

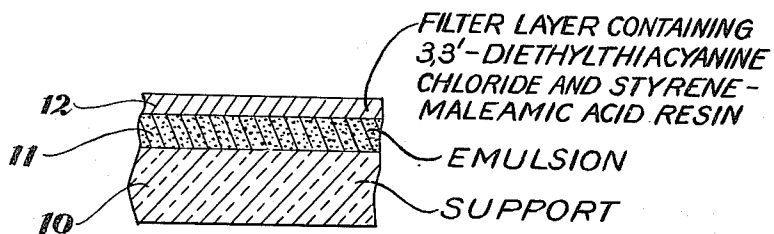
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2,691,579

ULTRAVIOLET ABSORBING LAYERS

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ULTRAVIOLET ABSORBING LAYERS

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10 Claims. (Cl. 95—2)

1

This invention relates to new photographic elements protected against the harmful effects of ultraviolet radiation.

It is known that certain materials, such as cellulosic films and photographic layers, are adversely affected by ultraviolet radiation when such materials are exposed to daylight. In the case of photographic layers, the ultraviolet radiation sometimes causes undesired exposure of the layer, or layers, since photographic silver halide emulsions are sensitive to blue, violet and ultraviolet regions of the spectrum, in addition to any other sensitivity which may be given them, and in the exposure of such material, it is frequently desirable to prevent the action of ultraviolet light on the sensitive emulsion. This is especially true in the case of photographic materials designed for use in color photography where the film has been sensitized to the longer wavelength regions where it is desirable to record only the rays of the visible spectrum.

Color photographs on multilayer photographic material, particularly where the dye images are formed in sensitive emulsion layers by color development, are susceptible to fading and discoloration by the action of ultraviolet radiation to which the photographs are subjected during viewing. It is also known that the residual couplers contained in the emulsion layers after formation of the picture images in certain processes, are attacked by ultraviolet radiation and form a stain which is undesirable in the finished photograph. The action of ultraviolet radiation on finished color photographs is particularly noticeable in positive prints on paper or other opaque supports, since this type of print is frequently viewed in daylight where there is a high content of ultraviolet radiation. This dye fading and yellowing appears to be caused primarily by those wavelengths of light which lie close to the visual region of the spectrum, i. e. 360–400 millimicrons.

I have now found that certain cyanine dyes are useful in absorbing harmful ultraviolet radiation when such dyes are incorporated in a gelatin layer containing a certain type of synthetic resin which acts as a mordant for the cyanine dye.

It is, therefore, an object of my invention to provide new photographic elements protected against the harmful effects of ultraviolet radiation. A further object is to provide photographic color materials which have been protected against the harmful effects of ultraviolet radiation. Other objects will become apparent from a consideration of the following description and examples.

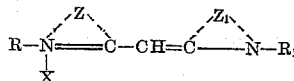
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The accompanying drawing illustrates schematically a cross-sectional view of a sensitive photographic element having an ultraviolet filter layer containing a synthetic resin which acts as a mordant for the ultraviolet absorbing compounds used according to my invention. Advantageously, the ultraviolet absorbing compound is incorporated in the photographic element by bathing the photographic element, which contains a gelatin layer having incorporated therein one of the synthetic resins mentioned above, in an aqueous solution of the ultraviolet absorbing compound. Alternatively, the ultraviolet absorbing compound, which in this case is a particular type of cyanine dye, can be incorporated directly in the gelatin layer before or during coating. Instead of using gelatin as the binder, other water-permeable, hydrophilic colloids can be used, such as synthetic resins (e. g. polyvinyl acetals, hydrolyzed polyvinyl acetate, etc.), hydrolyzed cellulose esters, etc.

