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COLOR PHOTOGRAPHIC PROCESS TO PREVENT DISCOLORATION BY ULTRAVIOLET LIGHT

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No Drawing. Continuation of abandoned application Ser. No. 707,481, Feb. 23, 1968. This application Mar. 16, 1971, Ser. No. 124,936

Claims priority, application Japan, Feb. 23, 1967, 42/11,670

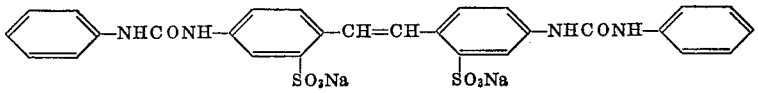
Int. Cl. G03c 7/00

U.S. Cl. 96—56 13 Claims

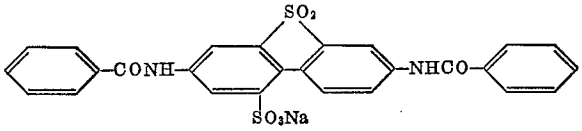
ABSTRACT OF THE DISCLOSURE

A method of processing a color photographic light sensitive material which comprises contacting it, after exposure and development, with a processing solution containing at least one ultra-violet absorbent selected from the group consisting of

Compound 1

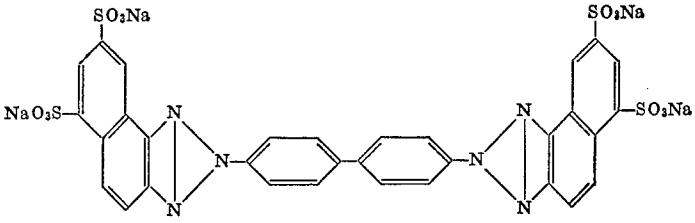


Compound 2



and

Compound 3



This application is a continuation of application Ser. No. 707,481 filed Feb. 23, 1968, now abandoned.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The present invention relates to a method of processing color photographic light sensitive materials and, in particular, to a method for processing color photographic light sensitive materials to prevent the color images thus formed from being faded or discolored by ultraviolet light.

(2) Description of the prior art

In general, when a color photographic image obtained by color developing a color photographic light sensitive material after light exposure is irradiated by ultraviolet light, the color image is faded or discolored in accordance

with the intensity and the wavelength of the ultraviolet light.

Also, if there remain in the photographic emulsion layers after the formation of color images materials other than those composing the color images, such as, couplers, the remaining materials are attacked by ultraviolet light to leave undesirable color stains in the finished photographic emulsion layers.

It is known that by incorporating preliminarily in at least one layer an ultraviolet absorbent during the preparation of photographic light sensitive materials, the aforesaid bad influences of ultraviolet light on the color images obtained by color development can be prevented. However, it is simple and economical to process a light-exposed color photographic light-sensitive material in a step of the photographic processing process by a solution containing an ultraviolet absorbent whereby the ultraviolet absorbent is applied to the color photographic light-sensitive material.

to prevent the color photographic image, obtained by

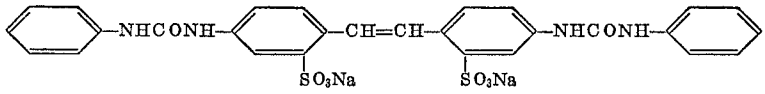
An object of this invention is to provide a method of processing a color photographic light sensitive material color developing a light-exposed color photographic light-sensitive material, from being faded or discolored by ultraviolet radiation. Another object of this invention is to provide a method of processing a color photographic light sensitive material to prevent the formation of color stains caused by the presence in the photographic emulsion layers of materials other than those forming a color photographic image, such as, couplers when they are irradiated by ultraviolet light. Still another object of the present invention is to provide a method of processing a color photographic printing paper for fluorescent-whitening the color-developed color photographic printing paper.

