United States Patent Office 3,352,681 Patented Nov. 14, 1967



3,352,681

# COLOR PHOTOGRAPHIC LIGHT-SENSITIVE ELEMENT CONTAINING ULTRAVIOLET ABSORBER

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No Drawing. Filed Sept. 12, 1966, Ser. No. 578,444
Claims priority, application Japan, Sept. 13, 1965, 40/55,636
10 Claims. (Cl. 96—84)

The present invention relates to color photography and more particularly to a color photographic light-sensitive element containing an ultraviolet absorber.

A color photographic image is generally inferior in light fastness to a black and white photographic image since the former is composed of dyes formed by color developments. It is natural to attempt to remove this drawback by eliminating ultraviolet rays having a large role in destroying the dyes by utilizing an ultraviolet absorber, and as a practical manner for using such an ultraviolet absorber there have generally been adopted the following two methods. In the one method, a print or a transparent positive picture is, after development, coated or impregnated with an ultraviolet absorber while in the other method an ultraviolet absorber is preliminarily incorporated in a light-sensitive element at the production thereof such that the ultraviolet absorber is not washed out at development processing. From the user's convenience the latter method is preferable and the instant invention is also concerned with the latter type.

The ultraviolet absorber to be employed for the purpose must be provided with the following properties:

(1) It absorbs effectively ultraviolet rays of 300–400 mμ in wave length but does not absorb visible rays of longer than 420 mμ.

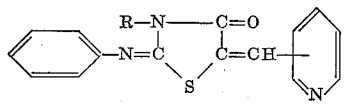
(2) It is not washed out or discolored by development processing.

(3) The ultraviolet absorber itself is not colored and the ultraviolet absorbing power thereof is not reduced by light exposure.

(4) It does not give a bad influence on the photographic light-sensitive element containing it at the preparation thereof, during preservation and at development.

Hitherto, various compounds have been known as ultraviolet absorbers, but a few of them satisfy the above-mentioned four factors, that is, many of the conventionally available ultraviolet absorbers are washed out during development. Several types of ultraviolet absorbers also affect adversely the photographic characteristics of light-sensitive emulsions.

The inventors have found that the above-mentioned factors are satisfied when the 2-phenylimino-3-alkyl-5-pyridylmethylene thiazolidone compound shown by the general formula.



wherein R represents an alkyl group having from 8 to 18 carbon atoms, is dissolved in a non-volatile solvent such as dibutyl phthalate and the resulting solution is incorporated in at least one coating layer of a photographic light-sensitive element as an emulsified dispersion thereof.

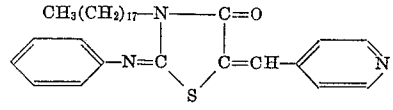
The coating layer in which the above-mentioned compound is incorporated may be a gelatin layer containing silver halide particles, that is, a light-sensitive silver halide layer or may be an intermediate layer or a protective layer containing no silver halide particles. Further, in



the light-sensitive element which will be exposed from the back side of the element, that is, from the support side as a transparent positive picture, the compound may be effectively incorporated in a subbing layer or a coating layer on the back side of the support. Moreover, if necessary, the compound in this invention may be incorporated in more than two coating layers. As these coating layers, a gelatin layer is most suitable, but the layer may contain other high molecular materials.

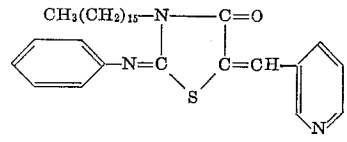
The typical examples of the compound included in the above-mentioned general formula to be used in this invention are shown below but it should be understood that the compounds to be used in this invention as ultraviolet absorbers should not be limited to these.

Compound 1



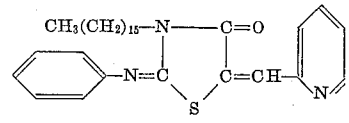
M.P. 67–68° C., λ max. 329 mμ, ε: $2.69\times10^4$,

Compound 2



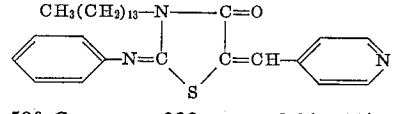
M.P. 71–72° C., λ max. 329 mμ, ε: $2.16\times10^4$,

Compound 3



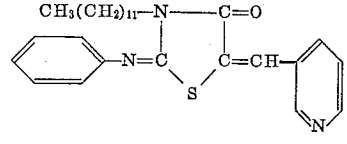
M.P. 107–108° C., λ max. 341 mμ, ε: $2.28\times10^4$,

Compound 4



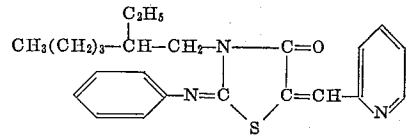
M.P. 57–58° C., λ max. 329 mμ, ε: $2.01\times10^4$,

Compound 5



M.P. 66° C., λ max. 329 mμ, ε: $2.16\times10^4$, and

Compound 6



M.P. 123–124° C., λ max. 341 mμ, ε: $2.27\times10^4$.

