Oct. 19, 1937.

G. S. BABCOCK

2,096,675

PHOTOGRAPHIC FILM

Original Filed June 19, 1935

2 Sheets-Sheet 1

Fig. 1.

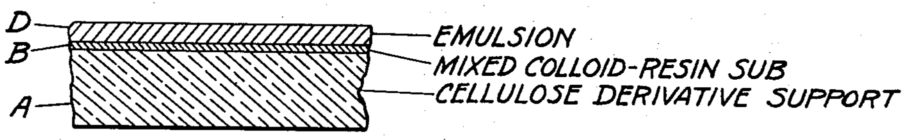

Fig. 2.

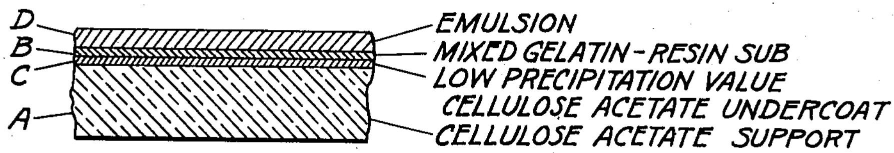

Fig. 3.

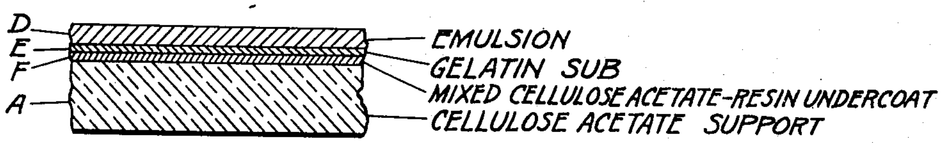

Fig. 4.

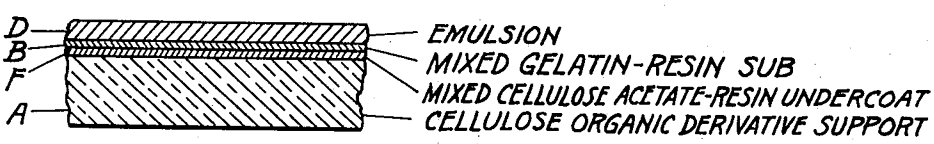

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Fig. 5.

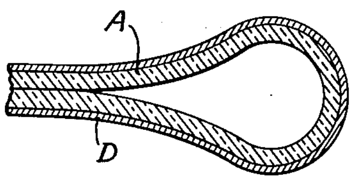


Fig. 6.

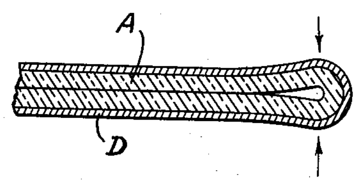


Fig. 7.

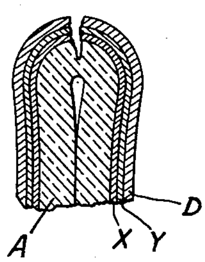


Fig. 8.

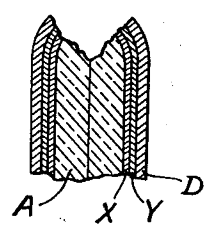


Fig. 9.

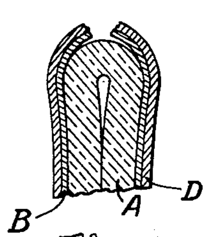


Fig. 10.

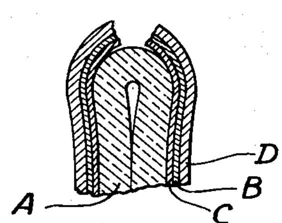


Fig. 11.

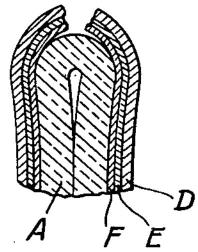
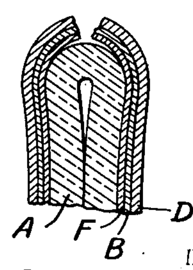


Fig. 12.



