Dec. 21, 1943. W. PARTRIDGE, JR 2,337,345

METHOD OF PROMOTING THE ADHERENCE OF CELLULOSE ESTER EMULSIONS ONTO FILM BASES

Filed March 5, 1942

FIG. 1.

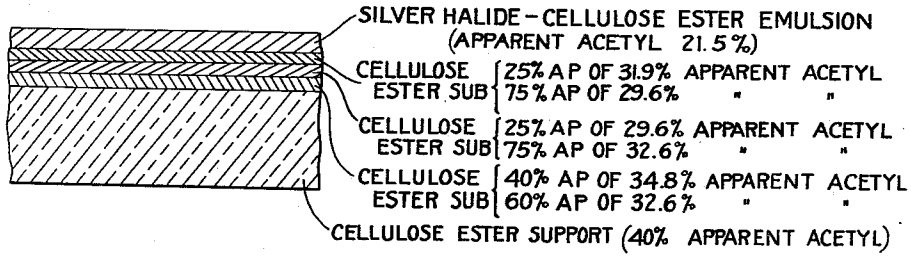
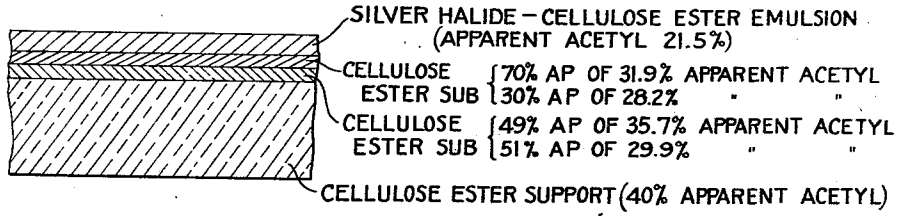


FIG. 2.



WINFIELD PARTRIDGE, JR.
INVENTOR
BY R. M. Perrins
Daniel J. Mayer
ATTORNEYS

Patented Dec. 21, 1943

2,337,345

UNITED STATES PATENT OFFICE

2,337,345

METHOD OF PROMOTING THE ADHERENCE OF CELLULOSE ESTER EMULSIONS ONTO FILM BASES

Winfield Partridge, Jr., Rochester, N. Y., assignor to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

Application March 5, 1942, Serial No. 433,476

11 Claims. (Cl. 95—9)

This application relates to the subbing of photographic film having thereon cellulose ester photographic emulsions to cause the adherence of those emulsions to the cellulose ester film base.

Recently the use of far-hydrolyzed cellulose esters, as carriers for the silver halide in photographic emulsions, has been described and claimed in U. S. Patent No. 2,110,491 of Salo. This patent points out that photosensitive emulsions, using acetyl cellulose esters particularly those having an acyl content of 20–28%, are eminently suitable for use in the photographic industry. The adherence, however, of these emulsions is poor when applied to a film base of an organic acid ester of cellulose and exhibits a tendency to pull away at the edges during coating and to exhibit poor adherence to the film base during the processing operations. Also, there is a tendency for these emulsions when supported by film base of an organic acid ester of cellulose to form blisters when treated in the conventional acid fixing baths. These characteristics have interfered heretofore with the use of cellulose ester emulsions for the preparation of photographic film.

One object of my invention is to provide a method of affixing cellulose ester emulsions to cellulose organic acid ester film base, whereby pulling, sliding, blistering and dry stripping of the emulsion layer from the film base is eliminated. Another object of my invention is to provide a gelatin-free photographic film having good permanence in ordinary use. Other objects of my invention will appear herein.

