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PHOTOGRAPHIC LAYERS WHICH CONTAIN UV-ABSORBERS

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U.S. Cl. 96—84 R 6 Claims

ABSTRACT OF THE DISCLOSURE

The light stability of color photographic images is improved by overcoating the image carrying layer with a UV-protective coating which contains a UV-absorbing compound.

The UV-absorbing layer contains as UV-absorbent a 2-phenolbenzotriazole, the benzo ring of which is substituted with 2 butyl groups.

The invention relates to photographic layers which contain UV-absorbent compounds.

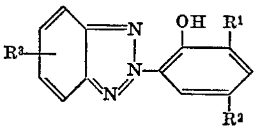
Numerous compounds are known which absorb light in the UV-region of the spectrum and are, therefore, suitable for the production of UV-filters and UV-protective coatings. Such coatings are used in photographic material for increasing the light fastness of color images. The UV-absorbent compounds should be incorporated in a separate protective layer in as high a concentration as possible in order to achieve the greatest possible effect. Generally, it is not possible to use the UV-absorbent compounds homogeneously or heterogeneously distributed with the image dyes in one layer, because the absorbent compounds and the dyes are very frequently found to interact with each other so that bleaching of the image is increased. The UV-absorbent compounds should be colorless and should have a high coefficient of extinction in the UV-region and should be as stable as possible.

The UV-absorbent compounds can be used in many different ways, e.g. in water insoluble binders. In this case, the finished color image is coated with such a solution in a separate working step. This procedure, however, is only economical for images of large shapes and sizes and is, therefore, not generally applicable. Incorporation of water soluble and water insoluble UV-absorbent compounds in a diffusion fast manner in a protective layer has also been described. In this case, the chemical and physical properties of the UV-absorbent compound must meet certain requirements, e.g. it must be possible for the absorbent compound to be used in a highly concentrated form in layers of a thickness of 1 to 2 μm. without precipitating from the protective layer in the form of crystals or an oil. The UV absorbent compound must, of course, be inert towards photographic processing baths and must not undergo yellowing on exposure to light.

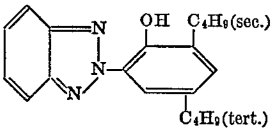
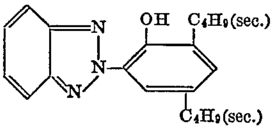
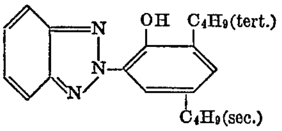
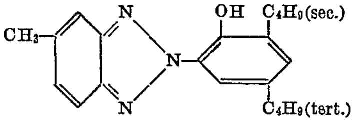
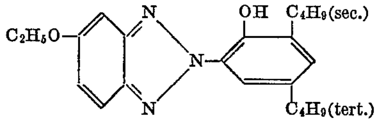
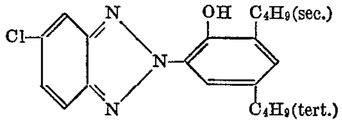
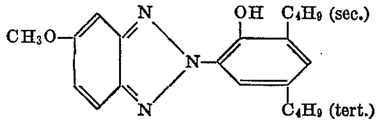
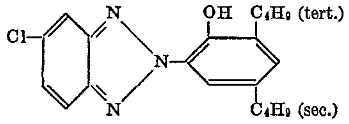
A very wide variety of UV-absorbent compounds have already been described for the present purpose. Many of these compounds, however, do not sufficiently satisfy the requirements in practice. Aromatic azines have, inter alia, been particularly recommended as UV-absorbent compounds, but these generally have a high melting point so that they are difficult to use because of their tendency to crystallize. Derivatives of this type which can easily be incorporated in photographic layers, which are described in German Pat. No. 1,182,066, are slightly yellowish so that they are detrimental to the white color images. The reason for this is that a slight absorption of light from the visible region of the spectrum occurs.

It is among the objects of the present invention to produce photographic layers which contain UV-absorbers, which must be easily incorporated in these layers, and as far as possible, must absorb only in the UV-region of the spectrum.