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Patented Oct. 19, 1937 2,096,675

UNITED STATES PATENT OFFICE

2,096,675

PHOTOGRAPHIC FILM

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Application June 19, 1935, Serial No. 27,409
Renewed March 30, 1937

21 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 in which an improved type of substratum or undercoat is employed between the light-sensitive emulsion and the film support.

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. It has accordingly always been found necessary heretofore to effect some sort of compromise between adherence on the one hand and brittleness on the other, and it is well known that one property is invariably 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 an emulsion is applied to a gel-subbed base, the emulsion and gel sub tend to merge and form what, for all intents and purposes, 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 if any. 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" gel 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 the 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 when dealing with the so-called safety types of films in which the support is 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, to keep the adherence (and consequently brittleness) down to approximately the proper value, but with cellulose organic derivative supports, such as those formed of cellulose acetate, or cellulose acetate propionate, for example, much stronger subbing solutions must be employed with the result that excessive adherence, and therefore excessive brittleness occurs. It has accordingly been necessary with this latter type of support, first to apply a thin cellulose nitrate undercoat (which can itself be subbed with relatively weak subbing solutions), and then to apply a gel sub to the nitrate surface, followed by the emulsion coating, but this is 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.

A number of expedients have been proposed in the prior art in an attempt to solve this problem of obtaining proper flexibility without an undue sacrifice of emulsion adherence. For example, the use of an undercoat of rubber or similar cushioning material underneath the emulsion has been suggested, 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 that 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 rubber-like 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 cement, or deposited, as 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. 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. A specific object is to provide a film having a colloid-resin mixed sub between the light-sensitive gelatin layer and the film base or support. Other objects will appear hereinafter.

I have found that if the film support is subbed or coated with a thin layer consisting essentially of a mixture of a colloidal material such as gelatin and a glyptal resin, subbing solutions of widely varying strength may be employed in the subbing operation and the gelatin emulsion may be bound to the mixed gelatin-resin sub or other substrata as tightly as desired without giving rise to brittleness of the finished photographic film as a whole. In other words, the use of gelatin-glyptal mixed subs renders the matter of flexibility of such films substantially independent of the degree of adherence existing between the emulsion and the underlying substrata.

I have also found that a mixed gelatin-glyptal sub may be used alone to take the place of the various substrata heretofore employed, since it is compatible with and can be made to stick to the cellulose derivative material of the film base or support and is of such character that the gelatin emulsion will readily adhere thereto. In some cases it may be desirable to employ this mixed type of sub in connection with other substrata or undercoats as will more fully appear hereinafter.

I have found that the glyptal resins, when used in accordance with the invention herein described, are entirely compatible with the material of the film base and are also compatible with the photographic emulsion, in that they do not fog or reduce the sensitivity thereof, or adversely affect any of the various processing steps to which the film is subjected during development.

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

Fig. 1 is a section through the body of a completed photographic film produced in accordance with my invention and comprising a single colloid-resin sub underlying the emulsion.

Fig. 2 is a section through another modification in which a cellulose derivative undercoat has been employed underneath a mixed sub.

Fig. 3 is a section through a modification in which a cellulose-derivative-resin mixed layer has been used as an undercoat and a gel sub laid over the undercoat.

Fig. 4 is a further modification in which a cellulose-derivative-resin mixed undercoat has been employed in connection with a gel-resin mixed sub.

Figs. 5 and 6 illustrate the manner of carrying out a brittleness test as described herein.

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

Figs. 9, 10, 11, and 12 illustrate the behavior of films such as shown in Figs. 1, 2, 3, and 4, respectively, when subjected to the brittleness test.

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, the film base or support, which is preferably composed of a cellulose organic ester material, such as cellulose acetate or cellulose acetate propionate, is subbed or coated with an extremely thin layer of a colloid-resin mixture, such as a gelatin-glyptal resin mixture. The resin to be employed in this mixed sub is preferably a glyptal resin (sometimes sold under the trade name Rezyl). These resins are the products formed by reacting a polyhydric alcohol, such as glycerin, with a polybasic acid, such as phthalic acid or its anhydride. A typical method of preparation is described on page 293 of the 1923 edition of the text by Carleton Ellis, entitled "Synthetic Resins and Plastics", published by the Chemical Catalog Company. Also included in this category are the alkyd resins, a modified type of glyptal which may be prepared, for example, by reacting a polybasic organic acid with an alcohol having three or more hydroxyl groups in the molecule, a dihydric alcohol, and a dibasic acid. The nature of these resins is more fully described in an article beginning on page 971 of volume 25 of the Journal of Industrial and Engineering Chemistry, (1933).

