Oct. 11, 1938. G. F. NADEAU 2,133,110

MANUFACTURE OF PHOTOGRAPHIC FILM

Filed Dec. 10, 1937 2 Sheets-Sheet 1

FIG. 1

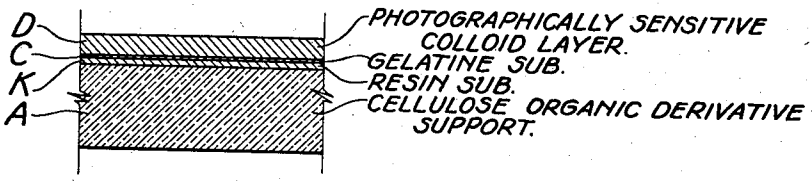


FIG. 2

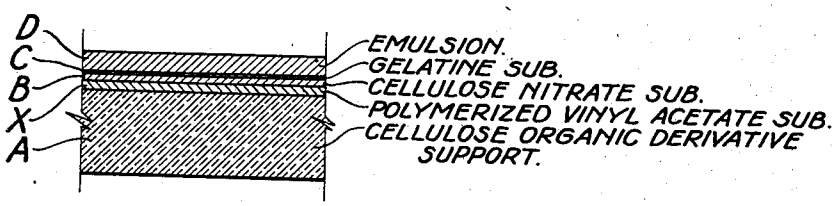


FIG. 3

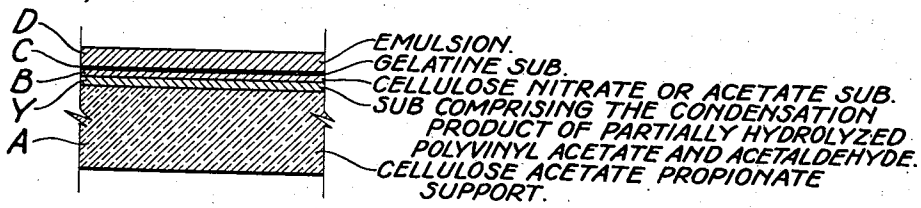
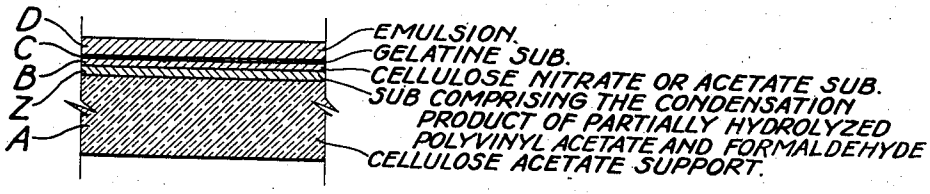


FIG. 4



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MANUFACTURE OF PHOTOGRAPHIC FILM

Filed Dec. 10, 1937 2 Sheets-Sheet 2

FIG. 5

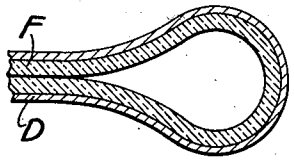


FIG. 6

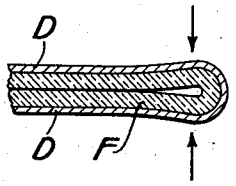


FIG. 7

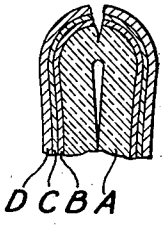


FIG. 8

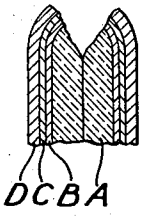


FIG. 9

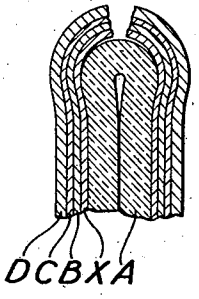
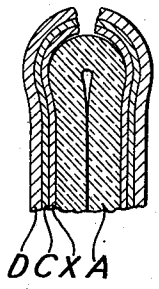


FIG. 10



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UNITED STATES PATENT OFFICE

2,133,110

MANUFACTURE OF PHOTOGRAPHIC FILM

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Application December 10, 1937, Serial No. 179,174

20 Claims. (Cl. 95—9)

This invention relates to photographic materials and more particularly to photographic film having a high degree of flexibility and satisfactory emulsion adherence characteristics in which an improved type of substratum or undercoat is employed between the light sensitive emulsion and the support.