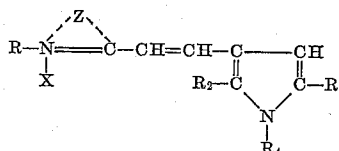
Where the photographic element is a material intended for use in color photography, the ultraviolet filter need not be an outer layer, but this layer can be placed over one of the layers subject to the harmful effects of ultraviolet radiation. For example, in a multilayer material comprising three differentially sensitized layers, the red sensitive layer being adjacent to the support, the green sensitive layer being superposed on the red sensitive layer, and the blue sensitive layer being outermost with respect to the other light-sensitive layers, the ultraviolet filter layer can be placed between the blue and green sensitive layers. Alternatively, the ultraviolet filter layer can be placed between the green and red sensitive layers. The amount of ultraviolet absorbing compound can be varied, depending upon the effect desired and the use to which the material is to be put.

The particular ultraviolet absorbing compounds useful in practicing my invention can advantageously be represented by the following two general formulas:

45 I.



50 II.



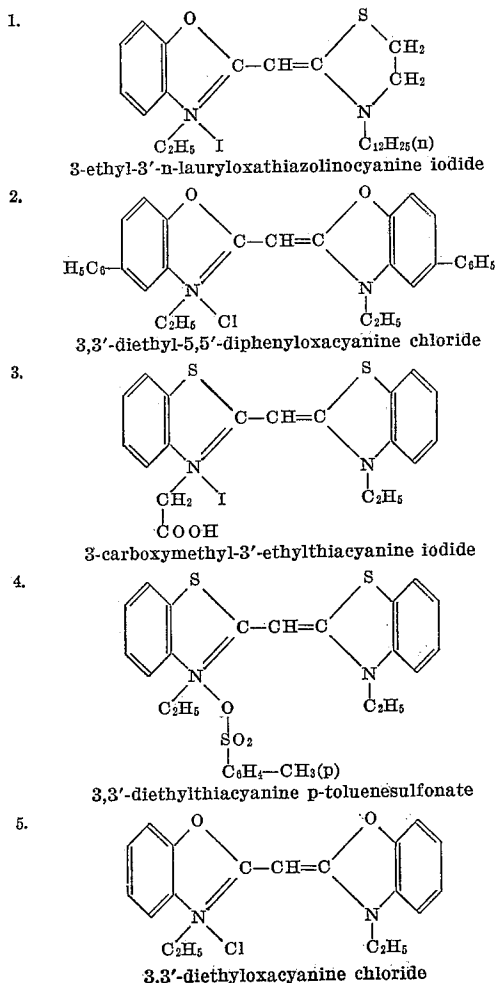
wherein R and R₁ each represents an alkyl group, such as methyl, ethyl, n-propyl, isopropyl, n-

3

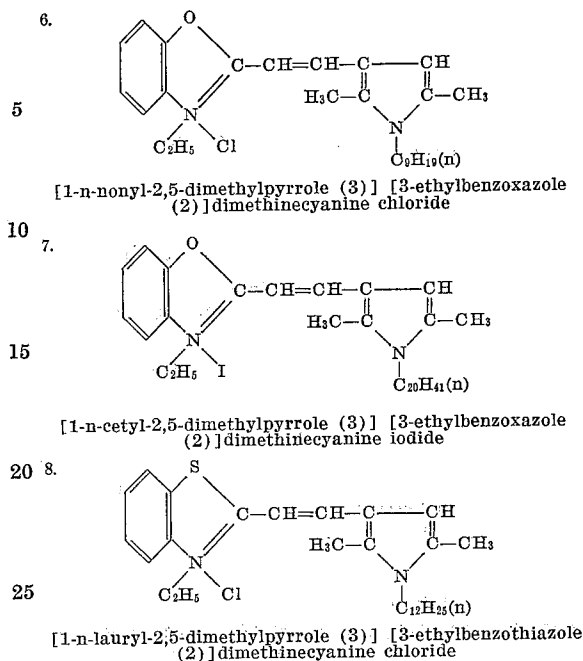
butyl, carboxymethyl, carbethoxymethyl, n-lauryl, benzyl (phenylmethyl), etc., R_2 and R_3 each represents an alkyl group, such as methyl, ethyl, n-propyl, etc., R_4 represents an alkyl group containing at least 9 carbon atoms, such as n-nonyl, n-decyl, n-lauryl, n-cetyl, etc., X represents an acid radical, such as chloride, bromide, iodide, perchlorate, p-toluenesulfonate, benzenesulfonate, etc., and Z and Z_1 each represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of those of the benzothiazole series, such as benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 5-methylbenzothiazole, 5-phenylbenzothiazole, 6-methoxybenzothiazole, etc., those of the benzoxazole series, such as benzoxazole, 5-chlorobenzoxazole, 5-phenylbenzoxazole, 5-methoxybenzoxazole, etc., those of the thiazoline series, such as thiazoline, 4-phenylthiazoline, 5-methylthiazoline, etc., and those of the thiazole series, such as thiazole, 4,5-diphenylthiazole, 4-phenylthiazole, 5-phenylthiazole, etc.

