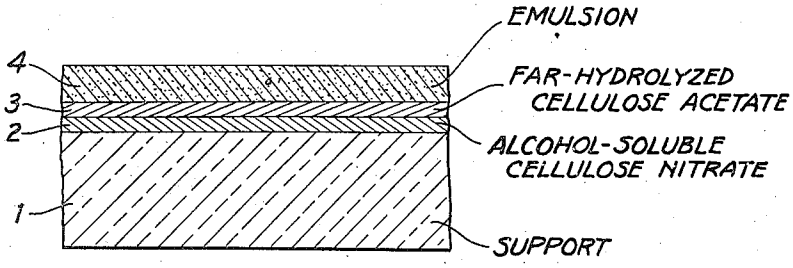
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PHOTOGRAPHIC FILM EMPLOYING HYDROLYZED CELLULOSE ACETATE EMULSIONS

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PHOTOGRAPHIC FILM EMPLOYING HYDROLYZED CELLULOSE ACETATE EMULSIONS

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This invention relates to photographic film in which a hydrolyzed cellulose ester photosensitive emulsion is employed and in which the emulsion is made to adhere to the support by means of subbing layers of cellulose nitrate and of a hydrolyzed lower fatty acid ester of cellulose.

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 in which the emulsion will permanently adhere to the support. At one time photographic film using gelatin emulsions suffered from one or both of these difficulties but means were worked out by which the gelatin emulsion could be made to adhere to the support and at the same time a film resulted having satisfactory flexibility. It has been found, however, that none of the usual subbing techniques that had been developed for use with gelatin-type photographic emulsions is satisfactory for use in photographic film in which non-gelatin type of emulsions were to be employed.

Of late years various types of non-gelatin photographic emulsions have become of interest as illustrated by those described and claimed in U. S. Patent 2,110,491 of Martti Salo or in British Patent 496,049 of I. G. Various methods of subbing photographic film using emulsions of this type have been proposed but in the case of the hydrolyzed cellulose ester emulsions, none of those methods has been found to be particularly satisfactory. For instance, some instances in which the film has seemed to be satisfactory have shown, upon processing of the film, separation of the emulsion from the support.

One object of our invention is to provide a photographic film having thereon a cellulose ester photographic emulsion which is stable, both before and after processing and yet which exhibits good flexibility. Other objects of our invention will appear herein.

We have found that a satisfactory photographic film having a cellulose ester photographic emulsion thereon may be obtained by first applying to the support a thin layer of cellulose nitrate, followed by applying a layer thereover of a lower fatty acid ester of cellulose having an acyl content of 23–27%. In order to form the photographic film the cellulose ester

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emulsion is then applied and the resulting product is flexible but yet there is no separation or stripping of the emulsion from the support, whether the film is in dry or wet condition.

The attached drawing illustrates a film produced in accordance with our invention. In that drawing the numeral 1 designates a flexible support, 2 an adherent substratum of nitrocellulose, 3 a thin adherent coating of a hydrolyzed lower fatty acid ester of cellulose having an acyl content of 23–27%, and 4 the cellulose ester-silver halide photographic emulsion.

The cellulose nitrate layer is coated out in the form of a thin layer from a dilute solution of a cellulose nitrate, particularly a cellulose nitrate which is soluble in ethyl alcohol and has a low viscosity. A cellulose nitrate which is especially suitable for this purpose is one having an ethyl alcohol solubility of from 30–100%, a viscosity on the order of 2–5 seconds (as determined by the dropping ball method), and a nitrogen content of 11–12%, such nitrate having been described in numerous patents relating to photographic products. The substratum formed may be of the thickness desired, but preferably it is on the order of .00005 inch in thickness. If desired, however, the cellulose nitrate substratum may be of any thickness from .00005 or less up to .0005 inch or even more in thickness without seriously interfering with the flexibility of the product obtained.

This cellulose nitrate layer will adhere to any of the commonly used transparent sheetings, and, therefore, the support of the photographic film may be cellulose nitrate, cellulose acetate, either triacetate or hydrolyzed, the latter usually being 40–41.5% acetyl, cellulose acetate propionate, cellulose acetate butyrate, cellulose ether such as ethyl cellulose or a synthetic resin such as polyvinyl butyraldehyde acetal, vinylacetate, vinylchloride resin, polyvinyl acetaldehyde acetal resin or the butyl ester of the co-polymer of maleic anhydride and vinyl acetate. The thickness of the support layer is not particularly critical, the only criterion being that it is of sufficient thickness to give some degree of rigidity to the photographic film. Ordinarily the support is of a thickness of approximately .005–.009 inch.