I have found that far-hydrolyzed cellulose organic acid ester emulsion layers can be attached to cellulose organic acid ester film base, if intermediate subbing layers are employed consisting of cellulose esters having acyl contents graduated between the cellulose ester of the emulsion layer and that of the cellulose ester employed for the film base. It is pointed out in the Salo patent, referred to above, that the cellulose esters employed for the photographic emulsion should be of a water-permeable nature in order to assist the processing of the silver halide emulsion. Cellulose esters, which are employed for film base, on the other hand, should be resistant to water so as to support a photographic emulsion during the processing operation and also to form a surface which is unaffected by water when the emulsion is coated thereon. In order to obtain a film base having these characteristics, a cellulose ester must be employed having properties dissimilar to those of the cellulose ester which is suitable for use as the carrier for the silver halide. Not only do cellulose esters employed for the photographic emulsions differ from those employed for the photographic film base in the degree of hydrolysis, but also in many instances the composition of acyl in the film base ester differs from that of the ester employed as the carrier for the silver halide. This invention is primarily concerned with the preparation of photographic film in which the acyl of the cellulose esters employed essentially consists of fatty acid radicals of 2–4 carbon atoms. The far-hydrolyzed cellulose ester employed as the carrier for the silver halide in the emulsion may be a water-susceptible cellulose acetate such as one having an acetyl content between 20 and 28%, while the cellulose ester employed in the film base may be a cellulose acetate having a relatively high acetyl content (such as 38–42%) or a cellulose acetate propionate or a cellulose acetate butyrate which may be substantially fully esterified or which may be hydrolyzed to some extent but not enough to appreciably diminish the water resistance of the ester when formed into sheeting. Instead of using a straight acetate, the cellulose ester employed, as the carrier for the silver halide, may be a water-susceptible cellulose acetate propionate which has been hydrolyzed down to an acyl content between 20 and 28%. To coat this emulsion upon a water-resistant film base would, to obtain good adherence, necessitate intermediate subbing coatings.

The accompanying drawing illustrates photographic film in accordance with my invention. Figure I illustrates a photographic film composed of a film support in which the cellulose ester is a cellulose acetate propionate having an acetyl content of 29%, a propionyl content of 14.5% and an apparent acetyl content of 40%, 3 subbing layers of the indicated acyl contents and an emulsion layer as shown. Figure 2 illustrates a photographic film in which only 2 subbing layers are employed.

By employing cellulose esters for the subbing layers, having characteristics as regards hydrolysis and as regards acyl composition substantially intermediate between the ester employed for the emulsion and that employed for the film base, good adherence of the emulsion to the film base is obtained and absence of stripping may be effected. I have also found that the number of subbing layers may be substantially decreased if a mixture of two or more esters is employed for each subbing layer. Where a mixture of esters is employed the difference between the ap-

parent acetyl contents of the cellulose esters in each subbing layer should be no more than 9%. It is desirable to employ a sufficient number of subbing layers that good adhesion is obtained between the film base and the emulsion. I have found that there is seldom any case in ordinary practice with cellulose ester emulsions and cellulose ester film base where more than three intermediate or subbing layers are required and, as a general rule, two subbing layers will be sufficient, particularly if mixtures of esters are employed in each subbing layer, although the use of a greater number of subbing layers is within the scope of my invention. However, the use of only one subbing layer also comes within the scope of my invention. When only one subbing layer is employed, it is preferable that it be composed of a mixture of esters and also that there be not too great a difference in type and proportion of acyl between the cellulose ester employed in the emulsion and the cellulose ester employed in the film base.

In accordance with my invention, the difference between the apparent acetyl content of the film base ester and the average apparent acetyl content of the subbing layer adjacent thereto should be no more than 11%. Also, in accordance with my invention, it is desirable that the average apparent acetyl content of any subbing layer be no more than 3½% different from that of any adjacent subbing layer. The average apparent acetyl content of the subbing layer adjacent the emulsion layer should be no more than 12 percent different than the apparent acetyl content of the cellulose ester of the emulsion. In the preferred embodiment of my invention, it is desirable that the apparent acetyl contents differ as follows:

	Per cent
Between film base and adjacent subbing layer	About 6
Between adjacent subbing layers	About 2
Between emulsion and adjacent subbing layer	About 7

The cellulose ester emulsions to which my invention is applicable are those described and claimed in the Salo Patent No. 2,110,491, referred to herein. The film base to which my invention is applicable is any base prepared from a lower fatty acid ester of cellulose in which the acyl consists of fatty acid radicals of 2–4 carbon atoms. For example, the film base prepared by coating out a slightly hydrolyzed cellulose acetate propionate and a plasticizer from propylene chloride-alcohol, as described and claimed in Malm Patent No. 1,960,185, would be quite suitable for use herewith. The film base might be a cellulose propionate or cellulose butyrate or even a cellulose triacetate. In preparing the film base, a solution of the cellulose ester is coated out onto a film-forming surface as a transparent layer, the composition containing, in addition to the cellulose ester, a plasticizer such as triphenyl phosphate in small amount and a volatile solvent therefor such as acetone, ethylene chloride or propylene chloride-methyl alcohol.. It is preferred that the conditions of coating be so controlled that, after evaporation of the solvent and the curing of the film, a sheet or film of cellulose ester, approximately .005–.010 in. thick is obtained. There is then deposited on this film base or film support a series of extremely thin layers of lower fatty acid esters of cellulose or preferably mixtures of these esters having characteristics intermediate and graduated between those of the film base ester and of the emulsion ester, as described herein. These layers may be deposited from appropriate solutions by any method known to those skilled in the art, such as by immersion, beading or the like, the support, being passed through or in contact with the solution at such a rate that a layer of the desired thickness will be laid down on the material. In general, these subbing layers are not more than a few one hundred thousandths of an inch in thickness (such as .000025 in. thick) although thicker layers may be applied in any case where excessive thickness is not objectionable. After each application of a subbing solution, the support is subjected to an appropriate drying operation at a temperature sufficient to evaporate the solvent. Many different subbing layers of cellulose ester may thus be deposited upon the film support prior to applying the emulsion thereto.

