Aug. 3, 1954 G. W. SAWDEY 2,685,512

PHOTOGRAPHIC ELEMENT CONTAINING ARYLIDENE DERIVATIVE OF FLUORENE

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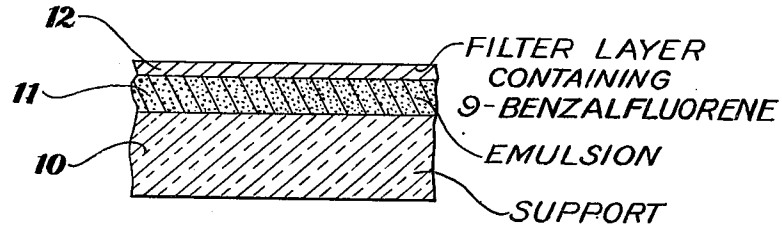

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PHOTOGRAPHIC ELEMENT CONTAINING ARYLIDENE DERIVATIVE OF FLUORENE

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5 Claims. (Cl. 95—8)

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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 effected 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 ultraviolet absorbing compounds can be used to overcome the afore-mentioned difficulties, without attending harmful action by the ultraviolet absorbing compound itself.

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

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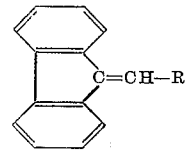
color materials which have been protected against the harmful effects of ultraviolet radiation. Other objects will become apparent from a consideration of the following description.

The ultraviolet absorbing compounds which I propose to employ in my invention are advantageously represented by the following general formula:



wherein R represents an aryl group, such as phenyl, o-, m-, and p-tolyl, o-, m-, and p-chlorophenyl, o-, m-, and p-bromophenyl, o-, m-, and p-methoxyphenyl, o-, m-, and p-sulfophenyl, o-, m-, and p-carboxyphenyl, etc.

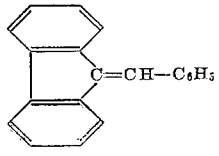
The accompanying drawing illustrates schematically a cross-sectional view of a sensitive photographic element having an ultraviolet filter layer containing one of the compounds represented by the above general formula. These ultraviolet absorbing compounds can be incorporated in the photographic element in a variety of ways, depending on the ultimate use of the photographic element and the degree of protection desired. Advantageously, the ultraviolet absorbing compound can be dissolved or dispersed in a solvent medium together with a colloidal binder, such as gelatin, cellulose esters (e. g. cellulose acetate, etc.), synthetic resins (e. g. polyvinyl acetals, hydrolyzed polyvinyl acetate, etc.), etc., and the resulting mixture coated over the light-sensitive layer of the photographic element. Where the photographic element is a material intended for use in color photography, the ultraviolet filter layer 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 the red sensitive layers. If desired, the material useful in absorbing the ultraviolet radiation can be incorporated directly in the light-sensitive emulsion instead of. or in addition to, being present in another layer. The amount of ultraviolet absorbing compound used can be varied, depending upon the effect desired and the use to which the material is to be put.

The support of the photographic element can be transparent, such as a cellulose ester support, for the support can be opaque, such as a paper support. Other supports, such as glass, metal, etc., can be employed, if desired.

The following example will serve to illustrate the manner whereby the compounds represented by the above general formula can be prepared.

Example 1



2.0 g. (0.087 g. atom) of sodium were dissolved in 100 cc. of absolute ethanol. To this solution were added 10.0 g. (0.060 mole) of fluorene (92% purity) and 6.0 g. (0.57 mole) of benzaldehyde.

The reaction mixture was allowed to stand for two days, at the end of which time the solution was evaporated to crystallization. The crude product was twice recrystallized from ethanol. There was thus obtained a cream-white crystalline powder having a melting point of 74–75° C., in a yield of approximately 65% of the theoretical quantity. Analysis of the product gave the following results:

Calculated for $C_{20}H_{14}$: Carbon, 84.4%; hydrogen, 5.6%. Found: Carbon, 84.0%; hydrogen, 5.6%.

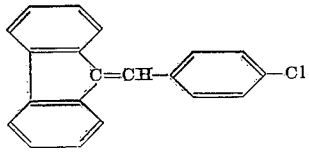
The above method is similar to that described by Thiele in "Berichte," vol. 33, pages 852–3.