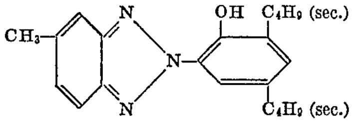
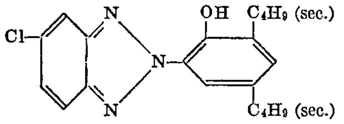
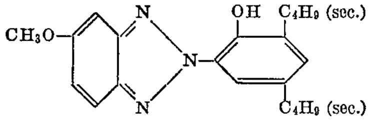
We now have found a photographic material with a UV-absorbent layer which contains a UV-absorber of the following formula



in which R^1 and R^2 stand for sec.-butyl or tert.-butyl and R^3 represents hydrogen, alkyl or alkoxy having up to 3 carbon atoms or halogen such as chlorine or bromine. But at least one of the substituents R^1 and R^2 represents sec.-butyl. The phenol ring may also be further substituted e.g. by alkyl or alkoxy having up to 3 carbon atoms or halogen for example chlorine or bromine. Particular utility is exhibited by the following compounds:

		M.P., °C.
(1)		80-81
(2)		36.5-37
(3)		73-74
(4)		74-75
(5)		79-80
(6)		43-44
(7)		67-68
(8)		72

TABLE—Continued

		M.P., °C.
(9)		41–42
(10)		Oil.
(11)		Oil.

The compounds to be used according to the invention are prepared in known manner. Preferably one starts from a diazotized o-nitraniline which is coupled with the butyl-substituted phenol to yield the o-nitrophenylazo compounds. The last mentioned compounds are reduced in alkaline medium with zinc dust whereby the benzotriazols are formed.

The preparation of Compound 1 is described in the following:

COMPOUND 1

138 g. (1 mol) of o-nitraniline are stirred up with 500 ml. of concentrated aqueous hydrochloric acid, mixed with 750 ml. of water and diazotized with 70 g. (1 mol) sodium nitrite in 150 ml. of water at a temperature of between 0 and 5° C. Thereafter it is stirred for another half hour.

The resulting diazonium solution is added quickly drop by drop while stirring at a temperautre of 5° C. to a solution of 206 g. 2-sec.-butyl-4-tert.-butyl-phenol (1 mol), 140 g. of sodium acetate and 400 g. of concentrated (45%) aqueous sodium hydroxide in 2.3 l. of methanol. The mixture is stirred for some hours and left standing over night.

The precipitated red dye is filtered off, washed with water and dried (M.P. ca. 80° C.). The raw product is recrystallized from methanol, the precipitate filtered off and washed with cold methanol (M.P. 92–93° C.).

355 g. (1 mol) of 2-nitro-phenylazo-2′-hydroxy-3′-sec.-butyl-5′-tert.-butylbenzene are refluxed in 2.5 l. of ethanol and mixed with 520 g. of sodium hydroxide in 2.5 l. water. Thereafter 230 g. of zinc dust are added portionwise under intensive stirring and the reaction mixture is refluxed until clarification the mixture. The non-reacted zinc dust is filtered off and the pH of the yellow solution is adjusted by addition of aqueous hydrochloric acid to a value of between 3–4. The yellow precipitate is recrystallized from methanol in the presence of charcoal. For further purification the yellow crystals can be recrystallized again from methanol or from light gasoline in the presence of bleaching earth. Yield: ca. 165 g.—M.P. 80–81° C.

The other compounds can be prepared in a similar manner.

The UV-absorbent compounds which are to be used according to the invention have exceptionally advantageous absorption properties. The absorption curve drops steeply at the beginning of the visible region of the spectrum.

The UV-absorbent compounds are readily soluble in those particular solvents which are used as so-called oil forming agents for the production of color photographic materials. The solution can easily be emulsified in the casting solutions for the layers.

The UV-absorbent compounds to be used according to the invention may also be used in combination with other UV-absorbent compounds.

The UV-absorbent compounds do not deleteriously affect the photographic properties of adjacent layers and in particular the color coupling reaction of dissolved dye derivatives is not reduced. Many of the known UV-absorbent compounds even of the benztriazole series are detrimental in this respect. The molar extinction coefficient is exceptionally high, so that the quantity of UV-absorbent compound used can be kept comparatively low.

The UV-absorbent compounds are preferably emulsified in the casting solutions for the particular layer in the form of their solutions in high boiling solvents, by using a suitable dispersing apparatus.

The proportions in which the UV-absorbent compounds are mixed with the solvents may vary between 1:1 and 1:0.1. Low boiling auxiliary solvents such as ethyl acetate, methylene chloride, alcohols and mixtures of these solvents may be used. After dispersion, the low boiling solvents are removed in thin layer evaporators under vacuum. Suitable water insoluble, high boiling compounds are, for example, dibutyl phthalate, tricresyl phosphate and particularly higher fatty acids, and preferably branched fatty acids having about 10 to 20 C-atoms.

The UV-absorbent compounds may be added directly to the silver halide emulsions which contain color couplers or to a gelatin-containing solution of the protective layer.

The gelatin layers which contain the UV-absorbent compound may be arranged in any position in the various layers of the photographic material, but are preferably positioned above the layers which contain the image dye.