This application is in part a continuation of my copending application Serial No. 1,547, filed January 12, 1935.

In the manufacture of photographic film, especially film of the so-called safety type in which a light sensitive emulsion is coated onto a flexible, relatively uninflammable cellulose derivative support, two rather serious problems are encountered. One is to get the emulsion to stick properly to the support and the other is to attain the requisite degree of flexibility. When the adhesion is good the film as a whole is often brittle and will fracture even with moderate bending. This is probably due to the fact that, since the emulsion adheres so closely to the support, it is, broadly speaking, substantially continuous with it. Accordingly, as soon as the emulsion breaks, the energy of impact produced by the fracture is transmitted directly to the support and causes it to break also. Experience has shown that when the emulsion adheres less tenaciously to the support, the film is often found to have unsatisfactory stripping qualities, that is, the emulsion can be lifted or stripped from the base or support too readily to meet the requirements of many photographic uses. Until the advent of the present invention it has always been found necessary to effect some sort of compromise between adherence on the one hand and brittleness on the other, and one property always gained at the expense of the other.

As is well known, gelatin emulsions (which are colloidal solutions or dispersions of gelatin in water) cannot be made to adhere directly to a cellulose derivative support, because water will not wet this type of surface. It is accordingly necessary to apply to the cellulose derivative support a thin layer, substratum, or "sub," as it is generally called, of gelatin in order to provide a surface to which the emulsion will stick. Although a gelatin emulsion, as such, will not adhere to the support, a gelatin sub can be made to adhere if it is applied from a subbing solution containing solvents, which, not only wet, but superficially attack, soften or swell the cellulose derivative material and thus assist in anchoring the gelatin thereto. Once the gel sub is applied, it is a relatively simple matter to make the light sensitive aqueous emulsion stick to the support, since water will readily wet and soften the surface of the gel coating and the emulsion can thus be made to adhere to it.

It should be pointed out that when the emulsion is applied to the gel-subbed base, the emulsion and gel sub merge and form what may be considered a single, continuous gelatin layer on the film and that the degree of adherence of the emulsion to the support is dependent upon the degree of adherence of the gel sub to the support or to the intervening substrata. This adherence of the gel sub is controlled in practice by controlling the "strength" of the gel subbing solution, that is, the solvent or softening power of the subbing solution on the cellulose derivative material, or intervening substrata. This control of solvent or softening power of the solution is accomplished by regulating the kind or amount of each of the solvents used in compounding it. A "strong" subbing solution is, accordingly, one which has a relatively strong solvent, softening or swelling action on the support material and causes the deposited gel sub to adhere tenaciously thereto, while a "weak" subbing solution is one which is only weakly solvent with respect to the support material and will cause the deposited gelatin coating to adhere only slightly. In general, it may be said that the stronger the gel subbing solution, the greater will be the degree of adherence of sub to the support and the greater the brittleness of the completed film.

The problem of obtaining proper adherence of the emulsion without an undue increase in brittleness is a difficult one, especially with the so-called safety types of film in which the support is generally formed from a cellulose organic derivative, such as cellulose acetate. When employing cellulose nitrate as the support, it is possible to use a relatively weak gel subbing solution and thus, to a certain extent, keep the adherence (and consequently brittleness) down to approximately the proper value. With cellulose organic derivative supports, such as those formed of cellulose acetate, or cellulose acetate propionate, for example, much stronger subbing solutions than those which can be satisfactorily employed with cellulose nitrate supports must be used, with the result that excessive adherence, and therefore excessive brittleness, results. It has accordingly been necessary with this type of support first to apply a thin cellulose nitrate sub (which can itself be subbed with relatively weak subbing solutions), and then to apply the gel sub to the nitrate surface, followed by the

emulsion coating, but this has been disadvantageous because of the fact that it introduces a certain amount of cellulose nitrate into the finished film, making it difficult to meet the underwriters specifications for safety film. Aside from this phase of the matter, the problem of brittleness has remained substantially the same and even films containing nitrate subs have proved to be insufficiently free from this defect to meet the rigid requirements of cinematographic use.

