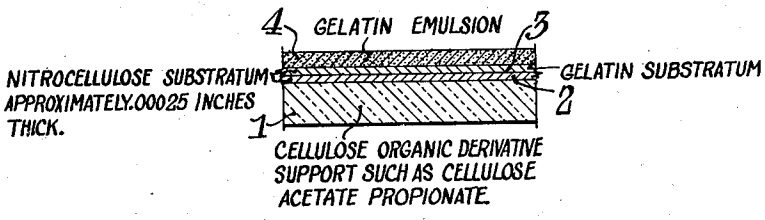
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PHOTOGRAPHICALLY SENSITIVE ELEMENT

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PHOTOGRAPHICALLY SENSITIVE ELEMENT

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This invention relates to photographic materials and more particularly to a photographic film in which a light-sensitive gelatin emulsion is coated on a flexible cellulose derivative support and in which substrata of cellulose derivative material and gelatin, respectively are employed between the emulsion and the support.

In the manufacture of photographic film two rather serious problems are encountered. One is that of obtaining the desired degree of flexibility, while the other is that of producing a film which will have the proper stripping (emulsion adherence) properties. When a gelatin emulsion is coated upon a flexible cellulose organic derivative support which has previously been substrated, it is often found that the desired degree of flexibility can be attained only at the expense of adhesion of the emulsion and other layers to the support. Conversely, proper adhesion is attained only at the expense of flexibility. Until the advent of the present invention it has always been necessary to effect some sort of compromise between these two factors in order to obtain products of the desired qualities. This has necessitated many delicate adjustments of the details of manufacture, composition of materials dealt with, and similar matters.

This invention has as its principal object to overcome the defects of prior art materials of the general character referred to above and to provide a photographic film having an especially high degree of flexibility and satisfactory stripping (emulsion adherence) properties. Another object is to produce a photographic film having a particular type of substratum between the material of the support and the gelatin sub or undercoat which substratum gives the film a high degree of flexibility without a corresponding decrease of emulsion adherence. Other objects will appear hereinafter.

These objects are accomplished by the following invention which, in its broadest aspects, comprises the use of an extra heavy substratum of cellulose nitrate between the support and the gelatin undercoat underneath the emulsion. I have found that this extra heavy nitrate layer gives the product a surprising and unexpected degree of flexibility without decreasing the adherence of the emulsion or other layers of which the film may be composed.

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

The single figure of the drawing represents a section through one form of photographic film made in accordance with my invention.

My invention can be conveniently illustrated by reference to the manufacture of the so-called safety types of film, for example, portrait, X-ray and cine film, in which the base or support consists of a cellulose organic ester material, such as cellulose acetate, cellulose acetate propionate, or similar relatively non-inflammable material. As is well known, before the gelatin emulsion can be permanently applied to such supports, it is necessary to treat the support surface in such manner that gelatin can be made to adhere thereto. This is done by applying various substrata or "subs", as they are generally known. In dealing with cellulose acetate or cellulose acetate propionate supports, it is customary to apply a thin cellulose nitrate layer over the cellulose acetate surface and then apply a thin gelatin undercoat or gel sub over the nitrate layer. The gelatin emulsion can then be readily applied to the coated support and adheres thereto with a sufficient degree of tenacity.

It should be pointed out that brittleness (or its opposite, flexibility) has been found to depend to a very considerable extent upon the degree of adherence of the various layers of the film one to another. It has been found, for example, that if the cellulose nitrate and gel subs are made to adhere to the support with a high degree of tenacity, the emulsion-coated film will be brittle with the result that a crack starting in the emulsion coating will be carried through the various substrata and on into the support itself. When the degree of adherence is less, the brittleness is decreased, that is, the flexibility is increased, but such films have poor stripping characteristics, that is the emulsion layer and possibly the substrata underneath the emulsion, are too easily stripped off.

The cellulose nitrate layers heretofore employed in film structures of the type referred to above, have in all cases been extremely thin, namely, of the order of .00002 inch in thickness. I have made the surprising discovery, as indicated above, that if the thickness of this nitrate layer is increased approximately tenfold, that is, if the nitrate layer is deposited in such manner as to lay down a coating, say, .00025 inch in thickness, a remarkable and unexpected increase in flexibility (decrease in brittleness) takes place. I have found, for example, that films produced in accordance with the procedure described below are anywhere from

50 to 100 percent free of brittleness, as compared to similar products of the prior art which do not run, in most instances, over 0 percent free of brittleness.