The following examples illustrate my invention:

Example I

A film base having a thickness of approximately .005 in. prepared by coating out a solution of a slightly hydrolyzed cellulose acetate propionate, having an acetyl content of 29% and a propionyl content of 14.5% (apparent acetyl 40%) and a plasticizer, from propylene chloride-alcohol as described and claimed in Malm Patent No. 1,960,185, dated May 22, 1934, was coated with an extremely thin coating consisting of a mixture of two cellulose acetate propionates A and B, ester A which made up 40% of the mixture having an acetyl content of 24.4%, a propionyl content of 13.9% and ester B which made up 60% of the mixture having an acetyl content of 22.5% and a propionyl content of 12.8%. The layer was coated out on to the film base from a 2% solution of the ester mixture in a solvent composed of acetone 28%, methanol 62% and cellosolve 10%.

After the first subbing layer on the film base had set and dried, a second layer was applied thereover consisting of a mixture of two cellulose acetate propionates A′ and B′, ester A′ which comprised 75% of the mixture having an acetyl content of 22.5% and a propionyl content of 12.8%, and ester B′ which made up 25% of the mixture having an acetyl content of 20.8% and a propionyl content of 12.6%. After this subbing layer had set and dried, a third subbing layer was applied thereover. This layer consisted of a mixture of two cellulose acetate propionates A″ and B″, ester A″ which made up 25% of the mixture having an acetyl content of 19.8% and a propionyl content of 14.6%, and ester B″ which made up 75% of the mixture having an acetyl content of 20.8% and a propionyl content of 12.6%. Both the second and third layers were respectively coated from 2% solutions of the mixture of the cellulose esters in a solvent having the same composition as employed in applying the first subbing layer. This solvent composition can be varied, however, as desired by the individual operator or, if desired, other suitable solvent compositions may be employed.

After the last subbing layer had set and dried, a photographic emulsion layer was applied thereto. The photographic emulsion was made up of silver halide carried by a far-hydrolyzed cellulose acetate propionate having an acetyl content of 15.2%, a propionyl content of 7.9% and an apparent acetyl content of 21.5%, dissolved in a solvent mixture consisting of 49% ethyl alcohol,

49% water and 2% monoacetin. The emulsion may, if desired, contain a sensitizing dye or any other added materials to impart the desired properties thereto. The emulsion layer was dried thus giving a photographic film which is readily susceptible to developing and fixing in the usual manner.

Example II

To a film base the same as employed in Example I, a layer was applied consisting of approximately equal parts of two cellulose acetate propionates, one having an acetyl content of 23.3% and a propionyl content of 16.5% and the other an acetyl content of 19.8% and a propionyl content of 12.8%. This layer was applied from a very dilute solution in organic solvents such as employed for the same purpose in the preceding example. After the subbing layer had set and dried, a second layer was applied thereto consisting of a mixture of two cellulose acetate propionates, one which made up 70% of the mixture having an acetyl content of 19.8% and a propionyl content of 14.6%, and the second which made up the remainder of the mixture having an acetyl content of 20.7% and a propionyl content of 10.4%. After this subbing layer had dried, a photo-sensitive emulsion layer was applied thereto of the same nature and in the same manner as described in the preceding example.

Example III

To a film base, the same as employed in Example I, a thin layer was applied consisting of 58% of a cellulose acetate propionate having an acetyl content of 23.3% and a propionyl content of 16.5% and of 42% of a cellulose acetate propionate having an acetyl content of 19.3% and a propionyl content of 12.1%. This layer was coated out onto the film base from a 2% solution of the ester mixture in the same solvents as employed for that purpose in Example I. After the subbing layer had set and was dried, a photographic emulsion layer was applied thereto, which layer was made up of silver halide carried by a far-hydrolyzed cellulose acetate propionate having an acetyl content of 15.2%, a propionyl content of 7.9% and an apparent acetyl content of 21.5%, coated out from a solvent mixture containing ethyl alcohol and water in equal amounts. The emulsion layer was dried and there resulted a photographic film.