The dyes represented by Formula I above can advantageously be prepared according to the methods described in U. S. Patent 2,108,485 or British Patent 423,792, or other methods known in the art. Also the dyes of Formula I can be prepared according to the method described in Jones et al. U. S. application Serial No. 291,302, filed June 4, 1952. The cyanine dyes of Formula II above can be prepared according to the method described in British Patent 529,440, for example.

Typical dyes which can be employed in my invention comprise those represented by the following formulas:



4



Synthetic resins which can be employed as mordants for the above dyes comprise interpolymers of styrene with maleamic acids, e. g. Amberlite W-1. These latter resins have been previously described in U. S. Patent 2,313,565 and Godowsky U. S. Serial No. 156,066, filed April 15, 1950. The process of making such resins comprises reacting a styrene-maleic anhydride resin with ammonia or an amine, such as aniline, n-butylamine, n-amylamine, etc. Alternatively, such resins can be prepared by hydrolysis (partial or complete) of interpolymers of styrene with maleinimide.

The advantages of my invention have been found to be particularly useful with respect to the use of the dyes represented by the above general formulas, and it has been found that other similar dyes do not provide the useful results obtained with the particular dyes of my invention; for example, such dyes as 4-[3-ethyl-2(3H)-benzoxazolylidene] ethylidene] - 3 - methyl - 1 - phenyl-5-pyrazolone and 2-[β-(1-piperidyl) vinyl]benzothiazole methiodide are not retained in gelatin layers during the washing operations to which such layers are customarily subjected. This is true even though substantial amounts of synthetic resin are present in the gelatin or colloidal binder.

The following examples will serve to illustrate more fully the manner whereby I practice my invention.

EXAMPLE 1

Amberlite W-1 was mixed with a gelatin solution and the mixture coated into a thin film containing about 50 mg. per square foot of the Amberlite. The coating was then dried and soaked in a 1% aqueous solution of 3,3'-diethylloxacyanine chloride for 10 minutes at 68° F. The pH of the solution was 5. The coating was then washed in running water for 5 minutes, dried, mounted and a spectrophotometric measurement made which showed that the coating absorbed substantially all radiation between 360 and 400 millimicrons, but transmitted substantially all radiation of wavelengths greater than 400 millimicrons.

5

EXAMPLE 2

A coating was made in substantially the same manner as that described in Example 1 above, except that styrene-maleamic acid resin obtained according to U. S. Patent 2,313,565 was employed instead of the Amberlite. The coating absorbed substantially all radiation between 360 and 400 millimicrons but transmitted substantially all radiation of wavelength greater than 400 millimicrons.

EXAMPLE 3

A series of cyanine dyes were adsorbed onto a coating containing only gelatin, and the same cyanine dyes were adsorbed onto a second coating containing styrene-maleamic acid resin plus gelatin. The following procedure was used:

0.1 g. of the cyanine dye was dissolved in 50 cc. of ethyl alcohol and then 50 cc. of water was added to the solution. The dyes remained in solution, and the two coatings were immersed in the solution for 5 minutes, then washed for 20 minutes in running water and dried. Density and wavelength of absorption were obtained to evaluate the retention characteristics of the dyes. The following results were noted.

