July 14, 1942. G. F. NADEAU ET AL 2,289,799

ANTIHALATION FILM

Filed March 4, 1941

FIG. 1

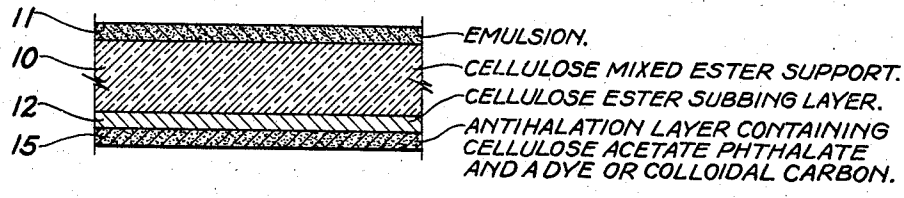


FIG. 2

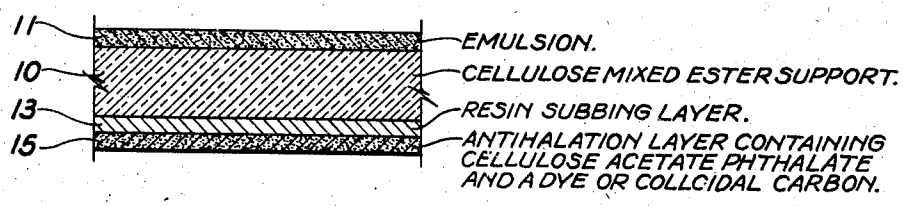
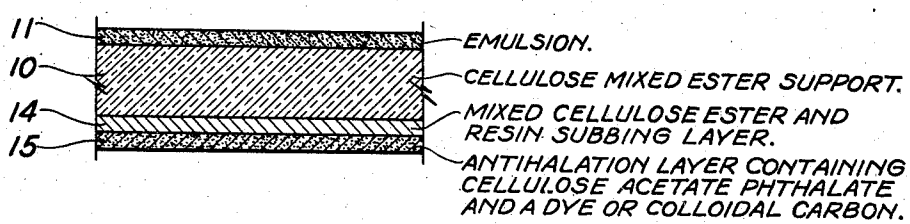


FIG. 3



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ANTIHALATION FILM

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Application March 4, 1941, Serial No. 381,694

12 Claims. (Cl. 95—9)

This invention relates to photographic film and more particularly to photographic film protected against halation.

Light-absorbing coatings on the backs of photographic films are well known to the art of halation prevention. Generally, these antihalation coatings consist of a carrier material and a light-absorbing material such as a dye or pigment, and are removable or non-removable according to the solubility characteristics of the carrier material. The coatings are applied, as a rule, to the rear side of a film support which may be a cellulose ester, a synthetic resin or other material.

Cellulose acetate dicarboxylic acid esters have been used as the carrier material in antihalation layers. The use of these esters has been limited almost entirely to antihalation layers for photographic films having supports of simple cellulose esters such as, cellulose acetate. The reason for this restricted usage lies in the fact that the adhesion of cellulose acetate dicarboxylic acid esters, such as cellulose acetate phthalate, to a cellulose acetate support is sufficiently good that it it is not necessary to employ an adhesive layer to join the antihalation layer to the film support. However, in the case of photographic film supports consisting of mixed esters of cellulose, such as substantially unhydrolyzed cellulose acetate propionate and cellulose acetate butyrate the adhesion of cellulose acetate dicarboxylic acid ester antihalation layers is so poor that an adhesive layer must be used between the film support and the antihalation backing layer to prevent stripping of the backing layer from the support.

The principal object of the present invention is to provide a cellulose mixed ester film support with an adhesive subbing layer to which antihalation layers of cellulose mixed organic acid dicarboxylic acid esters will adhere.

Another object is to describe the materials which may be used to adhesively join antihalation layers to cellulose mixed ester film supports.

Another object is to describe the types of cellulose mixed organic acid dicarboxylic acid esters which may be used for antihalation backing layers according to our invention.

Another object is to describe the method of applying, to film supports, cellulose mixed organic acid dicarboxylic acid esters which are removable in photographic processing solutions.

Another object is to describe the method of applying to film supports, cellulose mixed organic acid dicarboxylic acid esters which are non-removable in photographic processing solutions.