In an attempt to solve this problem of obtaining proper flexibility without an undue sacrifice of emulsion adherence, it has been proposed to employ an extra heavy cellulose nitrate undercoat underneath the gel sub, and, while this expedient has met with a certain amount of success, it suffers the disadvantage pointed out above, i. e., that it introduces a relatively large amount of cellulose nitrate into the finished product. Many other expedients looking toward the same end have been employed, for example, the use of an undercoat of rubber or similar material, but it has been found that, similarly to cellulose derivative undercoats, the impact arising from rupture of the emulsion is transmitted through the rubber layer, causing it to break and this break is carried on into the material of the underlying support. Somewhat similar to such products and suffering many of the same defects are various laminated structures in which bases consisting of cellulose organic derivatives or other materials have applied thereover a layer or layers of resinous or rubberlike materials of substantial thickness, these layers constituting a material part of the support and being applied, either in the form of separate sheets united to the base by appropriate cements, or deposited as relatively thick coatings from appropriate solutions.

It is the principal object of the present invention to overcome the above-mentioned prior art difficulties and to provide a photographic film having a high degree of flexibility or freedom from brittleness and at the same time satisfactory emulsion adherence characteristics. A further object is to provide an improved type of safety film in which flexibility is rendered completely independent of the degree of adherence between the emulsion and the underlying substrata. Other objects will appear hereinafter.

I have found that if the support is first subbed with an extremely thin layer comprising as a major constitutent a synthetic resin, preferably a polyvinyl resin, almost any strength of gel subbing solution may be employed in the subbing operation and the gelatin emulsion may be bound to the gel sub and other substrata as tightly as desired without giving rise to brittleness in the finished film. In other words, I have found that the use of these resin subs renders the matter of flexibility completely independent of the degree of adherence existing between the emulsion and the support or the substrata underlying the emulsion.

In the accompanying drawings, I have illustrated in greatly exaggerated section several film structures produced in accordance with my invention and certain tests by which the flexibility and emulsion adherence of such films may be determined.

Figures 1, 2, 3, and 4 are cross sections of films produced in accordance with my invention.

Figures 5 and 6 illustrate the manner of carrying out the brittleness test described herein.

Figures 7 and 8 illustrate the behavior of a relatively brittle film when subjected to the test illustrated in Figures 5 and 6.

Figures 9 and 10 illustrate the behavior of a film such as shown in Figures 2 and 1, respectively, upon being subjected to the test illustrated in Figures 5 and 6.

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.

After carrying out extensive work with various types of resinous materials, I have found that in order to fulfill the requirements of use as a substratum in a photographic film, the resin must be sufficiently adhesive when dissolved in appropriate solvents to stick properly to the cellulose derivative material of the support, i. e., so that the completed film will pass the stripping tests herein described. The material must be compatible with the cellulose derivative in the sense that it will adhere thereto and must also be compatible with photographic emulsions in the sense that it shall not fog or reduce the sensistivity thereof or adversely affect any of the various processing steps to which the film is subjected during development.

I have found that all of these qualities and others which will become apparent as the description proceeds, are possessed by various synthetic resins now commercially available. Of these I have found especially valuable the hydrolyzed or partially hydrolyzed vinyl resins such, for example, as those prepared by the method outlined in the U. S. Patent to Robertson 1,921,326, and particularly those resins known under the trade names Gelva (a polymerized form of vinyl acetate, the preparation of which is described in U. S. Patents 1,241,738, 1,586,803 and 1,710,825); Alvar, (an acetal derived from the condensation of partially hydrolyzed polyvinyl acetate with acetaldehyde,) and Formvar, (an acetal derived from the condensation of partially hydrolyzed polyvinyl acetate with formaldehyde, the preparation of which is described in U. S. Patent 2,036,092 and Reissue Patent 20,430 and British Patent 351,082). I also contemplate the use of the Santolites, which is a trade name for condensation products of formaldehyde with aromatic sulfonamides, the preparation of which is described on pages 101 and 102 of the text by Scheiber and Sandig entitled "Artificial Resins," published in 1931 by Isaac Pitman & Sons, Ltd., London, England, and at pages 299–303 of the book by Ellis entitled "Synthetic Resins and Their Plastics," published in 1923 by the Chemical Catalog Company, as well as the reaction or condensation products of polyhydric alcohols and polybasic acids, sold under various trade names especially the Glyptals, which are products of the reaction between glycerol and phthalic acid or phthalic anhydride, the preparation of which is described, for example, on page 293 of the 1923 edition of the above-mentioned Ellis text; the alkyds which are the products of reaction of a mixture of a polybasic acid, an alcohol having three or more hydroxyl groups in the molecule, a dihydric alcohol, and a dibasic acid, the preparation of which is described in an article beginning on page 972 of vol. 25 of the Journal of Industrial and Engineering Chemistry, 1933; ureaformaldehyde resins; the modified phenol formaldehyde resins and other similar resinous bodies.

