United States Patent [19]
Depoorter et al.

[11] **3,853,563**
[45] **Dec. 10, 1974**

[54] PHOTOGRAPHIC WATER-INSOLUBLE ANTIHALATION COATING

[75] Inventors: **Henri Depoorter**, Mortsel; **Felix Jan Moelants**, Wilrijk, both of Belgium

[73] Assignee: **AGFA-Gevaert**, Mortsel, Belgium

[22] Filed: **May 29, 1973**

[21] Appl. No.: **364,326**

[30] **Foreign Application Priority Data**

June 22, 1972 Great Britain 29388/72

[52] **U.S. Cl.** .... **96/84 R**, 96/87 R, 260/37 R, 260/37 N, 260/41 C, 260/240 F, 260/240.7
[51] **Int. Cl.** **G03c 1/84**
[58] **Field of Search** .... 96/84 R, 14 P

[56] **References Cited**

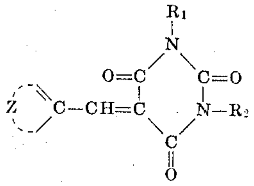
UNITED STATES PATENTS

3,653,905	4/1972	Depoorter et al.	95/84 R
3,687,670	9/1972	Rallaers et al.	96/84 R

Primary Examiner—Ronald H. Smith
Assistant Examiner—J. P. Brammer
Attorney, Agent, or Firm—A. W. Breiner

[57] ABSTRACT

Novel dyes are provided corresponding to the formula:



wherein the dye contains at least one carboxyl group, each of R_1 and R_2 stands for hydrogen, an alkyl group, allyl group, cycloalkyl group or aryl group and Z represents the atoms necessary to close a pyrrole ring. Provided the dyes contain no sulpho group they can be used in water-insoluble alkali-soluble polymeric antihalation coatings for photographic silver halide elements. They are fully compatible with the polymeric binder of the antihalation coating and leave no stain upon processing.

4 Claims, No Drawings

PHOTOGRAPHIC WATER-INSOLUBLE ANTIHALATION COATING

The present invention relates to photographic silver halide film material having on the back of the film support an antihalation coating comprising a water-insoluble, alkali-soluble polymeric binder.

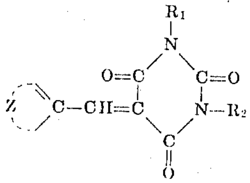
It is known to provide photographic silver halide film materials with an antihalation layer to prevent light that has penetrated through the light-sensitive emulsion layer(s) from being reflected by the support and affecting the emulsion layer(s) for a second time. The antihalation layer (which may be coated on the back of the film support) comprises dyes so chosen that they absorb the light penetrating through the emulsion layer(s).

The binders used for the antihalation layers applied to the side of the film support opposite to that of the emulsion layer(s) are usually hydrophilic colloids, more particularly gelatin. However, it is also possible to use water-insoluble, alkali-soluble polymeric binders so that the layers are completely removed in an alkaline processing bath more particularly the alkaline developing solution. The latter binders are preferred over gelatin for example where the gelatin layers, which are not removed upon processing, are too soft and give rise to handling problems as in microfilm material or where adhesion of polymeric layers to the hydrophobic film support, e.g., polyethylene terephthalate support is superior over the adhesion of gelatin layers.

Light-absorbing dyes should meet severe demands in order to be useful in photographic film material. They should not affect the inherent sensitivity or spectral sensitivity of light-sensitive emulsions with which they may come into contact. They should have good absorption characteristics and should not give rise to fogging. Further they should be readily rendered ineffective, i.e., decolourized or destroyed and removed, in at least one of the photographic processing liquids.

Though many dyes have been employed successfully in antihalation layers comprising gelatin as binder, most of them are unsuitable for use in antihalation layers comprising a water-insoluble, alkali-soluble polymeric binder. For example, some dyes are not readily or not completely discoloured in the alkaline developing solution so that, even though the polymeric layer is removed in the alkaline solution, the residual dye stains the photographic material and the developing bath. Other dyes are insoluble in the organic solvent, general a lower alcohol, from which the water-insoluble, alkali-soluble polymeric antihalation coating is applied or they are not compatible with the polymeric binder so that they precipitate or give rise to crystallization in the coating.

