my prior application, Serial No. 1,548, may be used. These include 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. Patents Nos. 1,231,738, 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, 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 Br. Patent No. 351,082 and in U. S. Patents Nos. 1,955,068 and 1,990,399. A still further type of resin which I may use are the alkyd resins, which are condensation products of a poly-basic acid and a polyhydroxy alcohol. An example of this type of resin is "Glyptal", which is a condensation product of glycerin and phthalic acid or phthalic anhydride. 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 other resins such as the polyacrylic esters, the urea-formaldehyde resins, the modified phenol-formaldehyde or Bakelite resins, and others.

My invention will now be described by reference to the accompanying drawing.

Fig. I is a sectional view of a film in which the support 10 is coated with a layer 11 of a suitable resin. This resin layer is followed by a layer 12 of a mixture of oxidized cellulose acetate and gelatin which is prepared in any suitable manner so that it adheres in the proper degree to the resin layer. The layer 12 is followed by the usual silver halide emulsion layer 13.

Fig. II shows a film in which a layer 11 of resin is first coated on the base, and this is followed by the oxidized cellulose acetate and gelatin layer 12 and by a gelatin subbing layer 14 which is coated from a weak gel solution. On this is laid the emulsion layer 13.

Fig. III is a section view of a film in which the support 10 is coated with a suitable resin 11 and this is followed by a layer 15 of oxidized cellulose acetate alone, coated from a suitable solvent. A layer of gelatin 14 is laid over the oxidized cellulose acetate, and the emulsion layer 13 is then coated directly over the gelatin layer.

Fig. IV shows a modification in which there is a sensitive emulsion layer on each side of the support 10. The support is coated on each side with a suitable resin 11 followed by the mixed gelatin and oxidized cellulose acetate protective layer and the emulsion layer 13. It is to be understood that in this modification the protective layer might be of oxidized cellulose acetate alone with a gelatin layer interposed between protective layer 12 and emulsion layer 13.

The following examples will illustrate the manner in which a film base may be coated according to my invention.

Example I

A film base of cellulose acetate is coated with a 5% solution of polyvinyl formaldehyde acetal resin dissolved in a mixture of 70% acetone and 30% methyl alcohol. This resin solution is coated at a linear speed of approximately three feet per minute. The film is then led through an appropriate drying apparatus maintained at a temperature of approximately 120 to 200° F. where the solvent is evaporated from the surface of the material and the resin layer becomes somewhat set or hardened, although it still remains slightly tacky. The resin coating is then treated with a solution of gelatin and oxidized cellulose acetate having approximately the following composition:

	Percent
Gelatin	1.25
Oxidized cellulose acetate	1.25
Acetic acid	1
Water	4
Acetone	50
Methyl Cellosolve	20
Methyl alcohol	22.5

The film is then dried at a suitable temperature after which the usual gelatino-silver halide emulsion coating is applied, by known technique, thus completing the film.

Example II

A film base of cellulose acetate or cellulose acetate-propionate of appropriate thickness is coated with a resin layer and a layer of mixed oxidized cellulose acetate and gelatin, as described in the preceding example. The oxidized cellulose acetate and gelatin protective layer is then coated with a weak gelatin solution having approximately the following composition:

	Percent
Gelatin	1
Acetic acid	1
Water	4
Methyl alcohol	74
Methyl Cellosolve	20

This additional gelatin produces a film which has better dry stripping than the film in which the emulsion layer is coated directly over the protective layer.

Example III

A film base of cellulose acetate or cellulose acetate propionate of appropriate thickness is coated with a 5% solution of a condensation product of glycerin and phthalic anhydride (Glyptal) in a mixture of 75% acetone and 25% methyl alcohol. This layer is dried as described in the preceding example and is then coated with a solution of oxidized cellulose acetate having approximately the following composition:

	Percent
Oxidized cellulose acetate	3
Water	40
Acetone	30
Methyl Cellosolve	27

This oxidized cellulose acetate protective layer is followed by a gel sub and then the usual gelatino-silver halide emulsion layer to complete the film.