Example IV

A film base prepared by coating out a solution of a slightly hydrolyzed cellulose acetate butyrate, having an acetyl content of 30% and a butyryl content of 17%, was coated with an extremely thin coating consisting of a mixture of equal parts of two cellulose acetate butyrates, A and B, ester A having an acetyl content of 28.9% and a butyryl content of 13% and ester B having an acetyl content of 27% and a butyryl content of 7%. This layer was applied from dilute solution in a mixture of organic solvents. After this subbing layer had dried, it was coated with a second layer consisting of a mixture of equal parts of two cellulose acetate butyrates, A' and B', ester A' having an acetyl content of 28.3% and a butyryl content of 11% and ester B' having an acetyl content of 26% and a butyryl content of 5%. After this subbing layer had dried, a photosensitive emulsion layer, in which the emulsion vehicle was a cellulose acetate of 25% acetyl content, was applied thereto as described in Example I.

The term "apparent acetyl," as employed herein, refers to the acyl content of the cellulose ester figured in terms of acetyl. For instance, if a cellulose ester was a diester containing one butyryl group for every acetyl group therein, the apparent acetyl would be the same as if both of the acyl groups were acetyl or, in other words, would be the same percentage as the acetyl content of a cellulose di-acetate. The term "average apparent acetyl content" refers to the average apparent acetyl content of a cellulose ester composition. If the composition consists substantially of all the same ester, obviously the apparent acetyl content and the average apparent acetyl content is substantially the same. However, if the composition consists of a mixture of esters, the average apparent acetyl content will be the average of the apparent acetyl contents of each of the esters present, weight being given the apparent acetyl content of each ester in accordance with the proportion of that ester which is present. For instance, if a composition consists of 75% of a cellulose ester having an apparent acetyl content of 34% and 25% of a cellulose ester having an apparent acetyl content of 30%, the average apparent acetyl content of the composition will be approximately 33%.

Anyone familiar with cellulose esters would be able to supply photographic film of the type refrred to in accordance with my invention. However, an alternative method, which might be employed for preparing a photographic film in accordance with my invention, would be to depend upon triangular graphs, such as shown in the prior art, for instance, in Malm Patent No. 2,078,261, dated April 27, 1937. For instance, suppose the preparation of a photographic film was desired in which the cellulose ester in the emulsion to be used was a cellulose acetate having an acetyl content of 20% and the cellulose ester employed for the film base was a cellulose acetate propionate having an acetyl content of 30% and a propionyl content of 14%. After plotting these points on the triangular graph, a line could then be drawn connecting these points. Although a straight line is preferred, in some cases a line connecting these two points could be an arc or a zigzag or other irregular line. Points could then be placed on the line so that the distance from the film base ester point and the first point selected would be no more than 11% figured in terms of apparent acetyl and the distance between the emulsion layer point and the first point on the line after that should be no more than 12% figured in terms of apparent acetyl. The intermediate points should be much closer together so that they are no more than 3½% different figured as apparent acetyl. It is preferable for the subbing layers that a mixture of cellulose esters be used, selected by taking alternative points for the esters which are to be mixed. In that case the points adjacent the emulsion ester and film base ester points would obviously be selected less than 12% and 11% respectively from the latter points so that the average apparent acetyl contents of the layers are within the terms of my invention. It has been my experience that by using a mixture of esters better results are obtained. With a line between the points designating the emulsion ester and the film base ester, anyone, even though unfamiliar with cellulose esters, can easily select a series of esters for subbing layers in accordance with the instructions in this description which will cause good adherence between the film base and the

emulsion without blistering or stripping of the emulsion from the film base.

Wherever the designations AP or AB are employed in this application they respectively refer to cellulose acetate propionate and cellulose acetate butyrate.

I claim:

1. A photographic film comprising a film base layer comprising a cellulose-organic acid ester of such relatively high acyl content that it has high water resistance, an emulsion layer containing as the protective colloid a far-hydrolyzed cellulose-organic acid ester and therebetween at least one cellulose-organic acid ester subbing layer the acyl contents of which are graduated between the cellulose ester of the emulsion layer and that of the film base, the difference between the apparent acetyl content of the cellulose ester of the film base and the average apparent acetyl content of the subbing layer adjacent thereto being no more than 11%, the difference between the average apparent acetyl contents of any subbing layers adjacent to each other being no more than 3½%, the difference between the apparent acetyl content of the cellulose ester in the emulsion and the average apparent acetyl content of the subbing layer adjacent thereto being no more than 12% and the difference between the apparent acetyl contents of substantially all of the cellulose esters in each subbing layer being no more than 9%.