In accordance with the present invention novel light-absorbing dyes are provided corresponding to the following general formula:



wherein:

each of R_1 and R_2 represents hydrogen, alkyl including substituted alkyl (e.g., aralkyl, hydroxyalkyl, carboxyalkyl, alkoxycarbonylalkyl), allyl, cycloalkyl, substituted cycloalkyl or aryl including substituted aryl (e.g., hydroxyphenyl, carboxyphenyl, alkoxycarbonylphenyl), and

Z represents the atoms necessary to close a pyrrole ring or a substituted pyrrole ring e.g. a 1-alkyl- or 1-aryl-, 2,5-dialkyl-4-pyrrolyl group in which the alkyl and aryl groups may be substituted,

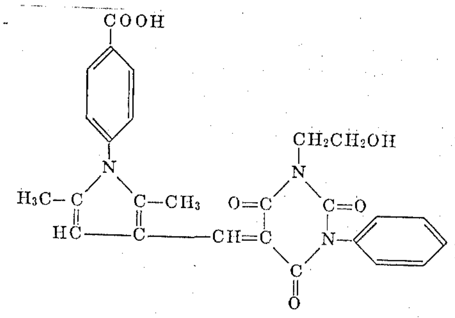
the dyestuff molecule containing at least one carboxyl group e.g. in a substituent of the barbituric acid nucleus and/or in a substituent of the pyrrole nucleus.

The dyestuffs corresponding to the above general formula, provided they do not comprise a sulpho group in acid or salt form lend themselves perfectly for use in antihalation coatings comprising as binder a water-insoluble, alkali-soluble polymer. They are highly compatible with the water-insoluble, alkali-soluble polymeric binders and do not give rise to crystallization therein. They can be easily dissolved in the organic solvent medium, e.g., a lower alcohol such as ethanol, used to dissolve and coat the polymeric material. They are discoloured in alkaline developing solutions without leaving an objectionable residual stain.

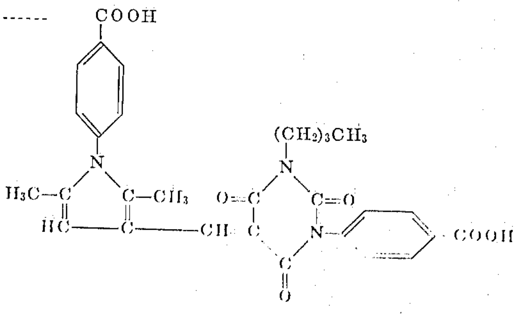
The present invention therefore also provides a coating of a water-insoluble, alkali-soluble polymeric binder comprising a dyestuff corresponding to the above general formula which comprises in its molecule at least one carboxyl group. It also provides a light-sensitive photographic element having a support and at least one light-sensitive silver halide emulsion layer, the said support carrying at the side opposite to that carrying the emulsion layer(s) an antihalation layer of a water-insoluble, alkali-soluble polymeric binder comprising a dyestuff, corresponding to the above general formula that contains in its molecule at least one carboxyl group and is free from sulpho group in acid or salt form.

Representative examples of light-absorbing dyes corresponding to the above general formula are:

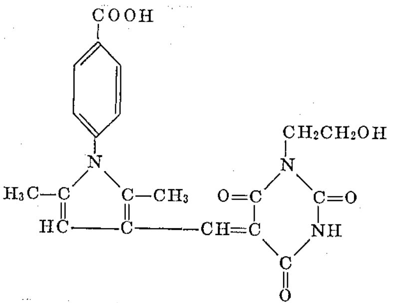
1. ....



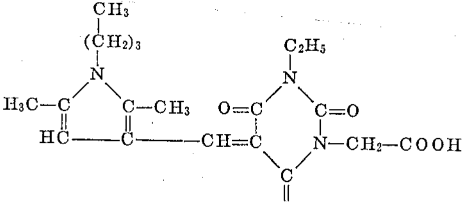
2. ....



