

[54] **PHOTOGRAPHIC LAYERS WHICH CONTAIN UV-ABSORBERS**  
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**Related U.S. Application Data**

[63] Continuation of Ser. No. 878,220, Nov. 19, 1969, abandoned.

[30] **Foreign Application Priority Data**

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

[58] Field of Search..... **96/84 UV; 252/300**

[56] **References Cited**

**UNITED STATES PATENTS**

3,253,921 5/1966 Sawdy..... 96/73  
 3,004,896 10/1961 Heller et al..... 252/300

**FOREIGN PATENTS OR APPLICATIONS**

879,144 Great Britain..... 96/84

*Primary Examiner*—Ronald H. Smith

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[57] **ABSTRACT**

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-phenolbenzo-triazole, the benzo ring of which is substituted with at least 1 alkoxy group.

**2 Claims, No Drawings**

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### PHOTOGRAPHIC LAYERS WHICH CONTAIN UV-ABSORBERS

This is a continuation of application Ser. No. 878,220, filed Nov. 19, 1969, and now abandoned.

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

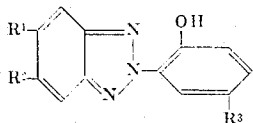
Numerous compounds are known which absorb light in the UV-region of the spectrum and are, therefore, suitable for the production of UV-filters and UV-protective coatings. Such coatings are used in photographic material for increasing the light fastness of colour images. The UV-absorbent compounds should 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 colourless 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 colour 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  $\mu\text{m}$  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. None of these compounds, however, sufficiently satisfies 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 crystallise. Derivatives of this type which can easily be incorporated in photographic layers, which are described in German Patent 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.

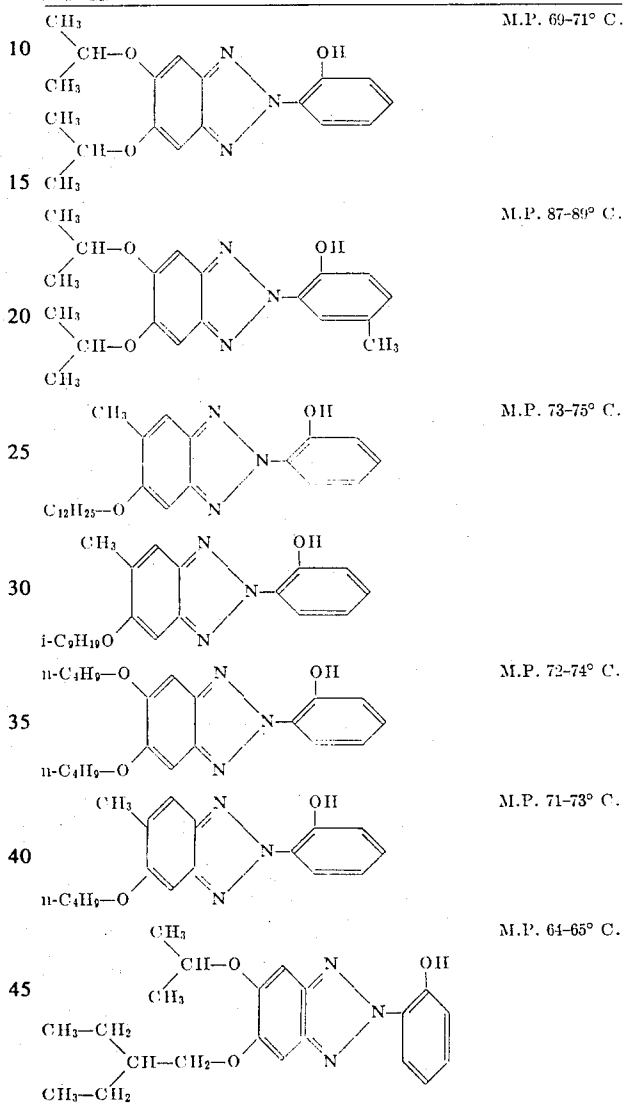
It is among the objects of the present invention to produce photographic layers which contain UV-absorbers, which must be easily incorporated in these layers, and as far as possible, must absorb only in the UV-region of the spectrum.

We now have found that compounds of the following formula are excellently suitable as UV-absorbers in photographic materials



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in which  $R^1$  and  $R^2$  are hydrogen, alkyl or alkoxy groups with up to 18 C-atoms, preferably with up to four C-atoms, in particular branched alkyl or alkoxy groups, but at least one of the substituents  $R^1$  and  $R^2$  is an alkoxy group;  $R^3$  stands for hydrogen or alkyl with up to five carbon atoms in particular methyl. Particular utility is exhibited by the following compounds:



Compounds to be used according to the invention are prepared in known manner. With compound 1, for example, 4-nitro-1,2-diisopropoxybenzene may be used, which can be obtained in known manner from 1,2-diisopropoxybenzene by nitration. The nitro compound is hydrogenated over Raney nickel and is then added in known manner to diazotised o-aminophenol. 4,5-diisopropoxy-2-amino-phenylazo-2'-hydroxy-benzene is obtained. Ring closure so as to form 5,6-di-isopropoxy-2-(2'-hydroxy-phenyl)-benzotriazol (compound 1) is carried out, e.g. by treatment with copper sulfate in methanolic solution in the presence of ammonia. Compound 1 can be recrystallized from propanol.

The other compounds can be prepared satisfactorily in a similar manner.

The UV-absorbent compounds which are to be used according to the invention have considerable advantages over known similar compounds. The exception-

ally advantageous absorption properties are unexpected. The absorption curve drops steeply towards the longwave region and is shifted by about 10 nm towards the shorter wavelengths compared e.g. with 2-o-

hydroxyphenyl-benzotriazole UV-absorbent compounds which only contain alkyl groups as the substituents.