The subbing of the film support with the resin solution may be carried out by any technique well

known to those skilled in the art. The solution may be conveniently applied to a cellulose acetate support, for example, from a 3–10% solution of vinyl resin in pure methyl or ethyl alcohol, methyl alcohol being preferred or in any suitable solvent for the resin in question. After drying a thin gelatin sub is then applied to the resin subbed support in order to form a proper surface upon which to deposit the final coating of emulsion as previously described. The application of the resin and gelatin subs may be accomplished by any well known subbing technique as by immersion, bead application, or otherwise. The support may be subbed on one or both sides, depending upon the type of film being produced. For some purposes it may have a coating of gelatin or other material on the surface opposite the emulsion layer in order to give greater flatness to the film, as is usually the case with portrait film. In X-ray film which has the emulsion deposited on both surfaces, the resin subs of the present invention may be advantageously employed on both sides of the base or support.

In some cases it may be desirable to employ a cellulose nitrate, cellulose acetate or other cellulose derivative sub between the gelatin sub and the resin sub, as illustrated in Figures 2, 3 and 4. This, however, is entirely optional and is employed merely as a means of coating the resinous surface of the subbed support to render it nontacky and thus facilitate handling on drying rolls and other parts of the film-making machinery.

It is desirable at this point to define the term "sub" or "sub layer" as used herein and in the appended claims. By the term "sub" I refer to extremely thin layers or undercoats of material having a thickness of the order of .000045" to .0002", that is, layers of only a few millionths of an inch in thickness. In the broad sense, the term sub may refer generically to any single layer or combination of layers lying between the emulsion and the film support itself. These extremely thin layers are to be particularly distinguished from the layers present in the coated or laminated structures of the prior art by virtue of the fact of their extreme thinness. As indicated above, my invention resides in the discovery that by providing on the support an extremely thin resin sub of the character and thickness herein described, the flexibility characteristics of a film including such a resin-subbed support, are rendered entirely independent of the degree of adherence existing between the deposited emulsion and the support and a rupture occurring in the emulsion layer of the film under flexure is thereby prevented from penetrating the support. It should be noted that all of the various layers of the film adhere, that is, are adhesively joined to adjacent layers. For example, the emulsion layer is joined to the gelatin layer, the gelatin to both emulsion and resin, and the resin to the gelatin and support. Thus, the emulsion adheres to the support through the medium of any intervening layers or subs which may lie between the emulsion and the support itself.

It will be understood that the thickness of the resin subs of my invention will vary somewhat in accordance with the type of film support with which they are used. The thicker types of support tolerate a slightly thicker sub than the thinner types and, although I have indicated the optimum range of thickness, it will be understood that this thickness may vary by a few millionths of an inch either above or below the preferred values. In no case, however, is the deposited layer of sufficient thickness to be regarded as a lamination in the ordinary sense of the word as in the case where a laminated film base is built up by the superimposition of a plurality of layers or coatings of appreciable or relatively substantial thickness. In fact, the use of resin layers of the type herein described as a means of controlling flexibility of a photographic film regardless of the degree of emulsion adherence, constitutes an entirely new concept in the art. The discovery that such extremely thin layers of resinous material would produce the results herein described is inobvious and wholly without precedent in the art of film manufacture.

Example I.—A film support consisting of a sheet or film of cellulose organic acid ester material such as cellulose acetate is led through an immersion type hopper containing a 5% solution of polyvinyl acetate resin in methyl alcohol at a linear speed of about 3 feet per minute. The support is then led through an appropriate drying apparatus maintained at a temperature of approximately 120–200° F. where the solvent is evaporated from the surface of the material leaving a resin layer of approximately .00008 inch in thickness. The resin coated material is then carried through a second immersion hopper containing a solution or dispersion of gelatin having approximately the following composition:

	Per cent
Gelatin	1.0
Acetic acid	2.0
Water	3.0
Acetone	70.0
Methanol	24.0

The gel subbed material is then dried at an appropriate temperature after which the usual gelatino-silver-halide emulsion coating is deposited upon the gel surface.