Applied over the cellulose nitrate layer is a thin layer of a lower fatty acid ester of cellulose

which has been hydrolyzed to an acyl content of 23–27%. The method of preparing esters of this type is disclosed in U. S. Patent No. 2,129,052 of Fordyce. Cellulose esters hydrolyzed to an acyl content between 23 and 27% have been employed for this layer and have been found to be suitable therefor, whether the photographic emulsion is made using a far-hydrolyzed cellulose acetate or a far-hydrolyzed mixed ester of cellulose. It is desirable that this cellulose ester subbing layer be no thicker than is necessary to cause good adherence of the photographic emulsion to the product. For instance, the substratum layer need only have a thickness of about 1 to 3% of the thickness of the support itself. For instance, if desired, it may be on the order of .00005 inch. It is desirable that the acyl content of the cellulose ester employed for the subbing layer approximate (within 2 or 3%) the acyl content of the cellulose ester used as the carrier for the silver halide in the photographic emulsion.

The subbing layer of cellulose nitrate may be obtained by applying to the film support a very dilute solution of the cellulose nitrate in low-boiling liquids, such as lower aliphatic alcohols. For instance, the solution employed is preferably on the order of about 3% concentration. Upon applying this solution to the film support and evaporating the solvent therefrom an extremely thin layer or sub of the cellulose nitrate is deposited on the support material and adheres and becomes permanently attached thereto. The hydrolyzed cellulose ester subbing layer may be applied from an even more dilute solution thereof in a solvent in which it is soluble, which solvent ordinarily contains some water to assist in the dissolving action. For instance, the concentration of the solution of the hydrolyzed cellulose ester employed to deposit that layer is preferably somewhat less than 1%, such as 0.25% concentration. It is desirable with this sub to apply it to the support while the latter is in contact on the opposite side with a heated metal drum, such as having a temperature of 130–150° F. After the sub has been applied to the film, it may be then completely dried or cured by further treating with warm, dry air, such as having a temperature of approximately 150° F. After the hydrolyzed ester subbing layer has been dried, the photographic film is completed by applying thereover a sensitive photographic emulsion comprising silver halide dispersed in a solution of a far-hydrolyzed cellulose ester, such as cellulose acetate having an acetyl content of 19–28%. The emulsion, for instance, may be in suspension in a mixture of water and acetone or water and alcohol from which it may be coated onto the film to form a layer of the emulsion of the desired thickness. This emulsion may be applied to the film so as to have a thickness of .0005 inch although this feature may be varied depending upon the emulsion used and its viscosity. With some types of film such as color film it is often desirable to employ more than one emulsion coating thereon.

Various methods of applying the layers in building up the photographic film may be used. For instance, in some cases it may be desirable to coat with the subbing layer by running the supporting 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 controlled so as to deposit a layer of the desired thickness. Instead of the immersion method, subbing layers may be applied by applicator rolls, beading, or other methods known to those skilled in the art.

The following examples illustrate the preparation of photographic film in accordance with our invention:

Example 1.—A cellulose nitrate film base was coated with the following composition forming a thin layer of cellulose nitrate thereon:

	Percent by weight
Cellulose nitrate (30–100% soluble in ethyl alcohol, viscosity 2.5 seconds and nitrogen content of about 11%)	3.0
Butanol	1.5
Acetone	35.0
Methanol	60.5

The use of a nitrate sub on cellulose nitrate film base is, however, optional. The dried nitrate coated support was then coated with an extremely thin layer of hydrolyzed cellulose acetate having an acetyl content between 23 and 27% using the following composition:

	Percent
Hydrolyzed cellulose acetate	0.25
Water	25.00
Methyl Cellosolve	20.00
Acetone	35.00
Methanol	19.75

This coating was dried and there was then applied thereover a photographic emulsion essentially consisting of silver halide in suspension in hydrolyzed cellulose acetate having an acetyl content of about 24.4% in solution in a mixture of water and beta methoxy ethyl alcohol. This coating operation was carried out under darkroom conditions using a slightly elevated temperature. After coating upon the support it was dried by a current of warm air resulting in a photographic film. This film was found to not separate into layers even after it had been subjected to processing in photographic processing solutions.

Example 2.—A film support of cellulose acetate having an acetyl content of approximately 41% was coated with cellulose nitrate, then with far-hydrolyzed cellulose acetate from its dilute solution and finally with cellulose ester emulsion as in the preceding example. A photographic film was obtained, resistant to the effects of photographic processing solutions, which film also exhibited good flexibility.

Example 3.—A film support of a polyvinyl butyraldehyde acetal resin was coated with subbing layers of cellulose nitrate followed by hydrolyzed cellulose acetate as in Example 1. A photographic emulsion consisting of silver halide dispersed in a cellulose acetate propionate having an acyl content of approximately 26% dissolved in a mixture of equal parts of ethyl acetate and water was applied thereto. The resulting photographic film obtained was found to have good flexibility and also good adhesiveness of the photographic emulsion to the film support.

Example 4.—A film support of vinylchloride-vinyl acetate resin was coated with subbing layers and then with a photographic emulsion as described in the preceding example. A photographic film having good flexibility and good adhesiveness even after photographic processing was obtained.