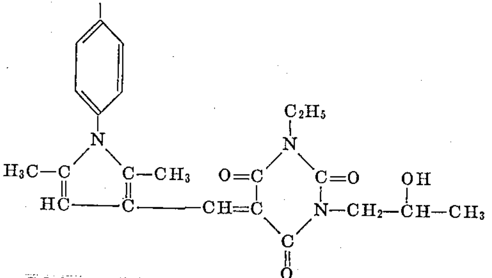
3



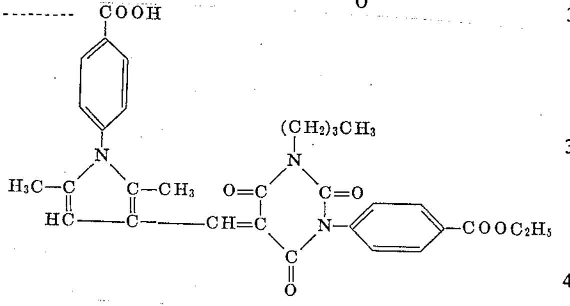
4



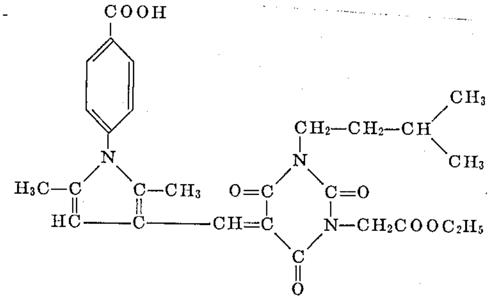
5



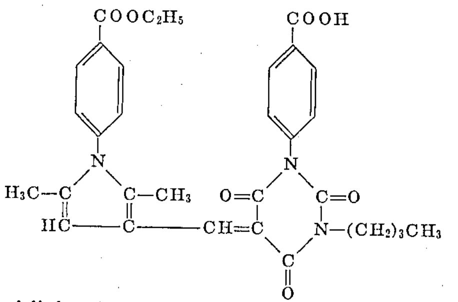
6



7



8



The novel light-absorbing dyes corresponding to the above general formula can be prepared by reaction of the appropriately substituted barbituric acid with a 3-pyrrolecarboxaldehyde.

The 3-pyrrole carboxaldehydes can be prepared from the corresponding pyrroles according to the Vilsmeier and Haack reaction (Ber. 60, 119, 1927) using dimethylformamide as formylating agent.

The required barbituric acids can be prepared without difficulty as known in the art by reaction of the appropriate urea with malonic acid in the presence of acetic anhydride. The urea can be obtained by reaction in an inert solvent such as benzene and chloroform, of an organic isocyanate or an inorganic cyanate, e.g., potassium cyanate with a primary amine. Preparations of some appropriately substituted bartiburic acids can be found in the U.K. Pat. Nos. 1,241,692 and 1,265,485 both filed May 21, 1968 by Gevaert-Agfa N.V.

The following preparation illustrates how the dyes of the present invention can be prepared.

Preparation

a. N-butyl-N'-(4-carboxyphenyl)urea

To 685 g (5 moles) of 4-aminobenzoic acid in 7.5 litres of chloroform, 550 g (5.5 moles) of butylisocyanate were added at room temperature with stirring. The mixture was refluxed for 90 minutes and then cooled. The precipitate formed was collected, boiled with 5 litres of methanol, cooled and collected by centrifuging.

Yield: 990 g (83 %). The product decomposes above 220°C.

b. N-butyl-N'(4-carboxyphenyl)barbituric acid

1,180 g (5 moles) of the above urea, 624 g (6 moles) of malonic acid and 5 litres of acetic acid were mixed and heated to 60°–70°C. 2.5 litres of acetic anhydride were added whereupon the mixture was stirred for 6 hours at 90°–95°C. The solvent was distilled off in a rotative evaporator under diminished pressure. The residue was poured into 5 litres of water and stirred for 1 hour at room-temperature. The precipitate was collected by suction and recrystallized from methanol-water.