These objects are accomplished in the present invention by subbing layers which adhesively join antihalation layers of cellulose mixed organic acid dicarboxylic acid esters to cellulose mixed organic acid ester film supports.

In the accompanying drawing are illustrated the various methods we use for affecting adherence between antihalation layers and photographic film supports.

Fig. 1 is an enlarged sectional view of a photographic antihalation film wherein a cellulose ester adhesively joins the antihalation layer to the film support.

Fig. 2 is an enlarged sectional view of a photographic antihalation film wherein a resin is used to join the antihalation layer to the support.

Fig. 3 is an enlarged sectional view of a photographic antihalation film wherein a mixture of a cellulose ester and a resin is used for joining the antihalation layer to the film support.

The method we use for accomplishing the objects of our invention depends upon the initial observation, above mentioned, that antihalation backing layers, such as cellulose acetate phthalate, adhere well to supports such as partially hydrolyzed cellulose acetate, however, do not adhere well to substantially unhydrolyzed cellulose mixed ester supports such as cellulose acetate propionate. Therefore, in the manner of our invention, we provide cellulose mixed ester supports such as cellulose acetate propionate, with an emulsion, and on the opposite side of the support, with a layer of cellulose acetate or partially hydrolyzed cellulose mixed organic acid ester, over which layer cellulose acetate dicarboxylic acid esters may be coated with good adherence. The backing layers are usually coated before the emulsion layer is applied.

On the other hand, when we wish to coat cellulose acetate butyrate film supports with an antihalation layer such as cellulose acetate phthalate, we find that cellulose acetate phthalate will not adhere well to either the uncoated support or to the support coated with cellulose acetate. Therefore, before coating the antihalation layer we provide such supports with a layer of a partially hydrolyzed cellulose acetate or cellulose mixed organic acid ester. We may even first coat the support with a layer of well esterified cellulose ester such as cellulose acetate propionate, followed by a layer of cellulose acetate to which the antihalation layer will adhere satisfactorily.

In a similar manner, when adapting our subbing layers to cellulose acetate phthalate backing layers having a wide range of phthalyl con-

tent and which may be either removable or non-removable in photographic processing solutions, we choose a cellulose ester subbing layer which will satisfactorily join the particular backing layer to the particular cellulose mixed ester support.

In addition to the use of cellulose esters for the adhesive layers we may use synthetic resins or mixtures of synthetic resins and cellulose esters. Such resins are the commercially well known Glyptal and Santolite resins.

For the light absorbing component of the antihalation backing layers we may use dyes or colloidal carbon. The use of cololidal carbon in antihalation layers similar to those of the present invention has been disclosed in a prior application Staud and Weyerts, Serial No. 343,254, filed June 29, 1940.

Our invention will now be described with particular reference to the accompanying drawing.

In Fig. I is shown a sectional view of a film having a cellulose mixed ester film support 10 consisting of an ester such as cellulose acetate propionate or cellulose acetate butyrate, coated on one side with an emulsion layer 11, and on the opposite side with a cellulose ester subbing layer 12 of a material such as cellulose acetate, cellulose acetate propionate or partially hydrolyzed cellulose acetate propionate, and a cellulose acetate phthalate layer 15 containing a dye or colloidal carbon.

In Fig. II is shown a sectional view of a film having a cellulose mixed organic acid ester support 10 provided, on one side, with an emulsion layer 11 and on the opposite side, with an antihalation layer 15 of cellulose acetate phthalate containing a dye or colloidal carbon, adhesively joined to the support by means of the resin subbing layer 13 consisting of a resin, such as, a Glyptal or Santolite resin.

In Fig. III is shown a modification of our invention wherein a cellulose mixed organic acid ester film support 10 is provided on one side with an emulsion layer 11, and on the opposite side with an antihalation layer 15 of a cellulose acetate phthalate adhesively joined to the support by means of layer 14 which consists of a mixture of a cellulose ester and a resin, such as a Glyptal or Santolite resin.

The following examples describe the method of coating antihalation backing layers in the manner of our invention.