a. 3-ethyl-3'-n-lauryloxathiazolinocyanine iodide.—This dye had an absorption maximum at 350 millimicrons and showed a density of 3.3 with the coating containing the resin, while the density of the coating with the gelatin alone was only 0.87, indicated preferential adsorption.

b. 3,3'-diethyl-5,5'-diphenyloxacyanine chloride.—This compound had a maximum absorption at 376-405 millimicrons and showed a density above 4 with respect to the coating containing the styrene-maleamic acid resin, although the density was only 1.5 with respect to the coating containing only gelatin.

c. [1-n-cetyl-2,5-dimethylpyrrole (3)][3-ethylbenzoxazole (2)]dimethinecyanine chloride.—This compound showed excellent adsorption to the coating containing the styrene-maleamic acid resin, having a density of 2.88 as contrasted to a density of 0.84 for the coating containing the gelatin alone. Maximum absorption occurred at about 440 millimicrons.

d. 3-carboxymethyl-3'-ethylthiacyanine iodide.—This dye was adsorbed tightly to the coating containing the styrene-maleamic acid resin, showing a density of 3.3 as contrasted to a density of 0.18 for the gelatin coating. Maximum absorption occurred at 400 millimicrons.

e. 3,3'-diethylthiacyanine p-toluenesulfonate.—This compound had maximum absorption at 400 millimicrons and was adsorbed to the coating containing the styrene-maleamic acid resin to give a density of 2.86, while the density of the coating containing only the gelatin was 0.1.

The coatings employed in Examples 1 and 2 respectively were two strips which had been developed in a complete color process. The coatings, after subjection to daylight for a substantial period of time, showed little change, insofar as fading or print-out were concerned.

The support employed in the photographic elements of my invention can be either transparent, such as cellulose acetate, cellulose nitrate, etc., or opaque, such as paper, metal, etc.

The accompanying drawing illustrates schematically a cross-sectional view of a photographic element containing a layer having incorporated therein 3,3'-diethylthiacyanine p-toluenesulfonate and a styrene-maleamic acid resin. As shown in the single figure of the drawing, a sup-

6

port 10 of any suitable material, such as cellulose acetate or paper, for example, having thereon a light-sensitive photographic silver halide emulsion layer 11 is coated with a filter layer 12 of gelatin having incorporated therein 3,3'-diethylthiacyanine p-toluenesulfonate and a styrene-maleamic acid resin. The filter layer 12 serves to protect the photographic element from the harmful effects of ultraviolet radiation both during exposure and after completion of photographic processes. It will be understood that the drawing is merely representative of other structures which can be employed in my invention, and that the element can have other layers, not shown, such as additional light-sensitive layers, subbing layers, antihalation layers, etc.

As noted above, the styrene-maleamic resins used in my invention have been previously described in the prior art. Such resins can be designated as having a polymeric hydrocarbon chain having substituted thereon at recurring intervals phenyl groups and carboxylic groups, together with carbonamide and/or carboxylic imide groups. Similar useful resins having such structure can be obtained from styrene-acrylic acid, styrene-methacrylic acid, or styrene-itaconic acid inter-polymers (instead of from styrene-maleic anhydride polymers as is described above).

The following two examples will serve to illustrate the manner whereby resins useful in practicing my invention can be prepared.

EXAMPLE A

Polystyrene-maleamic acid polymer

50 gm. of polystyrenemaleic anhydride were added gradually to 250 ml. of 28% ammonium hydroxide in a 500 ml. Erlenmeyer flask with stirring from a mixer to form a slurry. After stirring for eighteen hours at room temperature a viscous, clear colorless dope was obtained. 300 gm. of this dope was diluted to approximately 2% solids with water and 48% hydrobromic acid was added to it until it was just acid to Congo Red. The solid that was formed was separated by filtration, and leached with absolute alcohol until the wash solutions were bromide free. The solids were put to dry in an oven at 60° C.

20 gm. of the solid were doped to form a 5% dope by weight in water made alkaline with 13 ml. of 20% sodium hydroxide. pH=8.63.