Example 1.—A film support comprising a sheet or film of cellulose acetate propionate of approximately 0.008 inch in thickness is coated with a composition containing the following ingredients:

	Percent by weight
Cellulose nitrate (30–100% soluble in ethyl alcohol viscosity 2–5 seconds and nitrogen content of about 11%)	4.5
n-Butyl alcohol	10.0–15.0
Acetone	25.0
Methyl alcohol	55.5–60.5

The coating operation is conveniently carried out by running the support material through an immersion hopper at a temperature of 70–90° F., the composition of the subbing solution and the speed of the support therethrough being so controlled as to deposit on the support a layer which, when dry, is of approximately .00025 inch in thickness. A thin layer of gelatin is then deposited on the cellulose nitrate-coated support from an appropriate gelatin solution in order to provide a surface to which the emulsion coating can be made to adhere. Finally, the gelatin emulsion is coated onto the gelatin surface of the support by a known procedure.

Example 2.—A cellulose acetate support is given a coating of cellulose nitrate by the same general procedure as described in Example 1. The cellulose nitrate coated support is then treated with the same type of gelatin solution, thus producing a gel-coated surface for application of the emulsion, which is also carried out as before. In this case, the cellulose nitrate layer is approximately .00050 inch in thickness.

Example 3.—A cellulose acetate propionate support of the same general type as that described in Example 1 is coated with a composition containing the following ingredients:

	Percent by weight
Cellulose nitrate (30–100% soluble in ethyl alcohol, viscosity 2–5 seconds, and nitrogen content of about 11%)	4.5
n-Butyl alcohol	10.0–15.0
Acetone	25.0
Methyl alcohol	55.5–60.5

The coating operation is carried out as previously described by running the support through an immersion hopper at a temperature of 70 to 90° F., the composition of the subbing solution and the speed of the support therethrough being so controlled as to deposit a layer which, when dry, is of approximately .00035 inch in thickness. The dried nitrate-coated support is then coated with an extremely thin layer of cellulose nitrate, say, of the order of .00002 inch in thickness by depositing thereon a composition containing the following ingredients:

	Percent by weight
Cellulose nitrate (30–100% soluble in ethyl alcohol, viscosity 2–5 seconds, and nitrogen content of about 11%)	2.5
n-Butyl alcohol	10.0
Methyl alcohol	87.05

This coating is dried as before, after which a thin layer of gelatin is deposited on the cellulose nitrate surface from an appropriate gelatin solution. After drying of the gelatin coating, the light sensitive gelatin emulsion is coated onto the gelatin surface of the support by a known procedure.

It will be apparent from the above examples and description that I may deposit the extra heavy cellulose nitrate coating as a single layer, or I may deposit two or more such layers. I find that the double coating method is advantageous in that less extraction of plasticizer from the support by the solvents of the coating solution takes place than is the case with the single coating method. In either case the resulting nitrate layer is, to all intents and purposes, a single, continuous layer or undercoat.

A film produced in accordance with above procedure is illustrated in the single figure of the accompanying drawing in which the numeral 1 designates the flexible cellulose organic derivative support, 2 the extra heavy, adherent substratum of nitrocellulose approximately .00025–.00050 inch in thickness, 3 the thin adherent gelatin coating over the cellulose nitrate, and 4 the gelatino-silver halide emulsion.

Although I have described my invention by reference to the treatment of cellulose acetate and cellulose acetate propionate supports, it will be apparent that I may use any of the usual cellulose organic esters, such as cellulose acetate, cellulose propionate, cellulose butyrate, or the mixed esters such as cellulose acetate propionate, cellulose acetate butyrate, cellulose acetate stearate, and the like.

Although in the above example I have referred to the immersion method of depositing the cellulose nitrate layer on the support, it will be apparent that the cellulose nitrate may be applied by other methods, such as by applicator rolls, beading and similar methods known to those skilled in the art. Likewise, I may use various types of cellulose nitrate, although I prefer to use a nitrate having a relatively high ethyl alcohol solubility, say, from 30–100%, a viscosity of the order of 2–5 seconds (as determined by the dropping ball method), and a nitrogen content of about 11%.

Inasmuch as the present invention relates to photographic film of various types in which flexibility and stripping (emulsion adherence) properties are of prime importance, it is desirable to describe the usual tests by which these properties are determined. The most common tests to which photographic film is subjected are the so-called brittleness (flexibility) tests and the "stripping" test.

The brittleness test is carried out as follows: A strip of film of convenient size, say 6 to 8 inches wide and approximately 40 inches in length is heated for 45 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 by pressing suddenly between the forefinger and thumb. If the film is brittle, this sudden folding will cause it to break or snap in two at the fold. The flexibility is defined in terms of freedom from brittleness which may be figured directly in percentages. A film is, for example, said to be 60% free from brittleness if it ruptures at four out of the ten folds made as just indicated.

