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Paesschen et al.

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[54] **PHOTOGRAPHIC MATERIALS**

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** ..... **96/84 R,** 96/87 R

[51] **Int. Cl.** **G03c 1/84**

[58] **Field of Search** ..... 96/84 R

[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

To improve the adhesion of an antihalation layer to a polyethylene terephthalate film the antihalation layer is formed from a dye or finely divided pigment dispersed in a water-insoluble alkali-soluble binder consisting of 60 to 85 percent by weight of polymethylene-hydroxybenzoic acid and 40 to 15 percent by weight of a copolymer of 20 to 50 percent by weight of acrylic acid or methacrylic acid, 15 to 79 percent by weight of an alkyl acrylate and 1 to 50 percent by weight of an alkyl methacrylate.

When the photographic material comprising the antihalation layer thus formed is treated in a highly alkaline bath the antihalation layer can be rinsed away completely with pure water before entering the first photographic developer bath.

4 Claims, No Drawings

PHOTOGRAPHIC MATERIALS

This invention relates to photographic materials and particularly to photographic elements carrying light-sensitive silver halide emulsion layers.

The invention is an improvement of the invention described and claimed in our U. S. Pat. application Ser. No. 115,807 filed Feb. 16, 1971 hereinafter called "the main patent," now abandoned.

The problem of reducing halation in sensitive photographic materials is well known. Halation arises as a consequence of the reflection of light by the film support onto the light-sensitive coating or coatings. It can be neutralized by applying to the side of the film support opposite to the emulsion layer or layers, a light-absorbing layer, which is generally called antihalation layer. Such an antihalation layer may consist of a dye or pigment dispersed in a natural or synthetic binder. There is either selected a dye or pigment that is decolourized during the processing of the photographic element, or a natural or synthetic binder that is soluble in a processing bath. Both alternatives may be combined also.

In the main patent, there has been described a photographic material comprising a hydrophobic support, at least one light-sensitive silver halide emulsion layer, and at the side of the support opposite to said light-sensitive emulsion layer or layers an antihalation layer consisting of a dye or finely divided pigment dispersed in a water-insoluble alkali-soluble copolymer of 20 to 50 percent by weight of acrylic acid or methacrylic acid, 15 to 79 percent by weight of an alkyl acrylate, wherein the alkyl group comprises one to eight carbon atoms, and 1 to 50 percent by weight of an alkyl methacrylate, wherein the alkyl group comprises one to four carbon atoms.

It has now been found that the adhesion of the antihalation layer especially to polyethylene terephthalate film is improved by replacing part of the copolymer binding material described in the main patent, by polymethylene-hydroxybenzoic acid.

According to the invention there is provided a photographic material comprising a hydrophobic film support, at least one light-sensitive silver halide emulsion layer, and at the side of the support opposite to said light-sensitive emulsion layer or layers an antihalation layer consisting of a dye or finely divided pigment dispersed in a water-insoluble alkali-soluble binding material consisting of 60 to 85 percent by weight of polymethylene-hydroxybenzoic acid and 40 to 15 percent by weight of a copolymer of 20 to 50 percent by weight of acrylic acid or methacrylic acid, 15 to 79 percent by weight of an alkyl acrylate, wherein the alkyl group comprises 1 to 8 carbon atoms, and 1 to 50 percent by weight of an alkyl methacrylate, wherein the alkyl group comprises one to four carbon atoms.

The dyes used in the antihalation layer may belong to almost all known classes of dyes, but especially to the classes of triphenyl methane, oxonol, merocyanine, styryl-neutrocyanine, pyrrolecyanine, and styryl dyes. If a pigment is used, carbon black is preferred usually, though sometimes colloidal silver can be taken.

When black inert pigments are used, their amount may vary within a fairly wide range. They should be present, however, in sufficient amounts so that their layers prevent visible light from penetrating therethrough. A particle size of 10 to 100 nm represents a practical range and 30 to 80 nm a preferred range for the aforesaid pigments.

The quantity of black inert pigment dispersed in the binder with the aid of a dispersing agent may vary from 1 to 2 parts by weight of pigment to 1 to 20 parts of binder.

The thickness of the antihalation layer is not critical, though generally thicknesses of 0.5 to 3 μ are used. The thickness of the layer and the amount of pigment should be regulated so that the resulting layer has an optical density of about 0.5 to 3.