The following example briefly describes the manner of using the compound obtained in Example 1 in a photographic element.

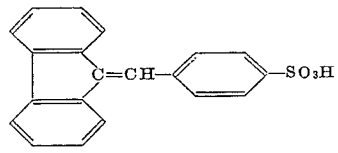
Example 2

The compound obtained in Example 1 above was dissolved in tricresyl phosphate in a 1:3 ratio, and this solution was mixed with a gelatin dispersion which was coated on film. A separate coating on paper was also made. After one week's exposure on an east window, the coatings showed neither fading nor print-out. A square of the film coating was placed over a paper coating containing a standard magenta coupler, and this was exposed in a similar manner to ultraviolet radiation. No fading nor print-out was observed in the magenta layer.

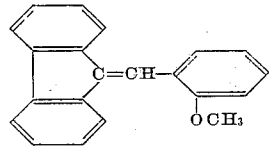
In a manner similar to that described above, other compounds selected from those represented by the above general formula can be employed. The following are typical compounds which can be employed in my invention.



9-p-chlorobenzalfluorene



9-p-sulfobenzalfluorene



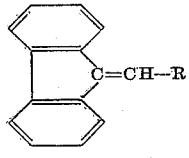
9-o-methoxybenzalfluorene

The accompanying drawing illustrates schematically a cross-sectional view of a photographic element containing a layer having incorporated therein 9-benzalfluorene, which is representative of the ultraviolet absorbing agents which can be employed in my invention. As shown in the single figure of the drawing, a support 10 of any suitable material, such as cellulose acetate or paper, having thereon a sensitive emulsion layer 11 is coated with a filter layer 12 having incorporated therein 9-benzalfluorene, or some other ultraviolet absorbing compound selected from those represented by the above general formula. 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.

In those cases where the ultraviolet absorbing compound contains a solubilizing group, such as carboxyl, hydroxyl, sulfo, etc., the compound can be incorporated into the photographic element by bathing the photographic element in an aqueous solution of the ultraviolet absorbing compound. When treating the photographic element in this manner, the ultraviolet absorbing compound is concentrated mostly in the outside gelatin overcoat, although it is also present in the remaining layers containing gelatin. The ultraviolet absorbing compound can be incorporated in the photographic element during the preparation thereof, or the ultraviolet absorbing compound can be incorporated in the finished and processed element in those cases where the element has an opaque support, such as paper, in which case, the ultraviolet absorbing compound functions primarily as a stabilizer for the images subject to fading upon exposure to ultraviolet radiation. Such would be the case where the photoraphic element is a multilayer material.

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

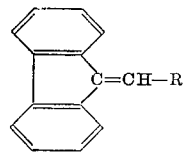
1. A photographic element having thereon a photographic silver halide emulsion layer and in one of the layers of said element a compound selected from those represented by the following general formula:



wherein R represents an aryl group.

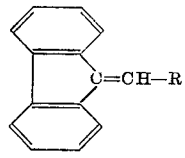
2. A photographic element comprising a support, at least one photographic silver halide emulsion layer, and incorporated in one of the layers of said photographic element a compound

selected from those represented by the following general formula:



wherein R represents an aryl group.

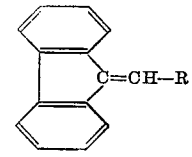
3. A photographic element comprising a support, at least one photographic gelatino-silver halide emulsion layer, and coated over said photographic gelatino-silver halide emulsion layer a gelatin layer containing a compound selected from those represented by the following general formula:



wherein R is an aryl group.

4. A photographic element comprising a support, at least one photographic gelatino-silver halide emulsion layer, and coated over said photographic gelatino-silver halide emulsion layer a gelatin layer containing 9-benzalfluorene.

5. A photographic element comprising a paper support, at least two photographic gelatino-silver halide emulsion layers differentially sensitized to light, and outermost with respect to at least one of said light-sensitive layers, a gelatin layer containing an ultraviolet absorbing compound selected from those represented by the following general formula:



wherein R represents an aryl group.

No references cited.