Example IV

In the process as described in Example III, a solution of oxidized cellulose acetate is used having the following composition:

	Percent
Oxidized cellulose acetate	1.5
Acetic acid	1
Water	4
Acetone	60
Methyl alcohol	33.5

Oxidized cellulose acetate is prepared by treating a hydrolyzed cellulose acetate with an acid permanganate solution. The hydrolyzed cellulose acetate used may vary from a slightly hydrolyzed acetate of about 41% acetyl, to a cellulose acetate hydrolyzed to 33% acetyl or less. In general, a hydrolyzed cellulose acetate of from 90% precipitation value to total acetone solubility may be used. The 90% precipitation value cellulose acetate corresponds in general to an acetate of 41% acetyl content. A preferred composition of starting material for the oxidation has a precipitation value of 72% and an acetyl content of 37%.

Oxidized cellulose acetate may be prepared in the following way. An acid permanganate solution is made up having the following composition:

Distilled water	140 lbs.
Sulfuric acid (95%)	640 cc.
Potassium permanganate	Dissolved by boiling 1 lb. in 20 lbs. of distilled water

This solution is placed on a 30 gallon crock fitted with a stirrer. To this solution is added 10 lbs. of cellulose acetate of 33% acetyl content finely broken up. The contents are stirred continuously for five minutes and then stirred one minute in every 15 minutes until the purple color of the permanganate has disappeared. The treatment is carried out at room temperature and requires about four hours at 85° to 90° F.

When the oxidation is complete, the liquid is drained off and the material washed several times with distilled water. The oxides of manganese are then removed by bleaching with sulfur dioxide. To accomplish this bleaching, sulfur dioxide is bubbled into distilled water placed in the crock, until the odor of sulfur dioxide persists. The bleaching is continued until the lumps of oxidized cellulose acetate are thoroughly decolorized. The bleach water is then discarded and the material washed thoroughly with distilled water and dried. The treatment in this way results in about seven pounds of dried material for ten pounds of initial cellulose acetate.

The oxidization described above, which is carried out with hydrolyzed cellulose acetate, has the effect of introducing acidic groups into the molecule. These acidic groups, probably carboxyl, are introduced at the places where there are free hydroxyl groups resulting from hydrolysis of the cellulose acetate. The chemical formula of this material is not known except that it is known to contain acid radicals. The material may, however, be distinguished in a number of ways, although the solubility in acetone and other solvents, of the oxidized material, is about the same as that of the unoxidized material. The precipitation value shows a steady decrease with increased time of oxidization. The adhesive properties and the dye absorptive properties, especially for basic dyes, of the oxidized material are much better than the corresponding properties of the undyed material. The water susceptibility of the material is also slightly increased by the oxidization. The most important means of determining the change which occurs in the hydrolyzed cellulose acetate on oxidization is its reaction with alkaline materials. Whereas, the original material has no free acid groups, the oxidized material has an appreciable degree of acidity. This acidity may be determined by treating it with an alkaline solution of known strength and measuring the amount of alkali required to neutralize the free acidity. With the material prepared as described above, the acidity is equivalent to about 100 to 200 cc. of normal alkali per 100 grams of oxidized cellulose acetate. This means that with a normal solution of alkali, for example, a normal solution of sodium hydroxide (i. e., a solution containing 40.01 grams sodium hydroxide per liter), about 100 to 200 cc. of the normal alkali solution will be required to neutralize 100 grams of the oxidized cellulose acetate.

The customary tests by which the properties of photographic film are determined will now be described. These are the so-called dry stripping, wet stripping and brittleness tests.

The dry stripping test is carried out as follows: A piece of the complete emulsion-coated film of a convenient size, say, 6 inches wide by 40 inches long, is held at one end with both hands with the emulsion side toward the operator and is then torn length-wise with successive quick motions of one hand, the tearing generally being carried out at a slight angle to the edge of the strip in order to obtain an oblique tear. The tears thus produced are more or less jagged. An attempt is now made to pull back the emulsion from the film with the fingernails and the degree to which the emulsion separates from the support is a measure of its adherence. It will, of course, be understood that the standards of emulsion adherence will vary for different types of film and what is considered satisfactory for one film may not be satisfactory for another. For example, stripping (emulsion adherence) is said to be satisfactory for X-ray film if the emulsion cannot be stripped back more than one or two inches. For Ciné film, on the other hand, the stripping should not be greater than about ¼ of an inch.