EXAMPLE B

Polystyrene-maleamic acid ammonium salt

The following reagents were put to reflux in an all glass reflux outfit equipped with a mechanical stirrer. Conditions were maintained anhydrous by calcium chloride tubes on all openings to the atmosphere.

49 gm. maleic anhydride (Eastman white label)
52 gm. distilled styrene
1500 ml. dry toluene
2.0 gm. benzoyl peroxide

The reaction mixture was heated for 2½ hours on a steam bath without stirring and then allowed to cool to room temperature. A small sample of the solids was withdrawn, washed with fresh benzene, and put to dry for analysis and viscosity purposes.

The stirrer was turned on and dry ammonia was bubbled into the reaction mixture continuously for 3½ hours. During this time the temperature within the reaction mixture rose from a starting temperature of 23° C. to 45° C. and

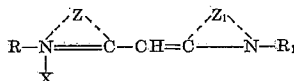
then returned to 23° C. The solids were filtered off on a Buchner funnel, washed with toluene, and put to dry in a vacuum oven at 60° C. overnight.

The residual toluene was then extracted with absolute alcohol by stirring the product with 2-3 liter portions of absolute ethyl alcohol and filtering onto a Buchner funnel. The product was then dried as above.

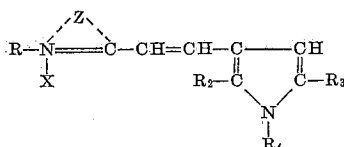
Forty grams of the polymer were gradually added to 200 ml. of water in an Erlenmeyer flask with mechanical stirring. The solution was kept slightly alkaline by the portion-wise addition of 28% NH₄OH. The pH was never allowed to exceed eight. A clear colorless dope was obtained which was then adjusted to 15% solids by weight by the addition of distilled water. The pH of this solution was 6.38.

What I claim as my invention and desire secured by Letters Patent of the United States is:

1. A photographic element comprising a support, a photographic gelatino-silver halide emulsion layer, and a gelatin layer containing (1) an interpolymers of styrene and an unsaturated, aliphatic carboxylic compound, said interpolymers having a polymeric hydrocarbon chain having substituted at recurring intervals phenyl groups and carboxylic groups, together with groups selected from the group consisting of carbonamide and carboxylic imide groups, and (2) an ultraviolet absorbing compound selected from those represented by the following two general formulas:

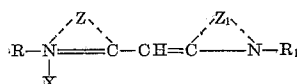


and



wherein R, R₁, R₂, and R₃ each represents an alkyl group, R₄ represents an alkyl group containing at least nine carbon atoms, X represents an acid radical, and Z and Z₁ each represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from those of the benzoxazole series, those of the thiazoline series, those of the thiazole series, and those of the benzothiazole series.

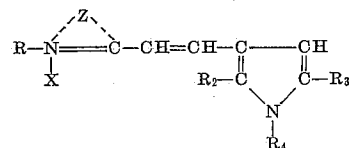
2. A photographic element comprising a support, a photographic gelatino-silver halide emulsion layer, and a gelatin layer superposed on said photographic gelatino-silver halide emulsion, said gelatin layer containing (1) an interpolymers of styrene and a maleamic acid, and (2) an ultraviolet absorbing compound selected from those represented by the following general formula:



wherein R and R₁ each represents an alkyl group, X represents an acid radical, and Z and Z₁ each represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of those of the benzoxazole series, those of the thiazoline series, those of the thiazole series, and those of the benzothiazole series.

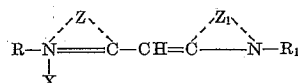
3. A photographic element comprising a sup-

port, a photographic gelatino-silver halide emulsion layer, and a gelatin layer superposed on said photographic gelatino-silver halide emulsion, said gelatin layer containing (1) an interpolymers of styrene and a maleamic acid, and (2) an ultraviolet absorbing compound selected from those represented by the following general formula:

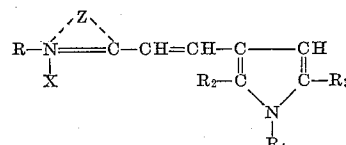


wherein R, R₂, and R₃ each represents an alkyl group, R₄ represents an alkyl group containing at least nine carbon atoms, X represents an acid radical, and Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of those of the benzoxazole series, those of the thiazoline series, those of the thiazole series, and those of the benzothiazole series.