Yield: 1,250 g (82 %). Melting point: 210°–212°C.

c. 1-(4-ethoxycarbonyl phenyl)-2,5-dimethyl pyrrole

A mixture of 495 g (3 moles) of ethyl 4-aminobenzoate, 387 g (3.3 moles) of hexan-2,5-dione, 375 ml of acetic acid and 1.5 litre of benzene was refluxed with stirring and the water formed was separated in a Dean-Stark apparatus. The benzene was removed by evaporation and the residue was crystallized from methanol. Yield: 583 g (89 %).

d. 1-(4-ethoxycarbonyl phenyl)-2,5-dimethyl-4-formylpyrrole

To 729 g (3 mole) of the above pyrrole in 3 litres of dimethylformamide, 276 ml (3 mole) of phosphoryl chloride were added dropwise with cooling so as to keep the temperature at 15°–20°C. The reaction mixture was then heated at 90°–95°C for 3 hours, poured into an aqueous solution of sodium acetate, stirred for 1 hour and left standing overnight at room temperature. The precipitate was collected by suction and the filtrate was kept for 3 days at room temperature to yield a second crop of product.

Total yield after washing with water: 764 g (94 %). Melting point: 118°C.

e. 1-(4-carboxyphenyl)-2,5-dimethyl-4-formyl pyrrole

To 813 g (3 moles) of the pyrrole aldehyde of step d, in 3.9 litres of ethanol which was heated to 50°–60°C, 1.95 litre of 2N sodium hydroxide was added. The mixture was heated at this temperature for 3 hours whereupon the ethanol was distilled off under reduced pressure. The residue was acidified by addition of 780 ml of 5N hydrochloric acid. The mixture was left overnight in a refrigerator whereupon the precipitate was collected by suction and washed with water.

Yield: 721 g (99 %). Melting point: above 260°C.

f. dye 2

A mixture of 912 g (3 moles) of the barbituric acid of step (b), 729 g (3 moles) of the pyrrole aldehyde of step (e) and 4.5 litres of ethanol was refluxed for 1 hour. After cooling, the crystallized dye was collected by suction.

Yield: 1,365 g (86 %).

Melting Point: above 260°C. Absorption maximum: 409 nm.

Extinction coefficient: $3.7.10^4$.

The polymeric binders for the antihalation layers of the present invention are water-insoluble but should be alkali-soluble so that they readily dissolve in alkaline photographic developer baths. These polymers may belong to different classes of polymers.

Suitable alkali-soluble polymers are, e.g.,

co(styrene/maleic acid)

partially or completely nitrated co(styrene/maleic acid)

co(vinyl acetate/maleic acid) (50:50 mole %)

co(styrene/acrylic acid) (70:30 % by weight)

co(styrene/methacrylic acid)(30:70 % by weight)

co(n-butyl acrylate/methacrylic acid)(70:30 % by weight)

co(methyl acrylate/acrylic acid)(80:20 % by weight)

co(styrene/mono-isobutylmaleate/maleic acid) (41:57:2 % by weight)

co(vinyl acetate/crotonic acid) (94:6 % by weight) and other copolymers of vinyl acetate and crotonic acid comprising from 5 to 20 % by weight of crotonic acid as described in French Pat. No. 2,078,629 filed Feb. 15, 1971 by Gevaert-Agfa N.V.