The wet stripping test is carried out as follows: A strip of film of convenient size is heated for forty-five minutes in a brittleness oven in which air having a controlled relative humidity of 20–25% and a temperature of 110–120° F. is circulated. The film is then removed from the oven and folded at ten different places along the strip by pressing the fold suddenly between the forefinger and the thumb. If the film is brittle, this sudden folding will cause it to break or snap in two at the fold. The flexibility may be defined in terms of freedom from brittleness which may be figured directly in percentages from the results of the test. For example, a film is said to be 60% free from brittleness if it ruptures at only four out of ten folds.

Precipitation value of a hydrolyzed cellulose acetate may be determined in the manner described in Sulzer U. S. Patent 1,833,136, page 1, line 95 to page 2, line 31. According to this method of stating precipitation value, a pre-

cipitation value of 0% represents a cellulose ester having complete acetone solubility.

The advantages realized by my improved subbing process include freedom from both wet and dry stripping and freedom from brittleness. Additional advantages are the reduction in number of the applications of subbing layers required and the freedom of the film from cellulose nitrate, thereby increasing the fire safety characteristics of the film. The elimination of the nitrate from the film also enables the use of slightly higher temperatures for curing the film containing nitrate is cured at higher temperatures. The use of higher temperatures enables a reduction in the length of time required for curing.

Although I have described my process as applied to the subbing of cellulose organic film base, I am not limited to treating this type of material. My method may also be used in subbing glass or paper supports or in subbing directly a film base formed of a resinous material. The modifications described are by way of example only and my invention is to be limited only by the scope of the appended claims.

This is a continuation in part of my application Serial No. 44,422, filed October 10, 1935.

What I claim is:

1. A flexible photographic film comprising a cellulose organic derivative support, and, in order, a synthetic resin layer, a layer comprising partially oxidized cellulose acetate having a free acidity equivalent of 100 to 200 cc. of normal alkali per 100 grams of oxidized cellulose acetate, and a photographic emulsion layer.

2. A flexible photographic film comprising a cellulose organic derivative support, and, in order, a synthetic resin layer, a layer comprising partially oxidized cellulose acetate having a free acidity equivalent of 100 to 200 cc. of normal alkali per 100 grams of ozidized cellulose acetate, and a light-sensitive phctographic emulsion layer.

3. A flexible photographic film comprising a cellulose organic derivative support, and, in order, a synthetic resin layer, a layer comprising partially oxidized cellulose acetate having a free acidity equivalent of 100 to 200 cc. of normal alkali per 100 grams of oxidized cellulose acetate, and gelatin, and a photographic emulsion layer.

4. A flexible photographic film comprising a cellulose organic derivative support, and, in order, a synthetic resin layer, a layer comprising partially oxidized cellulose acetate having a free acidity equivalent of 100 to 200 cc. of normal alkali per 100 grams of oxidized cellulose acetate and gelatin, and a light-sensitive photographic emulsion layer.

5. A flexible photographic film comprising a cellulose organic derivative support, and, in order, a synthetic resin layer, a layer comprising partially oxidized cellulose acetate having a free acidity equivalent of 100 to 200 cc. normal alkali per 100 grams of oxidized cellulose acetate and a silver halide emulsion layer.

6. A flexible photographic film comprising a cellulose acetate support, and, in order, a synthetic resin layer, a layer comprising partially oxidized cellulose acetate having a free acidity equivalent of 100 to 200 cc. of normal alkali per 100 grams of oxidized cellulose acetate, and a light-sensitive emulsion layer.

7. A flexible photographic film comprising a cellulose acetate support, and, in order, a synthetic resin layer, a layer comprising partially oxidized cellulose acetate having a free acidity equivalent of 100 to 200 cc. of normal alkali per 100 grams of oxidized cellulose acetate, and gelatin, and a light-sensitive emulsion layer.

8. A flexible photographic film comprising a cellulose acetate support, and, in order, a synthetic resin layer, a layer comprising partially oxidized cellulose acetate having a free acidity equivalent of 100 to 200 cc. of normal alkali per 100 grams of oxidized cellulose acetate and gelatin. and a silver halide emulsion layer.

GALE F. NADEAU.

CERTIFICATE OF CORRECTION.

Patent No. 2,135,524. November 8, 1938.

GALE F. NADEAU.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 25, for the patent number "1,231,738" read 1,241,738; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 7th day of February, A. D. 1939.

Henry Van Arsdale.

(Seal)

Acting Commissioner of Patents.

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