Example I

A cellulose acetate propionate film support, 16% propionyl and 29% acetyl, plasticized in a known manner and provided with a sensitive emulsion, was coated with a solution of cellulose acetate, containing about 38% acetyl, from a solvent mixture of the following composition:

	Per cent
Cellulose acetate	3.0
Acetone	70.0
Methyl alcohol	27.0

Over this layer was applied a solution of cellulose acetate phthalate, approximately 25–30% phthalyl and 22–24% acetyl, from a solvent mixture of the following composition:

	Per cent
Cellulose acetate phthalate	13.0
Water	20.0
Methyl Cellosolve	20.0
Ethyl alcohol	47.0

The cellulose acetate phthalate backing was then colored with an ethyl alcohol solution of spirit nigrosine dye (Color Index No. 846) containing 3% Aerosol AY. Over the tinted layer may be applied a carbon tetrachloride solution of carnauba wax or a basic material such as triethanolamine, ammonia, dioctylamine, tributylamine, diamylamine, etc. The antihalation layer is removable in alkaline photographic processing solutions.

Example II

Using the same film support and cellulose acetate undercoat as that described in Example I, the antihalation layer may consist of a dispersion of carbon in cellulose acetate phthalate coated from a mixture of the following composition:

	Per cent
Acetone	10.0
Methyl Cellosolve	26.0
Ethyl alcohol	40.0
Water	16.0
Cellulose acetate phthalate and carbon mixture in ratio 3 to 1	8.0

Carnauba wax may be coated over this layer.

Example III

A cellulose acetate butyrate film base, 31% acetyl and 20% butyryl, was coated with a layer of cellulose acetate propionate 29% acetyl and 15% propionyl, from a 3% solution of the ester in a solvent mixture of 70 parts acetone and 30 parts methanol. Over this layer may be applied the cellulose acetate phthalate and dye or carbon layer in the manner described in Examples I and II.

Example IV

Cellulose acetate propionate and cellulose acetate butyrate supports coated, respectively, with cellulose acetate and cellulose acetate propionate as described in Examples I and III, were overcoated with a layer of cellulose acetate phthalate containing 27% acetyl and 13% phthalyl, from a solvent mixture of 45% acetone and 55% methanol wherein the cellulose ester concentration was 3%. The backing layer was then tinted with a dye such as Acid Blue 3R using a 2.5% solution of the dye in a solvent mixture of 55% ethyl alcohol, 35% methyl Cellosolve, and 10% water. Over the tinted antihalation layer may be applied a thin layer of wax or basic material.

The above described antihalation layer is typical of the non-removable type previously referred to. When a photographic film so provided, is subjected to the action of photographic processing solutions the backing layer swells, exposing the dye to reagents which bleach and remove it from the film. Antihalation layers of this type are described in our application Nadeau and Slack Serial No. 381,695, filed March 4, 1941.

The above examples may be further amplified by the use of various partially hydrolyzed cellulose acetate propionates, such as, one containing 15% propionyl and 23% acetyl, for an undercoating on cellulose acetate propionate and cellulose acetate butyrate film supports of the composition shown in Examples I and III. These coatings may also be applied from solvent mixture of acetone and methanol, and are followed by a layer of cellulose acetate phthalate which is then tinted with a dye.

Example V

A cellulose acetate propionate film support plasticized in a known manner was coated with

a mixture of a resin and cellulose acetate, 38% acetyl, using a coating solution of the following composition:

	Per cent
Cellulose acetate	2.0
Glyptal (glycerol phthalic acid) resin	1.0
Acetone	70.0
Methanol	27.0

A cellulose acetate phthalate layer of the composition described in Example I, was coated over this layer and tinted with Nigrosine dye.

In addition to the above mentioned antihalation backing layers consisting of cellulose acetate phthalate we may use other cellulose mixed organic acid dicarboxylic acid esters with equal success, such as cellulose-propionate phthalate, acetate succinate, acetate maleate, etc. The method we use is to determine the composition of a cellulose ester to which these materials will adhere and use this ester as the adhesive joining layer between the antihalation layer and the film support.

The dicarboxylic acid acyl content of the backing layers is not critical, however, the higher this value is the more easily removable this layer will be. Where the dicarboxylic acid acyl content is low the antihalation layer is swellable, but non-removable in photographic processing solutions, providing that the organic acid ester content of the mixed organic acid dicarboxylic acid ester is not too low.