Example II.—A film support consisting of a sheet or film of cellulose acetate is led through an immersion type hopper containing a 5% solution of polyvinyl acetate resin in methyl alcohol at a linear speed of approximately 3 feet per minute. The support is then led through an appropriate drying apparatus maintained at a temperature of approximately 120–200° F. where the solvent is evaporated from the surface of the material and a resin layer of approximately .000045 inch in thickness is deposited. The resin-subbed material is then carried through a second immersion hopper containing a 2½% solution of a high alcohol-soluble, low viscosity nitrocellulose dissolved in a solvent comprising 90% of methyl alcohol and 10% of butyl alcohol. Following appropriate drying of the nitrate coating, which is also extremely thin (of approximately the same order of thickness as the resin coating), the material is given a third extremely thin gelatin coating by the immersion or equivalent method, the gelatin being applied from a solution or dispersion of approximately the following composition:

	Percent
Gelatin	1.0
Acetic acid	0.5
Water	10.0
Methanol	88.5

The gelatin-coated material is then dried at an appropriate temperature, after which the usual gelatino-silver halide emulsion coating is coated upon the gel surface by known technique.

Example III—A sheet or film of cellulose acetate-propionate of appropriate thickness is

coated with a layer of polymerized vinyl resin material having a thickness of .0002 inch by the same procedure as outlined in Example I, the resin in this case being the product known under the trade name Alvar, the product of condensation of partially hydrolyzed polyvinyl acetate with acetaldehyde prepared as above indicated. The resin layer or substratum is then coated as before with a thin protective layer of cellulose derivative, in this case cellulose acetate, upon which layer is deposited the thin gelatin substratum, from a solution of approximately the following composition:

	Percent
Gelatin	1.0
Acetic acid	0.6
Water	3.0
Acetone	70.0
Methanol	25.4

The light-sensitive gelatino-silver halide emulsion is applied as before.

Example IV.—A sheet or film of cellulose acetate-propionate of appropriate thickness is coated with a layer of polymerized vinyl resin material having a thickness of .000045–.0002 inch by the same procedure as outlined in Example I, the resin in this case being the product known under the trade name Formvar, the product of condensation of partially hydrolyzed polyvinyl acetate with formaldehyde prepared as above indicated. The resin layer or substratum is then coated as in Example III with a thin layer of cellulose acetate upon which is deposited a gelatin substratum, followed by the light-sensitive gelatino-silver halide emulsion.

As will be observed from the above examples, the material of the support may be composed of any suitable cellulose organic derivative material, such as cellulose acetate, cellulose propionate, cellulose butyrate, or a mixed cellulose organic ester, such as cellulose acetate-propionate, cellulose acetate-butyrate, cellulose acetate-stearate, and the like. Although not limited thereto, my invention relates primarily to the manufacture of the so-called safety types of photographic film in which the support is composed of a relatively non-inflammable material, such as the cellulose organic acid esters, since it is with this type of support that the problem of brittleness is most serious.

Although in the above examples I have found it convenient to illustrate my invention by reference to photographic film coated or subbed on one side only, the use of resin subs as herein described may be applied with equal success to products such as portrait film, in which a coating of gelatin is deposited on the surface opposite the emulsion coating to give greater flatness to the film. It will be apparent that in such products it is as necessary to prevent brittleness arising from the application of the gelatin on one side of the film as on the other. I have found that brittleness is as effectively prevented by the use of the thin resinous layers in accordance with my invention as in the case of those films which have gelatin layers or coatings on one surface only.

The customary tests by which the properties of my improved type of photographic films are determined will now be described. These are the so-called dry stripping, wet stripping, and brittleness or flexibility, 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 lengthwise 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 coating 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 three or four inches. For Cine 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 the emulsion-coated film of convenient size is soaked in water at 70° F. for ten minutes. It is then removed from the water and fixed on a flat surface with the emulsion side up. The emulsion is then gouged or creased with the fingernails at points near the middle and end of the strip, each nail scratch tearing the emulsion away from the support to a certain extent. The scratched places are then rubbed with considerable force with the balls of the fingertips for several seconds. A film is said to have satisfactory wet stripping (emulsion adherence) properties when no peeling, or substantially no peeling, of the emulsion occurs as a result of this rubbing action. Wet stripping is said to be unsatisfactory when an appreciable or large amount of the emulsion comes off. For most types of film it should not be possible, to remove pieces wider than ¼ inch by this test.