The colloidal component of the mixed sub is preferably gelatin, although it may be a cellulose derivative, such as cellulose acetate or similar colloidal materials which are compatible with the material of the film base to which they are applied.

The subbing operation may be carried out by any convenient technique well known to those skilled in the art of film making. The material may, for example, be applied from a 3-5% solution of the solid material in appropriate solvents. After drying, the usual light-sensitive gelatino silver halide emulsion may be coated directly onto the gelatin-glyptal-subbed surface to which it strongly adheres.

The application of the gelatin-resin mixture to the film support may be accomplished by any of the subbing operations well known to the art, such as immersion, bead application, or otherwise. The material may be subbed on one or both sides, depending upon the type of film being produced. For example, in making X-ray film the emulsion is deposited on both sides of the support. In producing this type of film in accordance with my invention the support is subbed on both sides with the gelatin-resin mixture and the emulsion coated on both the subbed surfaces.

Example 1

In producing a film in accordance with one form of my invention, a support consisting of a sheet or film of cellulose acetate is led through an immersion type hopper containing a solution prepared as indicated below.

A gelatin solution is made up having the following composition:

	Percent by weight
Gelatin	1.2
Acetic acid	1.2
Water	3.0
Acetone	70.0
Ethyl alcohol	24.6

To 97 parts by weight of this solution are added 3 parts by weight of a glyptal resin, for example, a resin such as that sold under the trade names "Bakelite BR51" or "Bakelite BR671."

The support after leaving the subbing apparatus is led through an appropriate drying apparatus maintained at a temperature of 120–200° F. where the solvents are evaporated from the surface of the material, with the result that a strongly adherent gelatin-resin layer of approximately .00008 inch in thickness is formed. An appropriate gelatino-silver halide emulsion coating is then applied in the usual manner, thus completing the film. A film produced as outlined above is illustrated in Fig. 1.

Example 2

A film support consisting of a sheet or film of 90% precipitation value cellulose acetate of the type customarily employed in the manufacture of safety film is subbed, preferably just after it has been stripped from the surface upon which it is formed, with a solution of the following composition, the percentages being by weight:

	Percent
Cellulose acetate (69% precipitation value—29 second viscosity by the dropping ball method)	2–6
Acetone	77
Ethyl alcohol (95%)	21–17

The coated film is then dried at approximately 120° F. producing thereon an extremely thin tightly adhering acetate layer, after which the film is subbed with a gelatin-glyptal resin solution such as described in Example 1, dried and finally coated with emulsion as in that example. The resulting product is illustrated in Fig. 2.

I prefer to use a cellulose acetate of low precipitation value (of the order of 69%) because of the greater ease of subsequent subbing with gelatin solutions as contrasted, for example, to an acetate of 90% precipitation value, although I do not exclude the use of the latter material nor of other types of acetate. The advantage of using the lower precipitation value material lies in the fact, which I have discovered, that it is easier to cause a gelatin-containing composition, such as the gelatin-resin mixture herein described or other gelatin subbing compositions, to adhere to a cellulose acetate surface of 69% precipitation value, for example, than to one composed of an acetate of 90% precipitation value. Although I do not confine myself to any particular explanation of this phenomenon, I believe it to be due to the greater proportion of hydroxyl groups present in the 69% material due to more extensive hydrolysis, the 69% material containing 38–39% acetyl, as compared to 40–41% acetyl for the 90% material.

Although I can produce a wholly satisfactory product without the use of the first (cellulose acetate) layer just described, I have found that there is a distinct advantage in doing so, since the thin acetate layer seals in the plasticizer or softener which is always present in the film base, and thus prevents its interference with the proper drying down and adherence of the gelatin-resin or other gelatin sub applied thereafter.