copolymers of 20 to 50 % by weight of acrylic acid or methacrylic acid, 15 to 79 % by weight of a C_1–C_8 alkylacrylate and 1 to 50 % by weight of a C_1–C_4 alkyl methacrylate as described in French Pat. No. 2,078,630 filed Feb. 15, 1971 by Gevaert-Agfa N.V. optionally together with polymethylene hydroxybenzoic acid which, as is described in the said specification, promotes the adhesion of the antihalation layer to the film support so that no special subbing layer is necessary. These copolymers include for example:

co(methacrylic acid/n-butyl acrylate/ethyl methacrylate) (30:67:3 % by weight) co(methacrylic acid/n-butyl acrylate/methyl methacrylate) (35:35:30 % by weight)

co(acrylic acid/n-butyl acrylate/methyl methacrylate) (20:70:1 % by weight)

co(methacrylic acid/2-ethylhexyl acrylate/methyl methacrylate (40:30:30 % by weight)

co-methacrylic acid/ethyl acrylate/n-butyl methacrylate) (20:78:2 % by weight)

co(methacrylic acid/ethyl acrylate/methyl methacrylate) (26:37:37 % by weight)

co-methacrylic acid/ethyl acrylate/methyl methacrylate) (35:15:50 % by weight)

co(methacrylic acid/n-butylacrylate/methyl methacrylate) (30:68:2 % by weight).

Normally, the above polymers in their acid form are insoluble in water but dissolve readily in an alkaline photographic developer so that the antihalation composition is eliminated from the photographic film support and a clear photographic film remains.

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

In order to obtain the desired absorption spectrum e.g. absorption of all light of the visible spectrum, one or more dyes according to the present invention can be used simultaneously or they can be used together with other suitable light-absorbing dyes e.g. those described in the two British Pat. applications Nos. 29385/72 and 29387/72 both filed June 22, 1972 by Agfa-Gevaert N.V. filed as Applications for Patents of Addition to British Pat. Nos. 1,265,485 and 1,241,692 both filed May 21, 1968 by Gevaert-Agfa N.V. respectively.

The coating composition for the antihalation layer may further comprise one or more surface-active agents as coating aids as well as matting agents, e.g., finely divided silicon dioxide, finely dispersed polymethylmethacrylate particles and finely dispersed particles of the reaction product according to U.K. Pat. No. 981,198 filed Jan. 1, 1962 by Gevaert Photo-Producten N.V. of starch with urea and formaldehyde.

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

In certain cases, especially when polyalkylene terephthalate films such as a film of polyethylene terephthalate are used as the film support to which the antihalation coating composition of the invention is to be applied, it may be preferable to provide the support before application of the antihalation layer, with a known subbing layer, or to pretreat the support superficially according to known techniques. For instance, the polyester film support may be provided with a subbing layer, comprising a copolymer of at least one of the chlorine-containing monomers vinylidene chloride and vinyl chloride. This subbing layer has been described in the British Pat. No. 1,234,755 filed Sept. 28, 1967 by Gevaert-Agfa N.V. Good results are also obtained when the surface of the subbing layer is exposed to a high voltage electric corona discharge as described in the British Pat. No. 1,286,457 filed Dec. 9, 1968 by Gevaert-Agfa N.V. Sometimes an electric corona discharge treatment of the polyester film support itself may suffice.

The polyester film support surface may also be treated with a solution of a swelling agent for the polyester as described e.g. in Belgian Pat. No. 754,145 filed July 30, 1970 by Gevaert-Agfa N.V.

In order to facilitate the elimination of the antihalation layer in the developing bath, there may be applied between the hydrophobic film support and the antihalation layer an intermediate layer which is formed from a mixture of 1 to 3 parts by weight of a cellulose ester, e.g., cellulose diacetate and 3 to 1 part by weight of at least one alkali-soluble polymer as referred to above. More details about such intermediate layers can be found in Belgian Pat. No. 773,588 filed Oct. 20, 1970 by Agfa-Gevaert N.V.

The following examples illustrate the present invention.

EXAMPLE 1

A biaxially oriented polyethylene terephthalate film of 100 micron thickness was provided with a subbing layer of a copolymer of vinylidene chloride, vinyl chloride, n-butyl acrylate and itaconic acid as described in example 3 of British Pat. No. 1,234,755 as mentioned hereinbefore.

The subbing layer was overcoated pro rata of 1 liter per 50 sq.m with the following antihalation composition:

dyestuff 2	6 g
co(styrene/acrylic acid) (70:30% by weight)	30 g
ethanol	450 ml
n-butanol	50 ml
acetone	500 ml

The dye of the antihalation layer is not extractable with water but discolours completely in a conventional photographic developing solution without staining the solution.