The brittleness 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.

My invention will be further understood by reference to the accompanying drawings. In Fig. 1, I have illustrated a section through a photographic film produced substantially as described in Example I in which the letter A designates a cellulose organic derivative support such as a cellulose acetate support. Superimposed on and tenaciously adhering thereto is an extremely thin sub K composed of a synthetic resin, this sub being approximately .00008 inch in thickness. C designates a thin gel sub which adheres to the resin sub K. D is the final gelatino-silver halide layer which adheres to the gelatin sub C.

In Fig. 2, I have illustrated a section through a photographic film produced substantially as described in Example II in which the letter A designates a cellulose derivative support, for example, a cellulose acetate support. Superim-

posed on and tightly adhering thereto is an extremely thin sub X composed of a resin as herein described, such as polymerized vinyl acetate this sub being approximately .000045 inch in thickness. B designates a thin protective layer of cellulose nitrate, while C is a thin gelatin sub which adheres to the cellulose nitrate or acetate layer B. D is the final gelatino-silver halide emulsion layer which adheres to the gelatin sub C.

Fig. 3 represents a film structure prepared as described in Example III and differing from that of Fig. 2 only in the fact that the resinous layer Y is about .0002 inch in thickness and is composed of the product of condensation of acetaldehyde with partially hydrolyzed polyvinyl acetate and the support consists of cellulose acetate propionate.

Similarly, the structure of Fig. 4 prepared by the procedure of Example IV corresponds to that of Figures 2 and 3 except for the fact that the resinous layer Z is composed of the product of condensation of formaldehyde with partially hydrolyzed polyvinyl acetate.

Figures 5 and 6 illustrate graphically the manner of carrying out the brittleness test above referred to. The film F, after removal from the brittleness oven, is folded at a given place into the form of a short loop, the gelatin layer D being outermost. This loop is then closed by means of the forefinger and thumb, the pressure being applied as suddenly as possible and in the direction indicated by the arrows in Fig. 6.

In Figures 7 and 8 there are illustrated the results obtained when an ordinary type of photographic film comprising, a support A, a thin cellulose derivative sub B over the support, a second gel sub C over the cellulose derivative sub, and the emulsion layer D over the gel sub, is subjected to the test. It will be seen that the crack starting in the emulsion penetrates through the two sub layers or undercoats B and C and goes on into the material of the support. This crack almost invariably continues on through the support with the result shown in Fig. 8. The film here illustrated is a typical prior art product and one from which the resinous sub or undercoat of the present invention is absent. This product is also one in which there is a high degree of adherence between the emulsion and gel sub layer and between these layers and underlying cellulose derivative material.

Fig. 9 illustrates the results obtained when a film employing the resin subs of my invention is subjected to the test illustrated in Figures 5 and 6. The film shown is in all respects the same as that illustrated in Figures 7 and 8, except that a layer X of vinyl resin, for example, has been applied to the support before application of the gel sub C, and the emulsion coating D. The emulsion is made to adhere to the support with the same degree of tenacity as in the product illustrated in Figures 7 and 8, but the product of Fig. 9 differs from that of Fig. 7 in the fact that, although the crack starting in the emulsion may continue through the gel sub and even through the resin layer itself, it does not in any case penetrate into the support itself.

Fig. 9 strikingly illustrates the fact that a photographic film produced in accordance with my invention is characterized by the unusual property of 100% freedom from brittleness or, in other words, it has 100% flexibility. In addition to this remarkable property, films produced in accordance with my invention respond satisfactorily to both the wet and dry stripping tests above described. In this connection it should be pointed out that one of the outstanding features of my invention is the fact that the adherence of the emulsion may be regulated without regard to the flexibility of the film. In other words, it is possible to produce a film in which the emulsion adheres with the highest practicable degree of tenacity to the support without inducing any brittleness whatever in the film as a whole or causing the support material itself to break on bending when subjected to the brittleness test herein described.

While I offer no particular explanation or theory to account for the unusual results obtained in the practice of my invention, it may be noted that the resin subs employed obviously afford some means of dissipating the impact of the rupturing emulsion. This effect is to be clearly distinguished from the mere cushioning effect characteristic of elastic or semi-elastic materials. In many, although not all, cases the break occurring in the emulsion will penetrate even the lowermost resin layer and these layers may even be slightly released from the support, but in no case does the break penetrate the material of the support itself.