Example 3

A sheet or film of 90% precipitation value cellulose acetate is coated with a solution having approximately the following composition, the percentages being by weight:

	Percent
Cellulose acetate (69% precipitation value—29 second viscosity by dropping ball method)	3.0
Glyptal resin (Bakelite BR51)	1.5
Acetone (or Methyl Cellosolve)	75.5
Ethyl alcohol (95%)	20.0

The coated support is dried as in the previous examples, after which it is subbed with a solution of approximately the following composition, percentages being by weight:

	Percent
Gelatin	1.2
Acetic acid	.12
Water	5.0
Acetone	70.0
Ethyl alcohol (95%)	23.68

After appropriate drying the support is then coated with emulsion, resulting in a product such as illustrated in Fig. 3.

Example 4

In a still further modification of my invention I may employ a resin as a component of both the cellulose acetate undercoat and the gelatin sub. In accordance with this modification a cellulose acetate support, for example, is coated with a cellulose acetate-resin composition of the type given in Example 3. After drying, the coated surface is subbed with a gelatin-resin composition of the type indicated in Example 1. After drying this coating, the emulsion coating is deposited on the subbed surface as before, the result being illustrated in Fig. 4.

The solvents employed for making up the various subbing solutions will of course be selected upon the basis of the particular resin dealt with and the material of the support or film base to which the solutions are to be applied. Inasmuch as the solvents for these materials are well within the knowledge of those skilled in the art no further explanation in respect to them is considered necessary.

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 esters, since it is with this type of material that the problem of brittleness is most severe.

Although in the above examples, I have found it convenient to illustrate my invention by reference to photographic films coated or subbed on one side only, the use of gelatin- or other colloid-resin mixed 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 or X-ray film which is gel- and emulsion-coated on both surfaces. It will be apparent that in such products, it is as necessary to prevent brittleness arising from the application of the gelatin or other subs on one side of the film as on the other. I have found that brittleness is as effectively prevented by the use of the colloid-resin layers in accordance with my invention as in the case of those films which have layers or coatings on one surface only.

The improvement made possible by my invention will now be made clear by a discussion of the results obtained in carrying out certain tests on the finished emulsion-coated film. 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 placed 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 test customarily employed for determining the brittleness of X-ray and portrait film 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.

Another test for brittleness customarily applied to Cine film consists in heating a sample of the film at 90–100° C. for one hour, after which the film is folded between the thumb and finger in several places, with the emulsion side up. If a break occurs all the way across, the film is said to be "brittle". If the break extends only half way across, the film is said to be "slightly brittle", while if the break does not extend more than a quarter of the way across, the film is said to be "very slightly brittle". If no break occurs, the film is "non-brittle."

Referring now to the drawings, in Fig. 1 I have illustrated a section through a photographic film of the so-called safety type produced substantially in accordance with Example 1 above, in which the letter A designates a cellulose derivative support composed of cellulose acetate, for example. Superimposed on and tightly adhering thereto is an extremely thin undercoat or substratum B composed of a mixed colloid-resin sub, such as a mixture of gelatin and a glyptal or alkyd resin, this undercoat being approximately .00008 inch in thickness. D is the final gelatino-silver-halide emulsion layer which adheres tightly to the mixed sub B.

Fig. 2 represents a film structure prepared substantially as described in Example 2 and differing from that of Fig. 1, in that the film base A has deposited thereon an extremely thin undercoat C of low precipitation value cellulose acetate. In this case the mixed gelatin-resin sub B, of substantially the same thickness as the undercoat, is deposited on, and adheres closely to, the undercoat C.

Fig. 3 represents a film structure in which the support or film base A is first provided with an undercoat F comprising a mixture of cellulose acetate and a resin. In this modification a gelatin sub E of the customary type is deposited upon the mixed acetate-resin undercoat F, the emulsion D being applied as in the previous modifications.

In Fig. 4 I have illustrated a still further modification of my invention in which the film base A is first provided with a mixed cellulose acetate-resin undercoat F upon which is deposited the mixed gelatin-resin sub B, followed by the emulsion D.

Figs. 5 and 6 illustrate graphically the manner of carrying out the brittleness test above referred to. The film A, 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 in the direction indicated by the arrows in Fig. 6.

In Figs. 7 and 8, there are illustrated the results obtained when a prior art type of photographic film is subjected to the test illustrated in Figs. 5 and 6. This film comprises a support A, a tightly adhering cellulose derivative undercoat X over the support, a gel sub Y over the cellulose derivative undercoat, and an emulsion layer D over the gel sub. It will be seen that the crack starting in the emulsion penetrates through the sub layer Y, the undercoat X, 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.