SUMMARY OF THE INVENTION

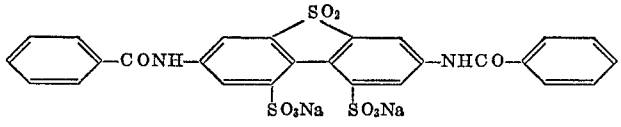
According to the method of this invention, a color photographic light-sensitive material is, after exposure,

processed in a processing solution containing an ultraviolet absorbent represented by the following formula:

Compound 1

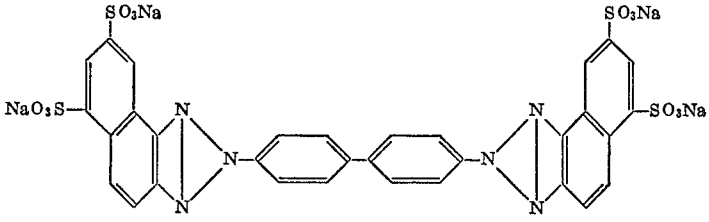


Compound 2



or

Compound 3



The ultraviolet absorbents used in this invention have water-soluble sulfonic acid groups, absorb ultraviolet light rays having wavelengths between 300 mμ and 400 mμ, transmit the light having wavelengths longer than 400 mμ, and are suitable for achieving the aforesaid objects of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In the method of this invention, a color photographic light sensitive material may of course be processed. After light-exposure, and color development, in any processing solution having incorporated therein the above-mentioned ultraviolet absorbent during subsequent necessary processings, after development, or it may be processed, after completion of the color photographic processings, in an additional processing solution containing the aforesaid ultraviolet absorbent.

The ultraviolet absorbent of this invention may be used as an aqueous solution alone or with an inorganic salt. For example, in the case of employing the ultraviolet absorbent together with sodium thiosulfate, the aqueous solution of the both components may be incorporated in a secondary fixing solution after bleaching by a ferricyanide and further when the above-mentioned ultraviolet absorbent is used together with borax, the deviation of the pH of the processing solution containing an aqueous solution of the ultraviolet absorbent alone may be considered.

By processing a color photographic light sensitive material, in particular, a color photographic light sensitive printing paper, after color development, in a processing solution containing the aforesaid ultraviolet absorbent in this invention in any step of the subsequent processings or by processing further a color photographic light sensitive material, after finishing the photographic processing, in an additional processing solution containing the ultraviolet absorbent, an extremely fluorescent-whitened color photographic image is obtained, fading and discoloration of the image by ultraviolet light are prevented, and the image has almost no color stains.

A suitable amount of the ultraviolet absorbent used in this invention is about 0.5–10 g. per liter of the processing solution in which the ultraviolet absorbent is incorporated, although the amount is not limited to this value.

The following are typical examples of the present invention showing the results of preventing fading and discoloration of the color photographic image by ultraviolet irradiation or preventing the formation of color stains by processing the color photographic light sensitive material in a solution containing the aforesaid ultraviolet absorbent, but it shall be understood that the invention is by no means limited only to these examples.

EXAMPLE 1

A color photographic light-sensitive printing paper having a silver halide red-sensitive emulsion layer containing a cyan coupler, a silver halide green-sensitive emulsion layer containing a magenta coupler, a silver halide blue-sensitive emulsion layer containing a yellow coupler, and other subsidiary layers such as intermediate layers were image-exposed and then subjected to conventional photographic processings, such as, color development, stop-fixing, water-washing, bleach-fixing, water-washing, hardening, and water-washing. Thereafter, the printing paper thus processed was processed in an aqueous solution containing 5 g./liter of each of the above shown ultraviolet absorbents for about one minute. The color photographic printing paper thus processed was further exposed to light for twenty hours by using a xenon tester and then the fading percentage, that is, the reduction percentage in each color image density of 1.0 was measured. The results are shown in the following table. The xenon tester used in the experiment was a light source having a spectral distribution and an intensity very similar to sun light.

	Compound			
	1	2	3	None
Cyan image, percent	10	12	11	40
Magenta image, percent	0	2	2	20
Yellow image, percent	10	10	12	40

As is clear from the results, by processing the color photographic light sensitive printing paper in the aqueous solution containing the ultraviolet absorbent in this invention, the fading of the color image by ultraviolet irradiation was markedly prevented. Also, the same results were obtained when a color photographic light sensitive film was processed in the aqueous solution of the ultraviolet absorbent instead of processing the color photographic printing paper.

Moreover, the formation of color stains on the color image of the color photographic light sensitive printing paper processed by the solution containing the ultraviolet absorbent was observed, the result of which is shown in the following table. In the measurement, a xenon tester was used as the light source for ultraviolet light and the extent of the formation of color stains was shown by the increase of blue density in the unexposed portion.