While we mention the use of only cellulose organic acid esters as components of the layers which are used to join antihalation layers to a film support—we may, however, use an inorganic acid ester of cellulose such as cellulose nitrate, in which case we prefer to use colloidal carbon in the antihalation layer rather than a dye, since cellulose nitrate has a tendency to absorb dyes and hold them fast to removal by photographic processing solutions.

It is to be understood that the disclosure herein is by way of example and that we consider as included in our invention all modifications and equivalents falling within the scope of the appended claims.

What we claim is:

1. A photographic film free from halation which comprises a substantially unhydrolyzed cellulose mixed organic acid ester support provided on one side with a light sensitive emulsion layer, and on the opposite side, with a layer comprising a hydrolyzed cellulose organic acid ester, and a layer containing a cellulose mixed organic acid dicarboxylic acid ester and a light-absorbing material.

2. A photographic film free from halation which comprises a substantially unhydrolyzed cellulose mixed organic acid ester support provided on one side with a light sensitive emulsion layer, and on the opposite side, with a layer comprising a hydrolyzed cellulose organic acid ester, and a layer containing cellulose acetate phthalate and a light-absorbing material.

3. A photographic film free from halation which comprises a substantially unhydrolyzed cellulose mixed organic acid ester support provided on one side with a light sensitive emulsion layer, and on the opposite side, with a layer comprising hydrolyzed cellulose acetate, and a layer containing cellulose acetate phthalate and a light-absorbing material.

4. A photographic film free from halation which comprises a substantially unhydrolyzed cellulose acetate propionate support provided on one side with a light sensitive emulsion layer, and on the opposite side, with a layer of hydrolyzed cellulose acetate, and a layer containing cellulose acetate phthalate and a light-absorbing material.

5. A photographic film free from halation which comprises a substantially unhydrolyzed cellulose acetate propionate support provided on one side with a light sensitive emulsion layer, and on the opposite side, with a layer of hydrolyzed cellulose acetate, and a layer containing cellulose acetate phthalate, 30 per cent phthalyl and 23 per cent acetyl, and a light-absorbing material.

6. A photographic film free from halation which comprises a substantially unhydrolyzed cellulose acetate propionate support provided on one side with a light sensitive emulsion layer, and on the opposite side, with a layer of hydrolyzed cellulose acetate, and a layer containing cellulose acetate phthalate and colloidal carbon.

7. A photographic film free from halation which comprises a substantially unhydrolyzed cellulose acetate butyrate support provided on one side with a light sensitive emulsion layer, and on the opposite side, with a layer of hydrolyzed cellulose acetate propionate, and a layer containing cellulose acetate phthalate and a light-absorbing material.

8. A photographic film free from halation which comprises a substantially unhydrolyzed cellulose acetate butyrate support provided on one side with a light sensitive emulsion layer, and, on the opposite side with a layer of hydrolyzed cellulose acetate propionate, and a layer containing cellulose acetate phthalate, 13 per cent phthalyl and 27 per cent acetyl, and a light-absorbing material.

9. A photographic film free from halation which comprises a substantially unhydrolyzed cellulose acetate butyrate support provided on one side with a light sensitive emulsion layer and, on the opposite side, with a layer of hydrolyzed cellulose acetate propionate, and a layer containing cellulose acetate phthalate and a dye.

10. A photographic film free from halation which comprises a substantially unhydrolyzed cellulose acetate propionate support provided on one side with a light sensitive emulsion layer, and on the opposite side, with a layer consisting of a mixture of hydrolyzed cellulose acetate and glyptal resin, and a layer containing cellulose acetate phthalate and a light-absorbing material.

11. A photographic film free from halation which comprises a substantially unhydrolyzed cellulose acetate propionate support provided on one side with a light sensitive emulsion layer, and on the opposite side, with a layer consisting of a mixture of hydrolyzed cellulose acetate and glyptal resin, and a layer containing cellulose acetate phthalate, 30 per cent phthalyl and 23 per cent acetyl, and a light-absorbing material.

12. A photographic film free from halation which comprises a substantially unhydrolyzed cellulose acetate propionate support provided on one side with a light sensitive emulsion layer, and on the opposite side, with a layer consisting of a mixture of hydrolyzed cellulose acetate and glyptal resin, and a layer containing cellulose acetate phthalate and colloidal carbon.

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