What I claim is:

1. A highly flexible photographic film of satisfactory emulsion adherence, comprising a cellulose organic derivative support, a thin synthetic resin sub adhesively joined to the support, a gel sub adhesively joined to the resin sub, and a photographically sensitive colloid layer adhesively joined to the gel-subbed surface of the support, said resin sub providing a means whereby the flexibility characteristics of the film as a whole are rendered independent of the degree of adhesion existing between the photographically sensitive layer and the subbed support and whereby a rupture occurring in the photographic layer of the film under flexure is prevented from penetrating the support.

2. The film of claim 1 in which the resin sub has a thickness within a few millionths of an inch of .000045–.0002 inch.

3. The film of claim 1 in which the resin sub has a thickness within a few millionths of an inch of .00008 inch.

4. A photographic film of satisfactory flexibility and free from brittleness, comprising a cellulose organic derivative support and a photographically sensitive colloid layer adhesively joined to the support by a composite intervening layer comprising an extremely thin resin sub adhesively joined to the support, a cellulose derivative sub adhesively joined to the resin sub, and a gel sub adhesively joined to the cellulose derivative sub and to the sensitive colloid layer, said intervening layer rendering the flexibility characteristics of the film as a whole independent of the degree of adhesion existing between the photographically sensitive layer and the subbed support.

5. A photographic film of satisfactory flexibility and free from brittleness comprising a cellulose organic derivative support and a photographically sensitive colloid layer adhesively joined to the support by a composite intervening layer comprising an extremely thin synthetic resin sub adhesively joined to the support, a cellulose derivative sub adhesively joined to the resin sub, and a gel sub adhesively joined to the cellulose derivative sub and to the sensitive colloid layer, said intervening layer rendering the flexibility characteristics of the film as a whole inde-

pendent of the degree of adhesion existing between the photographically sensitive layer and the subbed support.

6. A photographic film of satisfactory flexibility and free from brittleness comprising a cellulose organic derivative support and a photographically sensitive colloid layer adhesively joined to the support by a composite intervening layer comprising an extremely thin polymerized vinyl resin sub adhesively joined to the support, a cellulose derivative sub adhesively joined to the resin sub, and a gel sub adhesively joined to the cellulose derivative sub and to the sensitive colloid layer, said intervening layer rendering the flexibility characteristics of the film as a whole independent of the degree of adhesion existing between the photographically sensitive layer and the subbed support.

7. A photographic film of satisfactory flexibility and free from brittleness comprising a cellulose organic derivative support and a photographically sensitive colloid layer adhesively joined to the support by a composite intervening layer comprising an extremely thin polymerized vinyl acetate resin sub adhesively joined to the support, a cellulose derivative sub adhesively joined to the resin sub, and a gel sub adhesively joined to the cellulose derivative sub and to the sensitive colloid layer, said intervening layer rendering the flexibility characteristics of the film as a whole independent of the degree of adhesion existing between the photographically sensitive layer and the subbed support.

8. A photographic film of satisfactory flexibility and free from brittleness comprising a cellulose organic derivative support and a photographically sensitive colloid layer adhesively joined to the support by a composite intervening layer comprising an extremely thin polyvinyl acetal resin sub adhesively joined to the support, a cellulose derivative sub adhesively joined to the resin sub, and a gel sub adhesively joined to the cellulose derivative sub and to the sensitive colloid layer, said intervening layer rendering the flexibility characteristics of the film as a whole independent of the degree of adhesion existing between the photographically sensitive layer and the subbed support.

9. A photographic film of satisfactory flexibility and free from brittleness comprising a cellulose organic derivative support and a photographically sensitive colloid layer adhesively joined to the support by a composite intervening layer comprising an extremely thin resin sub composed of the product of condensation of partially hydrolized polyvinyl acetate with acetaldehyde adhesively joined to the support, a cellulose derivative sub adhesively joined to the resin sub, and a gel sub adhesively joined to the cellulose derivative sub and to the sensitive colloid layer, said intervening layer rendering the flexibility characteristics of the film as a whole independent of the degree of adhesion existing between the photographically sensitive layer and the subbed support.