Polymethylene-hydroxybenzoic acid is formed by polycondensation of hydroxybenzoic acid with formaldehyde as described more detailedly hereinafter. In this polycondensation reaction can be used the three isomeric forms of hydroxybenzoic acid, namely ortho-, meta- or para-hydroxybenzoic acid.

The water-insoluble alkali-soluble copolymer that constitutes part of the binder of the antihalation layer according to the invention can be prepared by emulsion-, solution, or bulk-polymerisation techniques. Examples of suitable copolymer are, e.g., :

co(methacrylic acid/n-butyl acrylate/ethyl methacrylate) (30:67:3),
co(methacrylic acid/n-butyl acrylate/methyl methacrylate) (35:35:30),
co(acrylic acid/methyl acrylate/methyl methacrylate) (20:79:1),
co(methacrylic acid/2-ethylhexyl acrylate/methyl methacrylate) (40:30:30),
co(methacrylic acid/ethyl acrylate/n-butyl methacrylate) (20:78:2),
co(methacrylic acid/ethyl acrylate/methyl methacrylate) (35:15:50),
co(methacrylic acid/n-butyl acrylate/methyl methacrylate) (30:68:2).

The numbers between brackets indicate the percent by weight of the respective monomer units present in the copolymer.

Both the polymethylene-hydroxybenzoic acids and the copolymer in their acid form are insoluble in water. In an alkaline photographic developer, however, the mixture of polymethylene-hydroxybenzoic acid and of copolymer dissolves readily, since they are converted therein into their alkali metal salts.

In certain development systems of colour photography there is used a preliminary bath, i.e., a highly alkaline bath with a high concentration of inorganic salts such as sodium sulphate. The mixture of polymers of the invention is usable here too since it does not dissolve in this preliminary bath as a result of a salting-out effect due to the high concentration of inorganic salts present. During the subsequent intermediate rinsing with water, before entering the first developer bath, the mixture can be brushed away very easily.

It may be very interesting to add to the coating composition of the antihalation layer a small amount of a wetting agent such as an alkali metal alkyl sulphate of eight to 20 carbon atoms, e.g., sodium octyl sulphate, sodium tetradecyl sulphate, sodium hexadecyl sulphate, ammonium octadecyl sulphate, and potassium oleyl sulphate.

It may be very interesting also to add to the coating composition of the antihalation layer a small amount of a matting agent, e.g., finely divided silicon dioxide or finely dispersed particles of the reaction product of starch with urea and formaldehyde. This reaction prod-

uct has been described in the U.S. Pat. No. 3,253,926 issued May 31, 1966 by Gevaert Photo-Producten N.V.

The antihalation coating composition may be applied to the hydrophobic film support by spray, brush, roller, doctor blade, air brush, or wiping techniques. Examples of hydrophobic film supports are films of cellulose triacetate, polystyrene, polyalkylene terephthalates, especially polyethylene terephthalate and polycarbonates.

The antihalation layers of this invention have all desirable characteristics of a commerically practical element. Their preparation does not present any coating difficulties. The layers are soluble in aqueous treating baths and may be removed from the film by treatment in such baths. They are photographically inert and hence do not adversely affect the light-sensitive layer or layers. Moreover, the layers show an excellent anchorage to hydrophobic film supports and they require no additional agents to form an effective bond.

In the main patent it has been described that the film support is preferably provided with a known subbing layer, especially when a film of polyethylene terephthalate is used as the hydrophobic film support. It has now been found that the replacement of part of the alkali-soluble copolymer by polymethylene-hydroxybenzoic acid makes it possible to renounce the use of special subbing layers. The adhesion of the antihalation layer of the invention to the polyethylene terephthalate film support is excellent in dry as well as in wet state.

The manufacture of polymethylene-hydroxybenzoic acid useful as part of the binding material in the antihalation layers of the invention is exemplified in the following preparation process.

Preparation of polymethylene-p-hydroxybenzoic acid

80 l of water at 40°C, 20 kg of p-hydroxybenzoic acid, 20 l of a 30 to 32 percent aqueous concentration of hydrochloric acid, and 14 l of a 30 percent aqueous solution of formaldehyde were mixed in the given sequence and kept for 2 hours at 45°C. Subsequently the mixture is stirred for 4 hours at 90°–95°C. The reaction product settled in the form of a coherent mass. It was washed twice with cold water and then immersed in water for one night.