4. A finished photographic element comprising a support having thereon a plurality of developed and fixed photographic emulsion layers containing coupled-dye images, at least one of said dye images being subject to fading by the action of ultraviolet radiation, said emulsion layer containing a coupled-dye image subject to fading lying between said support and a gelatin layer containing (1) an interpolymers of styrene and a maleamic acid and (2) an ultraviolet absorbing compound selected from those represented by the following two general formulas:



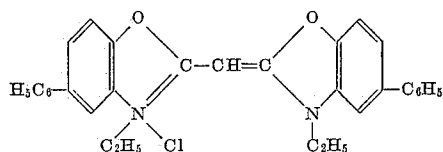
40 and



wherein R, R₁, R₂, and R₃ each represents an alkyl group, R₄ represents an alkyl group containing at least nine carbon atoms, X represents an acid radical, and Z and Z₁ each represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of those of the benzoxazole series, those of the thiazoline series, those of the thiazole series, and those of the benzothiazole series.

5. A photographic element according to claim 4 wherein the support is a paper support.

6. A photographic element comprising a support, a photographic gelatino-silver halide emulsion layer, and a gelatin layer containing (1) an interpolymers of styrene and a maleamic acid and (2) an ultraviolet absorbing compound having the following formula:

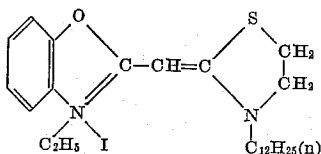


said photographic gelatino-silver halide emulsion layer lying between said support and said gelatin layer.

7. A photographic element comprising a support, a photographic gelatino-silver halide emul-

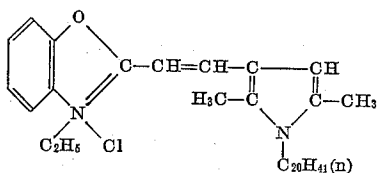
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sion layer, and a gelatin layer containing (1) an interpolymers of styrene and a maleamic acid and (2) an ultraviolet absorbing compound having the following formula:



said photographic gelatino-silver halide emulsion layer lying between said support and said gelatin layer.

8. A photographic element comprising a support, a photographic gelatino-silver halide emulsion layer, and a gelatin layer containing (1) an interpolymers of styrene and a maleamic acid and (2) an ultraviolet absorbing compound having the following formula:

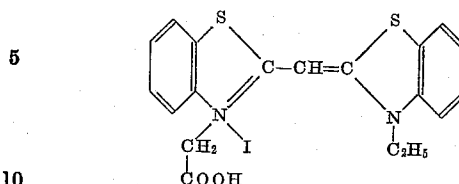


said photographic gelatino-silver halide emulsion layer lying between said support and said gelatin layer.

9. A photographic element comprising a support, a photographic gelatino-silver halide emulsion layer, and a gelatin layer containing (1) an interpolymers of styrene and a maleamic acid and

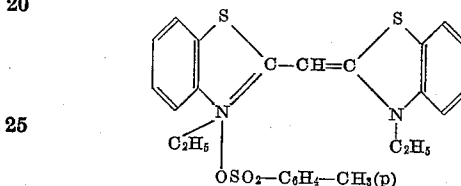
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(2) an ultraviolet absorbing compound having the following formula:



said photographic gelatino-silver halide emulsion layer lying between said support and said gelatin layer.

10. A photographic element comprising a support, a photographic gelatino-silver halide emulsion layer, and a gelatin layer containing (1) an interpolymers of styrene and a maleamic acid and (2) an ultraviolet absorbing compound having the following formula:



said photographic gelatino-silver halide emulsion layer lying between said support and said gelatin layer.

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35	Number	Name	Date
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