The UV-absorbent compounds are particularly readily soluble in those particular solvents which are used as so-called oil forming agents in the production of 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 particularly with those of the 2-hydroxyphenyl-benzotriazole series.

The UV-absorbent compounds do not deleteriously influence 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 benzotriazole 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 10 to 50 percent by weight, based on the binder in the layer, has proved to be sufficient.

When using multi-layered color photographic materials, the concentration 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 these protective layers which contain UV-absorbent compounds is 2 to 5  $\mu\text{m}$ .

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 color-less. 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

A solution of 30 g of compound 1, 3 g of bis-(2-ethyl)-hexyl-sulfosuccinate and 15 g of a mixture of highly branched aliphatic carboxylic acids having 15 to 19 C-atoms and 30 g of ethanol and 30 g of methylene chloride are emulsified at 50°C with 1 liter of a 10 percent gelatin solution which contains 50 ml of a 10 percent saponin solution as wetting agent.

A mixing siren is used as the emulsifying apparatus. The dissolved UV-absorbent compound is introduced near to the motor of the mixing siren through a tube. After the addition of the UV-absorbent compound, stirring is continued for another 15 minutes.

The above mixture is applied onto a processed multi-layer colorphotographic material bearing a color-image in true colors (layer thickness 3  $\mu\text{m}$ ).

The light fastness of the color photographic images is greater by a factor of 10 than that found when testing the protective layer which contains no UV-absorbent compound.

#### EXAMPLE 2

A casting solution for a layer containing UV-absorbent compound is prepared as follows:

A solution of 30 g of compound 6, 3 g of (2-ethyl)-hexyl-ester of sulfosuccinic acid and 15 g of a branched aliphatic carboxylic acid having 15 to 19 C-atoms in 60 g of dimethyl-formamide and 15 g of methylene chloride is emulsified at 50°C. with 1 liter of a 10 percent gelatin solution which contains 50 ml of a 10 percent saponin solution as wetting agent.

A commercial multi-layered color photographic material is coated with the above casting solution as described in Example 1. The light fastness of the finished image is greater by a factor of about 10 than that of an untreated photographic material.

#### EXAMPLE 3

The same procedure is used as described in Example 1 but in the casting solution for the layer which contains the UV-absorbent compound, the mixture of branched fatty acids is replaced by an equal quantity of dibutyl phthalate.

Equally good results are obtained from this procedure after suitable processing.

#### EXAMPLE 4

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:

Test 1: Into 1 liter of a 10 percent aqueous gelatin so-

lution which contains 2 ml of a 50 percent aqueous solution of phenol is emulsified at a temperature of 55°C during a time of 5 minutes, a solution of 100 g of a compound 7, 5 g of the bis-(2-ethyl)-hexyl ester of sulfosuccinic acid in 200 g of ethyl acetate. After emulsification it is stirred for 5 minutes and the ethyl acetate evaporized.

cessed 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.

TABLE

Test	After emulsifying	After evaporation of the solvent	Storage at 40° C.				Storage in the refrigerator at 5° C.	
			4 hours	20 hours	2 days	5 days	2 days	5 days
1.....	No.....	No.....	No.....	No.....	No.....	Beginning precipitation.	No.....	No.....
2.....	No.....	No.....	No.....	No.....	No.....	No.....	No.....	No.....
3.....	Beginning precipitation.	Beginning precipitation.	Advancing precipitation.	Strong precipitation.	Strong precipitation.	Strong precipitation.	Beginning precipitation.	Advancing precipitation.
4.....	No.....	No.....	Beginning.....	Beginning.....	Advancing.....	Strong.....	Beginning.....	Advancing.....

Test 2: The test is performed in the same manner with the exception that the ethyl acetate solution contained additionally 100 g of tricresyl phosphate.

Test 3: The test is performed in the same manner as test 1 with the exception that the ethyl acetate solution contained 400 g of the solvent and with 2-(2'-hydroxy-3', 5'-di-tert.-amylphenyl)-benzotriazol instead of compound 7.

Test 4: The test is performed in the same manner as test 2 with the exception that the ethyl acetate solution contained 400 g of the solvent and with the comparison compound of test 3 instead of compound 7.

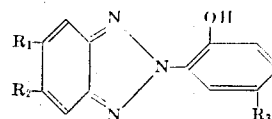
The above samples were stored at 40°C and in the refrigerator and the behaviour of the emulsions with respect to the precipitation of the UV-absorbing agents is observed. Results are shown in the following table.

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 pro-

What is claimed is:

1. A photographic material comprising at least one layer containing a silver halide emulsion and incorporated in a layer of said photographic material a UV-absorbing compound of the following formula:



in which

R<sub>1</sub> and R<sub>2</sub> are, independently of each other, branched propoxy or butoxy groups;

R<sub>3</sub> is hydrogen or an alkyl group having up to five C-atoms.

2. The photographic material of claim 1, wherein the UV-absorbent compound is contained in said layer in an emulsified form as a solution in a high boiling solvent.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,754,919 Dated Aug. 28, 1973

Inventor(s) Johannes Sobel et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Front page, the heading [75] should read as follows:  
-- Inventors: Johannes Sobel, Leverkusen, Germany;  
Fritz Nittel, Koeln 80, Germany; Wolfgang Himmelmann,  
Koeln 80, Germany; Willibald Pelz, Opladen, Germany. --

Signed and sealed this 30th day of April 1974.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents

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