The resulting product was dissolved with stirring in 150 l of water at 70°C and 13 kg of sodium carbonate. The solution was filtered through a fine paper filter and heated at 90°–95°C. After the addition of 2 l of methanol a mixture of 13.5 l of a 30 to 32 percent aqueous solution of hydrochloric acid and 11.5 l of water was added cautiously, until a clearly acid reaction was obtained. A small amount of methanol was then added yet. The precipitate was centrifuged, washed 5 min. with hot water and 5 min. with cold water, and finally dried for 2 to 3 days at 35°C. Yield : 14 to 15 kg. A solution of the polymer in propanol should have a clear appearance.

The ortho- and meta-derivatives are prepared in an analogous way.

The invention is illustrated by the following examples.

EXAMPLE 1

8.8 g of colloidal carbon having a particle size of approximately 50 nm was dispersed in a mixture of 300 ml of ethanol and 16 ml of a 27.6 percent by weight latex of co(methacrylic acid/n-butyl acrylate/methyl methacrylate) (35:35:30 percent by weight). This copolymer was obtained according to preparation 1 of the main patent.

A solution in 300 ml of ethanol of 17.6 g of polymethylene-p-hydroxybenzoic acid (prepared as described above) was added to the resulting dispersion of colloidal carbon whilst stirring. This solution was diluted afterwards with 370 ml of ethanol. After filtration 2 ml of a 40 percent by weight dispersion in water of the reaction product of starch with urea and formaldehyde was added. The dispersion thus formed was applied to the surface of a biaxially oriented polyethylene terephthalate film having a thickness of 100 μat a ratio of 35 sq.m/liter.

In order to improve the coefficient of friction of the material, the antihalation layer can be covered with a layer of wax, e.g., a layer formed from a 0.2 percent by weight solution of carnauba wax dissolved in equal parts of perchloroethylene and methylene chloride.

The other side of the support was coated with a known subbing layer and subsequently with a light-sensitive gelatin silver halide layer.

The antihalation layer adhered very well to the polyester film support.

The photographic film was exposed image-wise and then led through a preliminary bath having the following composition :

water — 1 l
sodium sulphite — 100 g
sodium tetraborate — 20 g
sodium hydroxide (up to pH 9.4)

As a result of the treatment with the preliminary bath the antihalation layer could be rinsed away completely by means of pure water. After this elimination the material was developed in the normal bath, washed, and fixed.

EXAMPLE 2

12 g of colloidal carbon having an average particle size of 23 nm were dispersed in a mixture of 560 ml of ethanol and 100 ml of n-propanol to which 40 ml of a 30.8 percent by weight latex of co(methacrylic acid-/ethyl acrylate/methyl methacrylate) (35:15:50 percent by weight) prepared according to the method described in Preparation 2 of the main patent had been added.

28 g of polymethylene-p-hydroxybenzoic acid dissolved in 300 ml of ethanol were added to the dispersion of carbon black and the solution was filtered, whereupon 0.8 g of silicon dioxide having an average particle size of 3 to 6 μ was dispersed therein.

The dispersion formed was applied to a biaxially oriented polyethylene terephthalate film having a thickness of 75 μ at a ratio of 35 sq.m/liter. This antihalation layer adhered very well to the polyester film support.

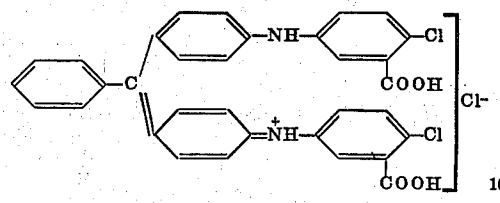
The other side of the polyester film was provided with the layers necessary for making a light-sensitive photographic film including a subbing layer or layers and a silver halide emulsion layer or layers.

The antihalation layer could be rubbed off completely and easily after a treatment with a preliminary bath as described in Example 1.

EXAMPLE 3

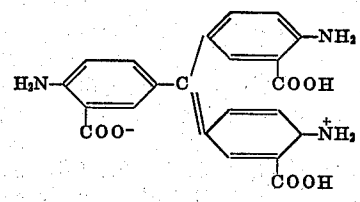
The following solution was prepared :
ethanol — 806 ml
triphenyl methane dye according to the formula :

5



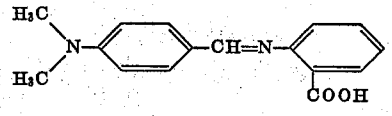
16.5 g.

triphenylmethane dye according to the formula :



11 g.

azomethine dye according to the formula :



5 g.