Fig. 9 illustrates the results obtained when a film prepared, for example, as described in Example 1 and employing the colloid-resin undercoats of my invention is subjected to the test illustrated in Figs. 5 and 6. Contrary to what would normally be expected, it is found that, notwithstanding the fact that the mixed gelatin-resin sub B has been bound tightly to the film base A and the emulsion D has been likewise tightly bound to the sub B, the crack starting in the two upper layers is not transmitted through the body of the film base. Corresponding results are obtained when the film structures of Figs. 2, 3, and 4 prepared, respectively, in accordance with Examples 2, 3, and 4 above, are subjected to this same test. While the emulsion and the underlying layers may crack when the film is flexed, the rupture in no case penetrates into the body of the film base. These results strikingly illustrate the fact that a photographic film produced in accordance with my invention is characterized by the unusual property of substantially 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 to the support with the highest practicable degree of tenacity without inducing any brittleness in the film as a whole, or causing the support material to break on bending, either during cinematographic or other use, or when subjected to the tests herein described. While I offer no particular explanation or theory to account for the unusual and unexpected results obtained in practice of my invention, it is evident that the mixed colloid-resin subs or undercoats herein described offer some means of dissipating the impact on the film base of the rupturing emulsion and underlying layers. This effect is to be 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 undercoat, and these layers may even be released from the support to a slight degree, but in no case does the break penetrate the material of the support itself.

What I claim is:

1. A photographic film having satisfactory flexibility and free from brittleness, comprising a cellulose organic derivative support and a photographically sensitive colloid layer adhesively joined to the support by an intervening layer comprising an extremely thin sub composed of a mixture of gelatin and a resin.

2. A photographic film having satisfactory flexibility and free from brittleness, comprising a cellulose organic derivative support and a photographically sensitive colloid layer adhesively joined to the support by an intervening layer comprising an extremely thin sub composed of a mixture of gelatin and a synthetic resin.

3. A photographic film having satisfactory flexibility and free from brittleness, comprising a cellulose organic derivative support and a photographically sensitive colloid layer adhesively joined to the support by an intervening layer comprising an extremely thin sub composed of a mixture of gelatin and a polybasic acid-polyhydric alcohol resin.

4. A photographic film having satisfactory flexibility and free from brittleness, comprising a cellulose organic derivative support and a photographically sensitive colloid layer adhesively joined to the support by an intervening layer comprising an extremely thin sub composed of a mixture of gelatin and an alkyd resin.

5. A photographic film having 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 layer comprising an extremely thin cellulose derivative sub adhesively joined to the support and an extremely thin sub composed of a mixture of gelatin and resin adhesively joined to the cellulose derivative sub and to the sensitive colloid layer.

6. A photographic film having 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 layer comprising an extremely thin cellulose derivative sub adhesively joined to the support and an extremely thin sub composed of a mixture of gelatin and a synthetic resin adhesively joined to the cellulose derivative sub and to the sensitive colloid layer.

7. A photographic film having 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 layer comprising an extremely thin cellulose derivative sub adhesively joined to the support and an extremely thin sub composed of a mixture of gelatin and a polybasic acid-polyhydric alcohol resin adhesively joined to the cellulose derivative sub and to the sensitive colloid layer.

8. A photographic film having 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 layer comprising an extremely thin cellulose derivative sub adhesively joined to the support and an extremely thin sub composed of a mixture of gelatin and an alkyd resin adhesively joined to the cellulose derivative sub and to the sensitive colloid layer.

9. A photographic film having satisfactory flexibility and free from brittleness comprising a cellulose acetate support and a photographically sensitive colloid layer adhesively joined to the support by an intervening composite layer comprising an extremely thin cellulose acetate sub adhesively joined to the support and an extremely thin sub composed of a mixture of gelatin and resin adhesively joined to the cellulose acetate sub and to the sensitive colloid layer.

10. A photographic film having 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 an intervening composite layer comprising an extremely thin sub composed of a mixture of a cellulose organic acid ester and a resin adhesively joined to the support and a gel sub adhesively joined to the mixed sub and to the sensitive colloid layer.