Such compounds may be prepared by condensing 2-phenylimino-3-alkylthiazolidone obtained by the reaction of an N-alkyl-N'-phenylthiourea and a monochloroacetic acid ethyl ester with pyridine aldehyde in ethanol under the presence of pyridine as the catalyst. The values of the elemental analysis about carbon, hydrogen and nitrogen almost coincide with the theoretical values. The values of λ max. and ε are ones measured in ethanol solution.

The use of a compound similar to the compound of this invention, that is, the use of 2-phenylimino-3-alkyl-5-

benzalthiazolidone is disclosed in U.S. Patent 2,739,888, but the compound of this invention is superior to the known compound in fastness to light. That is, as will be clear from the experimental results shown below, only 5–10% of the compound used in the present invention is decomposed under the same conditions by which 30% of the prior art compound is decomposed. It is a very important factor that an ultraviolet absorber itself is stable to light exposure for a long period of time and hence the compound used in this invention can be considered to have novelty and utility.

It has been confirmed by the following experiment that the compound used in this invention is excellent as the ultraviolet absorber for color photographic light-sensitive elements.

Fifty grams of any of above-illustrated Compounds 1–6 or the known ultraviolet absorber, 2-phenylimino-3-cetyl-5-benzalthiazolidone was added in 50 g. of dibutyl phthalate at a temperature not higher than 80° C. and the resulting solution was dispersed in a mixed solution of 1 kg. of a 10% gelatin solution and 100 g. of a 5% solution of sodium alkyl-benzene sulfonate in a colloid mill for 15 minutes, whereby a uniform dispersion of the ultraviolet absorber having an average particle size of about 0.3 micron was obtained.

Thereafter, the dispersion was applied to a transparent film base of triacetyl cellulose and dried. From the thus prepared film, the extent of the washing-out of the compound was detected. The results are as follows:

| | Time | Reduction percent in transmission density (370 mμ) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Comp. 1 | Comp. 2 | Comp. 3 | Comp. 4 | Comp. 5 | Comp. 6 |
| Water-washing | 30 min | 0 | 0 | 0 | 0 | 0 | 0 |
| Do | 2 hr | 0 | 0 | 0 | 0 | 0 | 1 |
| 3% $Na_2CO_3$ soln | 30 min | 0 | 0 | 0 | 0 | 0 | 0 |
| All photographic processing | 47 min | 1 | 2 | 1 | 2 | 2 | 3 |

From the results, it is clear that the above-mentioned Compounds 1–6 were not dissolved out of the gelatin layers in the photographic processing step and water-washing, fixing, bleach-fixing, water-washing, hardening, water-washing and drying or the steps of development, fixing, water-washing, bleaching, water-washing, fixing, water-washing, hardening, water-washing, and drying.

Then, these samples were exposed to a xenon tester for about 20 hours and thereafter the decomposition percentages of the compounds were measured, the results of which are shown in table below. In addition, the xenon tester used in this experiment is a light source having a spectral distribution of energy and intensity simlar to those of a sun beam.

DECOMPOSITION PERCENTAGE

| Compound | Comp. 1 | Comp. 2 | Comp. 3 | Comp. 4 | Comp. 5 | Comp. 6 | Known comp. |
|---|---|---|---|---|---|---|---|
| Percentage | 5 | 7 | 10 | 5 | 10 | 7 | 30 |

That is, as clearly evident from the experimental results shown in the above table, 30% of the known compound was decomposed under the condition, while only 5–10% of the compound in this invention was decomposed under the same condition.

The compound of this invention may be used alone or as a mixture thereof and there is no particular limitation about the proportion thereof to be incorporated in coating layers but 1–40 mg., in particular, 3–20 mg. per 100 sq. cm. of the area of coating layer is suitable. Furthermore, by the addition of the compound used in this invention, the preferable photographic properties of the photographic light-sensitive element are not reduced.

*Example 1*

A blue-sensitive silver iodo-bromide emulsion containing a yellow coupler, 3,5-dicarboxy-α-(4-stearoylamidobenzoyl)acetanilide was applied to baryta paper. The coupled had been added in the emulsion as an alkaline aqueous solution thereof. Thereafter, a green-sensitive silver chloro-bromide emulsion containing a magenta coupler, 1 - (3-sulfo-3-phenoxyphenyl)-3-stearoyl-5-pyrazolone was applied to the thus formed emulsion layer and further a red-sensitive chloro-bromide emulsion containing a cyan coupler, N-n-octadecyl-1-hydroxy-4-sulfo-2-naphthamide was applied on the layer. On the thus formed red-sensitive layer there was further coated a protective layer containing the above-mentioned compound of this invention in 20 mg./100 sq. cm. as the emulsified dispersion by the above-mentioned process.

The thus prepared color photographic printing paper was exposed and developed in a developer containing N,N' - diethyl-p-phenylene diamine followed by water-washing, fixing, water-washing, bleach-fixing, water-washing, hardening, water-washing and drying. Thus processed color photographic printing paper was exposed to a xenon tester for 20 hours and the reduction in percentage of the color image density was measured, the results of which are shown in the following table.