35 percent aqueous solution of hydrochloric acid 2 ml

10 percent solution in ethanol of co(methacrylic acid/ethyl acrylate/methyl methacrylate) (35:15:50 percent by weight) 120 ml

25 percent solution in ethanol of polymethylene-p-hydroxybenzoic acid 72 ml

This solution was applied to a biaxially oriented polyethylene terephthalate film having a thickness of 63 μ at a ratio of 35 sq.m/l.

The other side of the support was coated with the necessary layers to form a photographic film material including a subbing layer or layers and a silver halide emulsion layer or layers.

The antihalation layer adhered well to the support and was decolourized and dissolved in the developing bath.

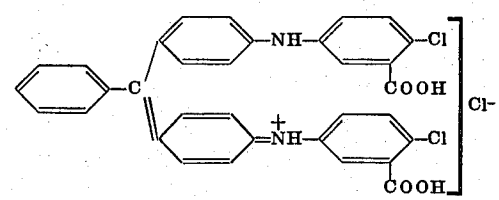
EXAMPLE 4

The following solution was prepared :

ethanol — 700 ml

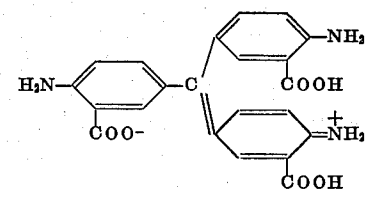
triphenyl methane dye according to the formula :

6



15 g.

triphenylmethane dye according to the formula :



10 g.

35 percent aqueous solution of hydrochloric acid — 3 ml

To this solution was added a solution of 24 g of polymethylene-o-hydroxybenzoic acid and 6 g of co(methacrylic acid/ethyl acrylate/methyl methacrylate) (35:15:50 percent by weight) in 300 ml of ethanol.

This solution was applied on one side of a biaxially oriented polyethylene terephthalate film at a ratio of 32 sq.m/l.

The other side of the support was coated with the necessary layers to form a photographic material including a subbing layer or layers and a silver halide emulsion layer or layers.

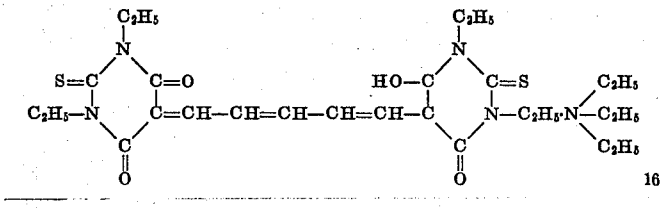
The antihalation layer adhered very well to the support and was completely decolourised in the developing bath.

EXAMPLE 5

To a solution of 16 g of polymethylene-m-hydroxybenzoic acid in 100ml of dimethylformamide was added the following solution :

co(methacrylic acid/ethyl acrylate/methyl methacrylate) (40:30:30 percent by weight) — 8 g

blue dyestuff corresponding to the formula :



16 g.

ethanol — 900 ml

This solution was applied to a polyester film at a ratio of 48 sq.m/l. The other side of the support was provided with the necessary layers to form a light-sensitive photographic material. The antihalation layer formed was completely decolourized when treating the material in a photographic developing bath.

We claim:

1. a photographic material comprising a hydrophobic polyester film support; at least one light-sensitive silver halide emulsion layer; and on the side of the support opposite to such light-sensitive emulsion layer, an antihalation layer consisting of a dye or finely divided pigment dispersed in a water-insoluble alkali-soluble binding material consisting essentially of a mixture of (a) 60 to 85 percent by weight of polymethylene hydroxybenzoic acid and (b) 40 to 15 percent by weight of a copolymer of 20 to 50 percent by weight of acrylic or methacrylic acid, 15 to 79 percent by weight of an alkyl acrylate, wherein the alkyl group comprises one to eight carbon atoms, and 1 to 50 percent by weight of an alkyl methacrylate, wherein the alkyl group comprises one to four carbon atoms.

2. A photographic material according to claim 1, wherein the hydrophobic film support is a film of polyethylene terephthalate.

3. A photographic material according to claim 1, wherein the finely divided pigment is carbon black having a particle size of 10 to 100 nm.

4. A photographic material according to claim 1, wherein the polymethylene hydroxybenzoic acid is polymethylene-p-hydroxybenzoic acid.

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