The stripping test usually comprises two parts, namely, dry stripping and wet stripping. The wet stripping test is carried out as follows: A strip

of the emulsion coated film of convenient size, say 6 to 40 inches, 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 finger nails at points near the middle and end of the strip. Each nail scratch tears the emulsion away from the support to a certain extent. The scratched places are then rubbed with considerable force with the balls of the finger tips 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 thus to remove pieces wider than ¼ inch by this test.

A modified form of this test is sometimes used in which, instead of employing water for soaking the test strip, the strip is put through the usual processing baths, including development, washing, fixing and the like after which it is subjected to the procedure outlined in the preceding paragraph.

In the dry stripping test, a piece of the emulsion-coated film, with the emulsion side toward the operator, is held at one end with both hands and is then torn lengthwise with successive, quick motions of one hand. The tearing is generally done 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 finger nails 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 is said to be satisfactory for X-ray film if the emulsion cannot be stripped back more than 3 or 4 inches. For cine film, on the other hand, the stripping should not be greater than about one-quarter of an inch.

In order to illustrate the remarkable increase in flexibility without an undue decrease in emulsion adherence of photographic films produced in accordance with my invention, as compared to those produced by ordinary methods, two films were prepared under identical conditions. One film, which may be referred to as sample A, consisted of a strip of cellulose acetate propionate support having deposited thereon a cellulose nitrate substratum of approximately .00002 inch in thickness, a thin gelatin substratum over the cellulose nitrate layer, and over the nitrate layer an emulsion coating. The second film, which may be referred to as sample B was prepared in accordance with the procedure of Example 1 given above. This film consisted of a similar strip of cellulose acetate propionate support having deposited thereon a cellulose nitrate substratum of approximately .00025 inch in thickness in accordance with my invention, a gelatin layer over the nitrate layer and the gelatin emulsion over the gelatin layer. The films and the undercoats thereof were identical except for the thickness of the cellulose nitrate layers.

These samples were subjected to the tests outlined above. In the brittleness test, sample A, showed ten breaks, indicating 100% brittleness or 0% flexibility. Sample B, on the other hand, was found to have broken only four times, thus indicating 60% freedom from brittleness. In both the wet stripping and dry stripping tests both samples A and B showed satisfactory emulsion adherence.

In this specification and the claims where a film is designated as having a high degree of flexibility and satisfactory stripping (emulsion adherence) it is a film which will satisfactorily pass the above-described tests. A film which is 60–100% free from brittleness is considered satisfactory as before described.

Although in the above examples I have referred to the manufacture of films which are coated or subbed on one side only, my invention may be applied with equal success to the manufacture of films which are coated or subbed on both sides, as is the case with portrait and X-ray film. In the case of portrait film, for example, I have found freedom from brittleness to run from 50% to as high as 100% when the film is provided with an extra heavy cellulose nitrate sub or undercoat in accordance with my invention. My invention is also applicable to the manufacture of safety cine film in which the same desirable properties may be obtained. In the broader sense the term "sub" or "substratum" as used herein and in the appended claims includes both a single layer of material such as cellulose nitrate, or a plurality of layers, one above the other, such as a layer of gelatin superimposed upon a layer of cellulose nitrate.

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

1. A photographic film having a high degree of flexibility and satisfactory stripping properties which comprises a flexible cellulose derivative support, a gelatino-silver-halide emulsion on the support, and a substratum between the emulsion and the support comprising a layer of cellulose nitrate .00025 to .00050 inch in thickness.

2. A photographic film having a high degree of flexibility and satisfactory stripping properties which comprises a flexible cellulose organic ester support, an adherent cellulose nitrate layer on the support, an adherent gelatin layer on the cellulose nitrate layer, and a gelatino-silver-halide emulsion layer on the gelatin layer, said cellulose nitrate layer having a thickness of .00025 to .00050 inch.

3. A photographic film having a high degree of flexibility and satisfactory stripping properties which comprises a flexible cellulose acetate propionate support, a thin adherent layer of cellulose nitrate of high alcohol-solubility, a viscosity of 2–5 seconds, and a nitrogen content of about 11%, said cellulose nitrate layer being approximately .00025 to .00050 inch in thickness, a thin gelatin layer over said cellulose nitrate layer and a gelatino-silver-halide emulsion layer over the gelatin layer.

4. A photographic film having a high degree of flexibility and satisfactory stripping properties which comprises a flexible cellulose acetate support, an adherent cellulose nitrate layer on the support, an adherent gelatin layer on the cellulose nitrate layer and a gelatino-silver-halide emulsion layer on the gelatin layer, said cellulose nitrate layer having a thickness of about .00025 to .00050 inch.

GEORGE S. BABCOCK.