11. A photographic film having 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 an intervening composite layer comprising an extremely thin sub composed of a mixture of a cellulose organic acid ester and a synthetic resin adhesively joined to the support and a gel sub adhesively joined to the mixed sub and to the sensitive colloid layer.

12. A photographic film having 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 an intervening composite layer comprising an extremely thin sub composed of a mixture of a cellulose organic acid ester and a polybasic acid-polyhydric alcohol resin adhesively joined to the support and a gel sub adhesively joined to the mixed sub and to the sensitive colloid layer.

13. A photographic film having satisfactory flexibility and free from brittleness, comprising a cellulose acetate support and a photographically sensitive colloid layer adhesively joined to the support by an intervening composite layer comprising an extremely thin sub composed of a mixture of cellulose acetate and a resin adhesively joined to the support and a gel sub adhesively joined to the mixed sub and to the sensitive colloid layer.

14. A photographic film having satisfactory flexibility and free from brittleness, comprising a cellulose acetate support and a photographically sensitive colloid layer adhesively joined to the support by an intervening composite layer comprising an extremely thin sub composed of a mixture of cellulose acetate and a synthetic resin adhesively joined to the support and a gel sub adhesively joined to the mixed sub and to the sensitive colloid layer.

15. A photographic film having satisfactory flexibility and free from brittleness, comprising a fully esterified cellulose acetate support and a photographically sensitive colloid layer adhesively joined to the support by an intervening composite layer composed of an extremely thin sub composed of a mixture of low precipitation value cellulose acetate and a polybasic acid-polyhydric alcohol resin adhesively joined to the support and a gel sub adhesively joined to the mixed sub and to the sensitive colloid layer.

16. A photographic film having satisfactory flexibility and free from brittleness, comprising a cellulose organic acid ester support and a photographically sensitive layer adhesively joined to the support by an intervening layer comprising an extremely thin sub composed of a mixture of a cellulose organic acid ester and a resin adhesively joined to the support and an extremely thin sub composed of a mixture of gelatin and a resin adhesively joined to the first named mixed sub and to the sensitive colloid layer.

17. A photographic film having 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 an intervening composite layer comprising an extremely thin sub composed of a mixture of a cellulose organic acid ester and a synthetic resin adhesively joined to the support and an extremely thin sub composed of a mixture of gelatin and a synthetic resin adhesively joined to the first named mixed sub and to the sensitive colloid layer.

18. A photographic film having 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 an intervening composite layer comprising an extremely thin sub composed of a mixture of a cellulose organic acid ester and a polybasic acid-polyhydric alcohol resin adhesively joined to the support and an extremely thin sub composed of a mixture of gelatin and a polybasic acid-polyhydric alcohol resin adhesively joined to the first named mixed sub and to the sensitive colloid layer.

19. A photographic film having satisfactory flexibility and free from brittleness, comprising a cellulose acetate support and a photographically sensitive colloid layer adhesively joined to the support by an intervening composite layer comprising an extremely thin sub composed of a mixture of cellulose acetate and a resin adhesively joined to the support and an extremely thin sub composed of a mixture of gelatin and a resin adhesively joined to the first named mixed sub and to the sensitive colloid layer.

20. A photographic film having satisfactory flexibility and free from brittleness, comprising a cellulose acetate support and a photographically sensitive colloid layer adhesively joined to the support by an intervening composite layer comprising an extremely thin sub composed of a mixture of cellulose acetate and a synthetic resin adhesively joined to the support and an extremely thin sub composed of a mixture of gelatin and a resin adhesively joined to the first named mixed sub and to the sensitive colloid layer.

21. A photographic film having satisfactory flexibility and free from brittleness, comprising a cellulose acetate support and a photographically sensitive colloid layer adhesively joined to the support by an intervening composite layer comprising an extremely thin sub composed of a mixture of cellulose acetate and a polybasic acid-polyhydric alcohol resin adhesively joined to the support and an extremely thin sub composed of a mixture of gelatin and a polybasic acid-polyhydric alcohol resin adhesively joined to the first named mixed sub and to the sensitive colloid layer.

GEORGE S. BABCOCK.