The UV-absorbent compounds are particularly suitable as the topmost layer for photographic multi-layered materials of the usual arrangement.

The concentration of the UV-absorbent compounds in the layers may vary within wide limits. An addition of 0.1–1.0 parts by weight, per part of the binding agent in the layer, has proved to be sufficient.

The binding agent for the UV-absorbing layers of the present invention is preferably gelatine which however can be replaced partially according to a preferred embodiment of the invention by homo- or copolymers of acrylic or methacrylic acid esters with aliphatic alcohols having up to 5 carbon atoms. In particular suitable are also anionic or cationic polyurethanes as described in U.S. patent specifications Nos. 3,374,095 and 3,397,989. The polyurethanes are also applied in combination with gelatine. The binding agents which are used in addition to gelatine are added preferably from an aqueous latex of the polymer. The concentration of the polymer in the layer is preferably 5–50% based on the total weight of the binding agent.

When using multi-layered color photographic materials, the concentration of the UV-absorbing compounds is so chosen that on exposure to light the stability of the image dyes is equally satisfactory in the three layers.

The layer thickness of the protective layers which contain UV-absorbent compounds is preferably 2 to 5 μm.

After the usual color photographic processing and testing of the resulting color image for its light fastness, the color photographic material is found to be improved by a factor of 4 to 10 compared with the same color photographic material which does not contain these protective layers.

The improvement in fastness is determined by exposing both images at the same color density to the same degree of bleaching. The ratio of lux hours required gives a measure of the improvement factor. The improvement factor depends not only on the concentration of the UV-absorbent compound but also on the thickness of the protective layer.

The layers which contain the UV-absorbent compound are completely transparent in the dry state and practically colorless. They are stable against the photographic processing baths, e.g. a colorforming development bath. No yellowing can be detected after prolonged exposure to light.

Example 1

On to a paper support which is laminated on both sides with a polyethylene layer containing a white pigment are applied the following layers:

(1) a red-sensitive silver chloro bromide gelatine layer containing a water-soluble diffusion-resistant cyan coupler,
(2) an intermediate gelatine layer,
(3) a green-sensitive silver chloro bromide gelatine emulsion layer containing a water-soluble diffusion-fast magenta coupler,
(4) an intermediate gelatine layer and
(5) a silver bromide gelatine emulsion layer containing a yellow color coupler fast to diffusion.

On to a stripe of the above material is applied a gelatine layer having a thickness of 3 μm. Another stripe of the above material is coated with a UV-absorbing layer from the following casting emulsion:

30 g. of Compound 1
4.5 g. of sulfosuccinic acid-bis-(2-ethyl)-hexylester
50 g. of a 30% methanolic solution of the monopotassium salt of pentadecylensuccinic acid (as described in British patent specification 1,222,753 or U.S. application Ser. No. 814,808) are dissolved in 60 ml. of diethylcarbonate and emulsified at a temperature of 55° C. into 1 l. of a 10% aqueous gelatine solution.

The UV-absorbing layer has a thickness of 3μm.

Both samples are processed in identical manner including exposure and color-forming development.

The light-fastness of the final image is determined as described above. The improvement factor lies in the range of 4–10 depending on the kind of the color coupler.

The UV-absorbing layer does not deleteriously affect the photographic properties of the adjacent emulsion layers or the time of color-forming development. Formation of a uniform dye fog is not observed.

Example 2

The same procedure is applied as described in Example 1 but the casting solution for the UV-absorbing layer is not applied as a separate top layer but is added to the blue-sensitive silver halide emulsion layer containing the yellow color coupler. The casting solution containing the UV-absorbent is changed in so far as 50 g. of the same UV-absorber and 75 g. of the 30% methanolic solution of pentadecylensuccinic acid is used.

Similar results are obtained as in Example 1.

Example 3

The procedure is the same as described in Example 1 the casting solution for the UV-absorbing layer has the following composition:

Into 1 l. of a 10% aqueous solution of gelatine is emulsified at a temperature of 55° C. the following solution:

30 g. of Compound 1
4.5 g. of sulfosuccinic acid-bis-(2-ethyl)-hexylester
30 g. of a 30% methanolic solution of the monopotassium salt of pentadecylensuccinic acid
10 g. dibutylphthalate in 60 ml. of diethylcarbonate.

Similar results are obtained as in Example 1.