10. A photographic film of satisfactory flexibility and free from brittleness comprising a cellulose organic derivative support and a photographically sensitive colloid layer adhesively joined to the support by a composite intervening layer comprising an extremely thin resin sub composed of the product of condensation of partially hydrolyzed polyvinyl acetate with formaldehyde adhesively joined to the support, a cellulose derivative sub adhesively joined to the resin sub, and a gel sub adhesively joined to the cellulose derivative sub and to the sensitive colloid layer, said intervening layer rendering the flexibility characteristics of the film as a whole independent of the degree of adhesion existing between the photographically sensitive layer and the subbed support.

11. 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 an extremely thin vinyl resin sub adhesively joined to the support, a cellulose derivative sub adhesively joined to the vinyl resin sub and a gel sub adhesively joined to the cellulose derivative sub and to the sensitive colloid layer, said intervening layer rendering the flexibility characteristics of the film as a whole independent of the degree of adhesion existing between the photographically sensitive layer and the subbed support.

12. 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 an extremely thin polyvinyl acetate resin sub adhesively joined to the support, a cellulose derivative sub adhesively joined to the resin sub and a gel sub adhesively joined to the cellulose derivative sub and to the sensitive colloid layer, said intervening layer rendering the flexibility characteristics of the film as a whole independent of the degree of adhesion existing between the photographically sensitive layer and the subbed support.

13. 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 an extremely thin polyvinyl acetal resin sub adhesively joined to the support, a cellulose derivative sub adhesively joined to the resin sub and a gel sub adhesively joined to the cellulose derivative sub and to the sensitive colloid layer, said intervening layer rendering the flexibility characteristics of the film as a whole independent of the degree of adhesion existing between the photographically sensitive layer and the subbed support.

14. 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 an extremely thin resin sub composed of the product of condensation of partially hydrolyzed polyvinyl acetate with acetaldehyde adhesively joined to the support, a cellulose derivative sub adhesively joined to the resin sub and a gel sub adhesively joined to the cellulose derivative sub and to the sensitive colloid layer, said intervening layer rendering the flexibility characteristics of the film as a whole independent of the degree of adhesion existing between the photographically sensitive layer and the subbed support.

15. 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 an extremely thin resin sub composed of

the product of condensation of partially hydrolized polyvinyl acetate with formaldehyde adhesively joined to the support, a cellulose derivative sub adhesively joined to the resin sub, and a gel sub adhesively joined to the cellulose derivative sub and to the sensitive colloid layer, said intervening layer rendering the flexibility characteristics of the film as a whole independent of the degree of adhesion existing between the photographically sensitive layer and the subbed support.

16. 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 an extremely thin vinyl resin sub adhesively joined to the support, a cellulose nitrate sub adhesively joined to the resin sub and a gel sub adhesively joined to the cellulose nitrate sub and to the sensitive colloid layer, said intervening layer rendering the flexibility characteristics of the film as a whole independent of the degree of adhesion existing between the photographically sensitive layer and the subbed support.

17. 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 an extremely thin polyvinyl acetate resin sub adhesively joined to the support, a cellulose nitrate sub adhesively joined to the resin sub and a gel sub adhesively joined to the cellulose nitrate sub and to the sensitive colloid layer, said intervening layer rendering the flexibility characteristics of the film as a whole independent of the degree of adhesion existing between the photographically sensitive layer and the subbed support.

18. 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 an extremely thin polyvinyl acetal resin sub adhesively joined to the support, a cellulose nitrate sub adhesively joined to the resin sub and a gel sub adhesively joined to the cellulose nitrate sub and to the sensitive colloid layer, said intervening layer rendering the flexibility characteristics of the film as a whole independent of the degree of adhesion existing between the photographically sensitive layer and the subbed support.

19. 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 an extremely thin resin sub composed of the product of condensation of partially hydrolized polyvinyl acetate with acetaldehyde joined to the support, a cellulose nitrate sub adhesively joined to the resin sub and a gel sub adhesively joined to the cellulose nitrate sub and to the sensitive colloid layer, said intervening layer rendering the flexibility characteristics of the film as a whole independent of the degree of adhesion existing between the photographically sensitive layer and the subbed support.

20. 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 an extremely thin resin sub composed of the product of condensation of partially hydrolized polyvinyl acetate with formaldehyde joined to the support, a cellulose nitrate sub adhesively joined to the resin sub and a gel sub adhesively joined to the cellulose nitrate sub and to the sensitive colloid layer, said intervening layer rendering the flexibility characteristics of the film as a whole independent of the degree of adhesion existing between the photographically sensitive layer and the subbed support.

GALE F. NADEAU.