2. A photographic film comprising a film base layer comprising a cellulose-organic acid ester of such relatively high acyl content that it has high water resistance, an emulsion layer containing as the protective colloid a far-hydrolyzed cellulose-organic acid ester and therebetween a plurality of cellulose-organic acid ester subbing layers, the acyl contents of which are graduated between the cellulose ester of the emulsion layer and that of the film base, the difference between the apparent acetyl content of the cellulose ester of the film base and the average apparent acetyl content of the subbing layer adjacent thereto being no more than 11%, the difference between the average apparent acetyl contents of any subbing layers adjacent to each other being no more than 3½%, the difference between the apparent acetyl content of the cellulose ester in the emulsion and the average apparent acetyl content of the subbing layer adjacent thereto being no more than 12% and the difference between the apparent acetyl contents of substantially all of the cellulose esters in each subbing layer being no more than 9%.

3. A photographic film comprising a film base layer comprising a cellulose-organic acid ester of such relatively high acyl content that it has high water resistance, an emulsion layer containing as the protective colloid a far-hydrolyzed cellulose-organic acid ester and therebetween subbing layers made up of a mixture of cellulose esters, the acyl contents of the subbing layers being graduated between the cellulose ester of the emulsion layer and that of the film base, the difference between the apparent acetyl content of the cellulose ester of the film base and the average apparent acetyl content of the subbing layer adjacent thereto being no more than 11%, the difference between the average apparent acetyl contents of any subbing layers adjacent to each other being no more than 3½%, the difference between the apparent acetyl content of the cellulose ester in the emulsion and the average apparent acetyl content of the subbing layer adjacent thereto being no more than 12% and the difference between the apparent acetyl contents of substantially all of the cellulose esters in each subbing layer being no more than 9%.

4. A photographic film comprising a film base layer comprising a cellulose-organic acid ester of such relatively high acyl content that it has high water resistance, an emulsion layer containing as the protective colloid a far-hydrolyzed cellulose-organic acid ester and therebetween a plurality of subbing layers made up of mixtures of cellulose esters, the average acyl contents of the subbing layers being graduated between the cellulose esters of the emulsion layers and that of the film base, the difference between the apparent acetyl content of the film base and the average apparent acetyl content of the subbing layer adjacent thereto being no more than 11%, the difference between the average apparent acetyl contents of any subbing layers adjacent to each other being no more than 3½%, the difference between the apparent acetyl content of the cellulose ester in the emulsion and the average apparent acetyl content of the subbing layer adjacent thereto being no more than 12% and the difference between the apparent acetyl contents of substantially all of the cellulose esters in each subbing layer being no more than 9%.

5. A photographic film comprising a film base layer comprising a cellulose-organic acid ester of such relatively high acyl content that it has high water resistance, an emulsion layer containing as the protective colloid a far-hydrolyzed cellulose-organic acid ester and therebetween at least one cellulose-organic acid ester subbing layer the acyl contents of which are graduated between the cellulose ester of the emulsion layer and that of the film base, the difference between the apparent acetyl content of the cellulose ester of the film base and the average apparent acetyl content of the subbing layer adjacent thereto being approximately 6%, the difference between the average apparent acetyl contents of the subbing layers adjacent to each other being approximately 2% and the difference between the apparent acetyl content of the cellulose ester in the emulsion and the average apparent acetyl content of the subbing layer adjacent thereto being approximately 7% and the difference between the apparent acetyl contents of substantially all the cellulose esters in each subbing layer being approximately 7%.

6. A photographic film comprising a film base layer comprising a cellulose-organic acid ester of such relatively high acyl content that it has high water resistance, an emulsion layer containing as the protective colloid a far-hydrolyzed cellulose-organic acid ester and therebetween a plurality of cellulose-organic acid ester subbing layers, the acyl contents of which are graduated between the cellulose ester of the emulsion layer and that of the film base, the difference between the apparent acetyl content of the cellulose ester of the film base and the average apparent acetyl content of the subbing layer adjacent thereto being approximately 6%, the difference between the average apparent acetyl contents of the subbing layers adjacent to each other being approximately 2% and the difference between the apparent acetyl content of the cellulose ester in the emulsion and the average apparent acetyl content of the subbing layer adjacent thereto being approximately 7% and the difference between the apparent acetyl contents of substantially all the cellulose esters in each subbing layer being approximately 7%.