Example 4

The procedure is the same as described in Example 1. The casting solution for the UV-absorbing layer has the following composition:

Into 1 l. of a 10% aqueous gelatine solution containing 50 g. of a 40% aqueous dispersion of an anionic polyurethane as described in U.S. patent specification 3,374,095 is emulsified at a temperature of 55° C. the following solution:

30 g. of Compound 2
3 g. of sulfosuccinic acid-bis-(2-ethyl)-hexylester and
50 g. of a 30% methanolic solution of the monopotassium salt of pentadecylensuccinic acid in
40 ml. of diethylcarbonate.

Similar results are obtained as in Example 1.

Example 5

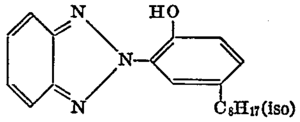
The exceptionally high compatibility with conventional binding agents for photographic UV-absorbing layers in the presence of oil formers in opposition to chemically similar known compounds such as described in U.S. Pat. No. 3,253,921 is shown in the following example:

Into 1 l. of a 10% aqueous solution is emulsified at a temperature of 55° C. the following solution:

30 g. of the UV-absorber referred to below
3 g. of the bis(2-ethyl)-hexylester of sulfossucinic acid in 60 g. of ethyl acetate.

Sample 1: UV-absorber Compound 1
Sample 2: UV-absorber Compound 2
Sample 3: The UV-absorber of the following formula

(A)



The above samples were stored at 40° C. and in the refrigerator and the behaviour of the emulsions with respect to the precipitation of the UV-absorbing agents is observed. The results are shown in the following table.

Compound	Digestion			Refrigerator 3 days
	1 hour	6 hours	24 hours	
1	Good	Good	Good	Good.
2	do	do	do	Do.
A	Slightly crystallized.	Crystallized.	Completely crystallized.	Crystallized.

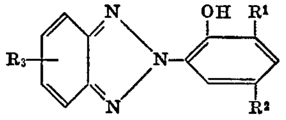
It is readily apparent from the above results that the casting solutions of the compounds used in accordance with the invention are far more stable, therefore far better to handle than the prior art compounds.

The above samples were also applied onto a processed multilayer color photographic material in the manner described in Example 1. Compounds of the invention do not crystallize in the layer. The protective action of the UV-absorbing layers containing compounds of the present invention is considerably higher than the protective action of layers containing the above prior art compound.

Precipitation of the UV-absorber of sample 3 can be reduced by a sufficiently high addition of an oil former such as dibutylphthalate or tricresyl phosphate. The required amount of about 0.5 to 1 part by weight of oil former per part of UV-absorber is however so high that the layers are getting hydrophobic which effects processing of the exposed color-photographic material. The diffusion of the aqueous processing baths into the photographic layers is made difficult, which is in particular relevant with hydrophilic color-forming developers such as N-butyl-N-ω-sulfobutyl-p-phenylenediamine.

We claim:

1. A photographic element comprising a support, at least one hydrophilic photographic silver halide emulsion layer and incorporated in one of the hydrophilic layers of said photographic element a UV-absorbing compound of the following formula:



wherein represents

R^1=sec.-butyl or tert.-butyl,

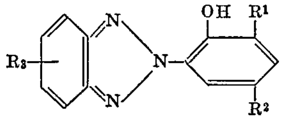
R^2=sec.-butyl or tert.-butyl, whereby at least one of the substituents R_1 or R_2 stands for sec.-butyl and

R^3=hydrogen, alkyl or alkoxy having up to 3 carbon atoms or halogen.

2. The element of claim **1** wherein the UV-absorber is contained in an amount of 0.1–0.5 parts by weight per one part by weight of binding agent of the layer.

3. The photographic element of claim **1** wherein the UV-absorbing compound is finally distributed in the layer in the form of a solution in a high-boiling solvent.

4. The finished photographic element comprising a support having thereon a plurality of developed and fixed photographic emulsion layers containing dye images formed upon color-forming development, at least one of said dye images being subject to fading by the action of ultraviolet radiation, said emulsion layer containing the dye image subject to fading laying between said support and an UV-absorbing layer containing an ultraviolet absorbing compound of the following formula:



wherein represents

R^1=sec.-butyl or tert.-butyl,

R^2=sec.-butyl or tert.-butyl, whereby at least one of the substituents R_1 or R_2 stands for sec.-butyl and

R^3=hydrogen, alkyl or alkoxy having up to 3 carbon atoms or halogen.

5. The finished photographic element of claim **4** wherein the UV-absorber is contained in an amount of 0.1–0.5 parts by weight per one part by weight of binding agent of the layer.

6. The photographic element of claim **4** wherein the UV-absorbing compound is contained finally distributed in the layer in the form of a solution in a high-boiling solvent.

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RONALD H. SMITH, Primary Examiner

U.S. Cl. X.R.

117—33.3; 252—300