EXAMPLE 2

A cellulose triacetate film of 140 micron thickness comprising 15 % by weight of triphenyl phosphate was coated at a ratio of 1 liter per 45 sq.m with the following coating composition:

cellulose diacetate (56% by weight of acetic acid)	2.5 g
acetone	850 ml
methanol	75 ml
butanol	75 ml

After drying, this intermediate layer was overcoated at a ratio of 1 litre per 45 sq.m with the following antihalation coating composition:

dye 2	5 g
25 % by weight ethanolic solution of co(styrene/acrylic acid) (70:30% by weight)	120 ml
methanol	780 ml
t.butanol	100 ml

The antihalation dyestuff could not be extracted with water. The layer discoloured and dissolved completely in a conventional alkaline developing solution without leaving any residual stain neither on the material nor in the solution.

EXAMPLE 3

A cellulose triacetate film of 140 micron thickness comprising 15 % by weight of triphenyl phosphate was coated at a ratio of 1 liter per 40 sq.m with the following coating composition:

10% by weight of aqueous solution of the sodium salt of completely suphonated polystyrene	30 ml
water	20 ml
methanol	250 ml
acetone	600 ml
5% by weight solution in acetone of cellulose diacetate (56% by weight of acetic acid)	100 ml

After drying, this clear intermediate layer was overcoated at a ratio of 1 liter per 32.5 sq.m with the following antihalation coating composition:

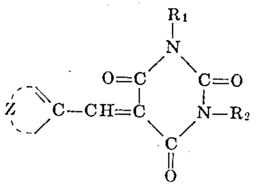
dye 3	10 g
co(vinyl acetate/malaeic acid)(50:50 mole%)	25 g
ethanol	1000 ml
35% bby weight aqueous solution of hydrogen chloride	1 ml

The other side of the cellulose triacetate film support was coated with a light-sensitive silver halide emulsion.

After exposure, the material was developed in a conventional alkaline silver halide developing solution. The antihalation layer was completely eliminated and discoloured in the developer leaving no residual stain.

We claim:

1. A light-sensitive photographic element comprising a support and at least one light-sensitive silver halide emulsion layer wherein the side of the support, opposite to that carrying the said silver halide emulsion layer(s) is provided with an antihalation layer of a water-insoluble, alkali-soluble polymeric binder and a dye corresponding to the formula:



wherein the dyestuff molecule contains at least one carboxyl group and is free from sulpho group in acid or salt form, and wherein

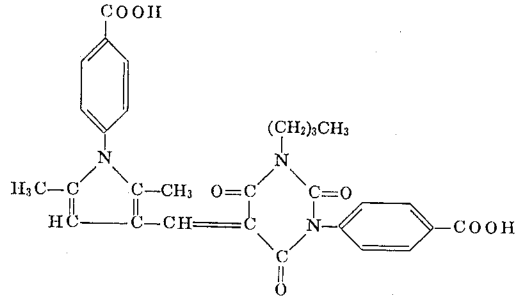
each of R_1 and R_2 stands for hydrogen, and alkyl group, an allyl group, a cycloalkyl group or an aryl group, and

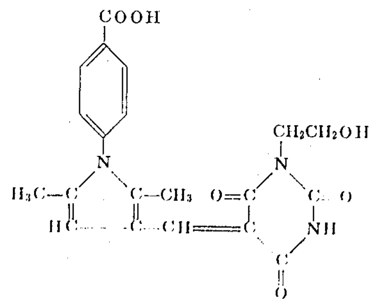
Z represents the atoms necessary to close a pyrrole nucleus.

2. A photographic element according to claim 1, wherein the said polymeric binder is co(vinyl acetate/-maleic acid) or co(styrene/acrylic acid).

3. A photographic element according to claim 1, wherein a subbing layer is provided between the support and the antihalation layer.

4. A photographic element according to claim 1 wherein the dye corresponds to one of the following formulae:





* * * * *