FADING PERCENTAGE OF COLOR IMAGE

| Color image | None | Comp. 1 | Comp. 2 | Comp. 3 | Comp. 4 | Comp. 5 | Comp. 6 |
|---|---|---|---|---|---|---|---|
| Cyan, percent | 40 | 15 | 20 | 23 | 15 | 20 | 23 |
| Magenta, percent | 20 | 0 | 2 | 3 | 0 | 2 | 3 |
| Yellow, percent | 40 | 15 | 18 | 20 | 15 | 18 | 20 |

As clear from the experiment, the fading of color image in the case of incorporating no ultraviolet absorbent in the protective layer was prevented or reduced by the use of the ultraviolet absorbent of this invention.

When the ultraviolet absorber of this invention was incorporated in the intermediate layer between the first light-sensitive emulsion layer and the second light-sensitive emulsion layer instead of incorporating it in the protective layer, the fading of color images formed in the light-sensitive layers under the intermediate layer containing the ultraviolet absorber was prevented as anticipated. Further, almost the same results were obtained when a film base was used as the support instead of the baryta paper.

*Example 2*

The dispersion of the compound the same as in Example 1 was added in the first emulsion layer in Example 1, that is, in the red-sensitive silver chlorobromide emulsion layer. The content of the compound was 5 mg./100 sq. cm. The magenta layer of the second emulsion layer and the yellow layer of the third emulsion layer were as in Example 1.

The thus prepared multi-layer color photographic light-sensitive element was exposed and subjected to development, water-washing, fixing, water-washing, bleach-fixing, water-washing, hardening, water-washing, and drying. Thereafter, the thus processed element was exposed to a xenon tester for 20 hours and the reduction in percentage of color image density was measured, the results of which are shown in the following table:

FADING PERCENTAGE OF COLOR IMAGE

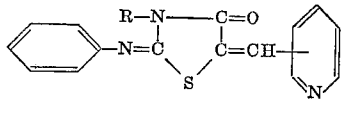
| Color image | None | Comp. 1 | Comp. 2 | Comp. 3 | Comp. 4 | Comp. 5 | Comp. 6 |
|---|---|---|---|---|---|---|---|
| Cyan, percent | 40 | 25 | 30 | 35 | 25 | 30 | 35 |
| Magenta, percent | 20 | 0 | 20 | 3 | 0 | 2 | 3 |
| Yellow, percent | 40 | 15 | 18 | 20 | 15 | 18 | 20 |

As clear from the experimental results the ultraviolet prevention effect could be obtained also in the case of incorporating the dispersion of the compound of this invention directly in a silver halide emulsion.

Further, in the case where the ultraviolet absorber was incorporated in a photographic light-sensitive emulsion layer, the photographic properties of the photographic light-sensitive emulsion was not infected by the compound.

What is claimed is:

1. A color photographic light-sensitive element having incorporated in at least one layer of photographic light-sensitive emulsion layers, intermediate layers, protective layers, subbing layer and backing layer of a support a compound represented by the general formula



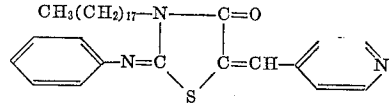
wherein R represents an alkyl group having from 8 to 18 carbon atoms.

2. The color photographic light-sensitive element according to claim 1 wherein said compound is incorporated in said layer by adding the compound in the coating solution for the layer as a solution thereof in a non-volatile solvent.

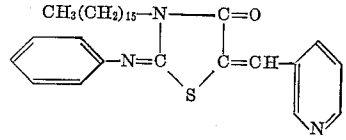
3. The color photographic light-sensitive element according to claim 2 wherein said non-volatile solvent is dibutyl phthalate.

4. The color photographic light-sensitive element according to claim 1 wherein the proportion of said compound is 1–40 mg. per 100 sq. cm. of the area of the layer.

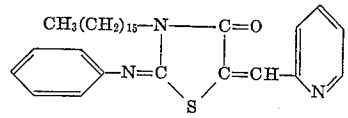
5. The color photographic light-sensitive element according to claim 1 wherein said compound is



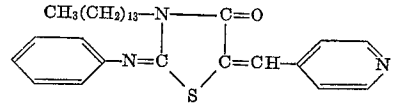
6. The color photographic light-sensitive element according to claim 1 wherein said compound is



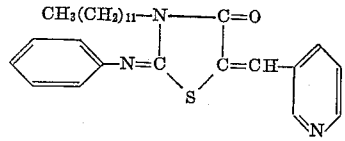
7. The color photographic light-sensitive element according to claim 1 wherein said compound is



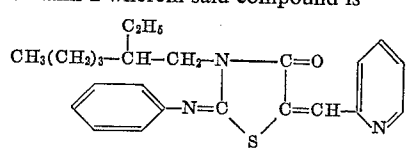
8. The color photographic light-sensitive element according to claim 1 wherein said compound is



9. The color photographic light-sensitive element according to claim 1 wherein said compound is



10. The color photographic light-sensitive element according to claim 1 wherein said compound is



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