7. A photographic film comprising a film base layer comprising a cellulose-organic acid ester of such relatively high acyl content that it has high water resistance, an emulsion layer containing as the protective colloid a far-hydrolyzed cellulose-organic acid ester and therebetween subbing layers made up of a mixture of cellulose esters, the acyl contents of the subbing layers being graduated between the cellulose ester of the emulsion and that of the film base, the difference between the apparent acetyl content of the cellulose ester of the film base and the average apparent acetyl content of the subbing layer adjacent thereto being approximately 6%, the difference between the average apparent acetyl contents of the subbing layers adjacent to each other being approximately 2% and the difference between the apparent acetyl content of the cellulose ester in the emulsion and the average apparent acetyl content of the subbing layer adjacent thereto being approximately 7% and the difference between the apparent acetyl contents of substantially all the cellulose esters in each subbing layer being approximately 7%.

8. A photographic film comprising a film base layer comprising a cellulose-organic acid ester of such relatively high acyl content that it has high water resistance, an emulsion layer containing as the protective colloid a far-hydrolyzed cellulose-organic acid ester and therebetween a plurality of subbing layers made up of mixtures of cellulose esters, the average acyl contents of the subbing layers being graduated between the cellulose esters of the emulsion layers and that of the film base, the difference between the apparent acetyl content of the cellulose ester of the film base and the average apparent acetyl content of the subbing layer adjacent thereto being approximately 6%, the difference between the average apparent acetyl contents of the subbing layers adjacent to each other being approximately 2% and the difference between the apparent acetyl content of the cellulose ester in the emulsion and the average apparent acetyl content of the subbing layer adjacent thereto being approximately 7% and the difference between the apparent acetyl contents of substantially all the cellulose esters in each subbing layer being approximately 7%.

9. A photographic film comprising a cellulose acetate film base layer having a relatively high acetyl content, an emulsion layer containing as the protective colloid a far hydrolized cellulose acetate and therebetween at least one cellulose acetate subbing layer, the acetyl contents of which are graduated between the cellulose acetate of the emulsion layer and that of the film base, the difference between the acetyl content of the cellulose acetate of the film base and the acetyl content of the subbing layer adjacent thereto being no more than 11%, the difference between the acetyl contents of any subbing layers adjacent to each other being no more than 3½%, the difference between the acetyl content of the cellulose acetate in the emulsion and the acetyl content of the subbing layer adjacent thereto being no more than 12% and the difference between the acetyl contents of substantially all of the cellulose acetates of each subbing layer being no more than 9%.

10. A photographic film comprising a cellulose acetate propionate film base of such relatively high acyl content that it has high water resistance, an emulsion layer containing as the protective colloid a far hydrolyzed cellulose acetate propionate and therebetween at least one cellulose acetate propionate subbing layer, the acyl contents of which are graduated between the cellulose ester of the emulsion layer and that of the film base, the difference between the apparent acetyl content of the cellulose ester of the film base and the average apparent acetyl content of the subbing layer adjacent thereto being no more than 11%, the difference between the average apparent acetyl contents of any subbing layers adjacent to each other being no more than 3½%, the difference between the apparent acetyl content of the cellulose ester in the emulsion and the average apparent acetyl content of the subbing layer adjacent thereto being no more than 12% and the difference between the apparent acetyl contents of substantially all of the cellulose esters in each subbing layer being no more than 9%.

11. A photographic film comprising a cellulose acetate butyrate film base layer of such relatively high acyl content that it has high water resistance, an emulsion layer containing as the protective colloid a far hydrolyzed mixed organic acid ester of cellulose and therebetween at least one cellulose mixed organic acid ester subbing layer, the acyl contents of which are graduated between the cellulose ester of the emulsion layer and that of the film base, the difference between the apparent acetyl content of the cellulose ester of the film base and the average apparent acetyl content of the subbing layer adjacent thereto being no more than 11%, the difference between the average apparent acetyl contents of any subbing layers adjacent to each other being no more than 3½%, the difference between the apparent acetyl content of the cellulose ester in the emulsion and the average apparent acetyl content of the subbing layer adjacent thereto being no more than 12% and the difference between the apparent acetyl contents of substantially all of the cellulose esters in each subbing layer being no more than 9%.

WINFIELD PARTRIDGE, JR.