Example 5—A cellulose nitrate film base was coated on both sides with a thin layer of subbing type cellulose nitrate from its 2% solution in ethyl alcohol and the coatings were dried. Both sides

of the support were then coated with thin layers (approximately .0005 inch) of hydrolyzed cellulose acetate having an acetyl content of approximately 25% from its solution in aqueous acetone of 0.2% concentration. The coatings were dried and there was applied to one side of the film base a silver halide-cellulose acetate photographic emulsion in a layer having a thickness of .0005 inch, the acetyl content of the acetate being approximately 24%. There was applied to the opposite side of the film an anti-curling layer of cellulose acetate from aqueous acetone, the acetate having an acetyl content of 24%, the thickness of the layer being approximately equal to that of the emulsion coating.

Example 6.—A cellulose acetate-propionate film base was coated on both sides with a thin layer of cellulose nitrate, dried and then on both sides with a thin layer of hydrolyzed cellulose acetate (acetyl 24%) and dried as described in the preceding examples. On one side of the film support was then applied a red-sensitive cellulose ester emulsion layer, a green-sensitive cellulose ester emulsion layer, a yellow cellulose ester layer to absorb blue light and on top of this a layer of a blue-sensitive cellulose ester emulsion. In each of these emulsion layers is also present coupler compounds to form colored images as previously described with reference to color sensitive photographic film, such as in U. S. Patent No. 2,318,788 of Leermakers et al.

The opposite side of the film was coated with a removable backing layer consisting of cellulose acetate phthalate having carbon dispersed therein as described in U. S. Patent No. 2,327,828 of N. L. Simmons. Instead, the backing layer may be a far-hydrolyzed cellulose acetate, of the kind ordinarily employed for photographic emulsions (see U. S. Patent no. 2,110,491 of salo) containing an anti-halation dye dispersed therein.

It is to be understood that the acetyl contents of the hydrolyzed cellulose esters employed in the subbing layer next to the photographic emulsion are preferably adjusted to correspond to the acyl contents of the cellulose esters which are employed in the photographic emulsions to be used. In view of the fact, however, that ordinarily the cellulose esters within the range of acyl content of 23–27% are the most suitable for use in photographic emulsions, it naturally follows that the cellulose esters having an acyl content within this range will be most suitable for the subbing layer adjacent thereto. It is to be understood that our invention includes for use in this subbing layer not only the far-hydrolyzed cellulose acetates but also the far-hydrolyzed lower fatty acid esters of cellulose generally, included in which are the cellulose acetate propionates, the cellulose acetate butyrates, the cellulose propionates and cellulose butyrates, having acyl contents of or near 23–27%.

As the present invention relates to photographic film of various types in which flexibility and emulsion adherence are both 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 1⅜ inches wide and approximately 12 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.

When a cellulose nitrate film base is used, the use of the cellulose nitrate subbing layer is optional and in most cases would be unnecessary. Therefore, our invention also includes photographic film consisting of cellulose nitrate base, a subbing layer thereover of a hydrolyzed lower fatty acid ester of cellulose having an acyl content approximating that of the cellulose ester of the emulsion (usually 23–27% acyl) and on the subbing layer, a photographic emulsion layer, the emulsion essentially consisting of silver halide and a far-hydrolyzed cellulose ester.

We claim:

1. A photographic film of satisfactory flexibility and stripping properties which comprises a flexible cellulose ester film support and a photographically sensitive layer essentially consisting of silver halide and a far-hydrolyzed lower fatty acid ester of cellulose having an acyl content of 19–28%, united to the support throughout its area by a composite intervening layer comprising a cellulose nitrate coating on the support, and a hydrolyzed lower fatty acid ester of cellulose coating on the cellulose nitrate, the cellulose ester in the latter coating having an acyl content of 23–27%.

2. A photographic film of satisfactory flexibility and stripping properties which comprises a flexible cellulose ester film support and a photographically sensitive layer essentially consisting of silver halide and a far-hydrolyzed lower fatty acid ester of cellulose having an acyl content of 23–27%, united to the support throughout its area by a composite intervening layer comprising a cellulose nitrate coating on the support, and a hydrolyzed lower fatty acid ester of cellulose coating on the cellulose nitrate, the cellulose ester in the latter coating having an acyl content of 23–27%, substantially that of the cellulose ester of the photographically sensitive layer.

3. A photographic film of satisfactory flexibility and stripping properties which comprises a flexible cellulose ester film support and a photographically sensitive layer essentially consisting of silver halide and a far-hydrolyzed lower fatty acid ester of cellulose having an

acyl content of 19–28%, united to the support throughout its area by a composite intervening layer comprising a cellulose nitrate coating on the support, and a hydrolyzed cellulose acetate coating on the cellulose nitrate, the cellulose ester in the latter coating having an acyl content of 23–27%.

4. A photographic film of satisfactory flexibility in stripping properties which comprises a flexible cellulose ester film support and a photographically sensitive layer essentially consisting of silver halide and a far-hydrolyzed cellulose acetate having an acyl content of 23–27% united to the support throughout its area by a composite intervening layer comprising a cellulose nitrate coating on the support and a hydrolyzed cellulose acetate coating on the cellulose nitrate, the cellulose acetate in the later coating having an acetyl content of 23–27%.

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