BLUE DENSITY BEFORE AND AFTER EXPOSURE TO XENON TESTER FOR 20 HOURS

	Compound			
	1	2	3	None
Before exposure	0.10	0.10	0.10	0.12
After exposure	0.13	0.13	0.14	0.20

From the above results, it is clear that by the aforesaid processing of this invention, the formation of color stains was effectively prevented. Furthermore, it was confirmed that in the case of processing color photographic light sensitive materials by an aqueous solution containing the ultraviolet absorbent in this invention, the whiteness of the processed color photographic material was remarkably increased as compared with that of a color photographic light sensitive material which was not processed by a solution containing the ultraviolet absorbent of this invention.

The processing temperature in this example was 24° C.

EXAMPLE 2

After exposure, a color photographic printing paper, as in Example 1, was subjected to photographic processings, such as, color development, stop-fixing, water-washing, bleaching, and water-washing and was processed for 2 minutes in an aqueous solution having the following composition followed by water-washing:

	G.
Sodium thiosulfate	80
Sodium sulfite	3
Sodium carbonate (mono-hydrate)	20
Sodium bicarbonate	15
Ultraviolet absorbent of the invention (Compound 1, 2 or 3)	5

Water to make 1 liter.

The color photographic printing paper thus processed was exposed to a xenon tester for 20 hours and then the reduction percentage in the color image density of 1.0 was measured. The results are shown in the following table.

FADING PERCENTAGE OF THE COLOR IMAGE AFTER EXPOSURE TO XENON TESTER FOR TWENTY HOURS

	Compound			
	1	2	3	None
Cyan image, percent	12	13	13	40
Magenta image, percent	0	2	2	20
Yellow image, percent	10	10	12	40

As is clear from the results, by processing color photographic light-sensitive materials in a processing solution containing the ultraviolet absorbent whereby the ultraviolet absorbent of this invention is incorporated in the emulsion layers of the printing paper, the fading of the color photographic image can be markedly prevented. When the process was applied to a color photographic light sensitive film instead of color photographic printing paper, almost the same results were obtained.

Moreover, the stain preventing effects in the case of processing the ultraviolet absorbent of this invention are shown below.

In the experiment, a xenon tester was used as a source of ultraviolet light and the extent of color stains was shown by the increase of the unexposed portions of the color photographic light sensitive material thus processed.

BLUE DENSITY AFTER EXPOSURE TO XENON TESTER FOR TWENTY HOURS

	Compound			
	1	2	3	None
Before exposure	0.11	0.11	0.11	0.13
After exposure	0.14	0.15	0.16	0.20

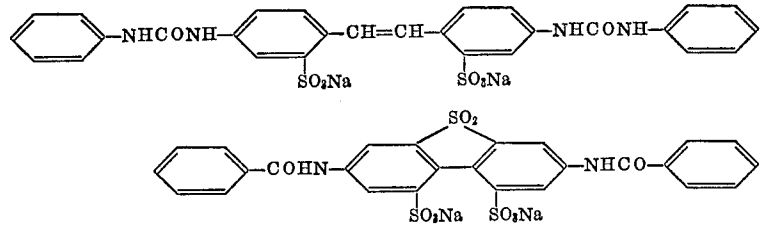
From the experimental results, it became clear that by the process of this invention, the formation of color stains could be markedly prevented. Also, in the case of processing with a solution containing the ultraviolet absorbent in this invention, the whiteness of the color photographic printing paper was markedly increased as compared with with a color photographic printing paper which was not processed in a solution containing the ultraviolet absorbent of this invention.

Furthermore, an aqueous solution of sodium thiosulfate having incorporated therein the ultraviolet absorbent of this invention was as stable as a sodium thiosulfate solution containing no ultraviolet absorbent of this invention. The aqueous solution of sodium thiosulfate containing the ultraviolet absorbent was used as a solution for the secondary fixing of color photographic light sensitive materials to provide a fixing action as well as the fading-prevention and color-stain prevention effects.

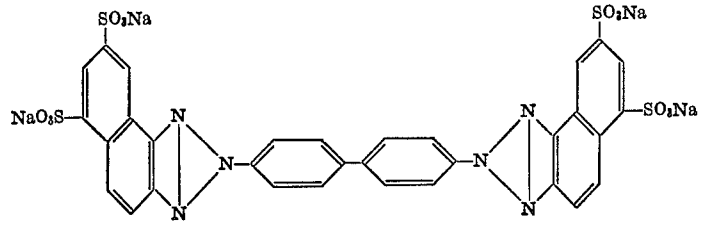
The processing temperature in this example was 24° C.

What is claimed is:

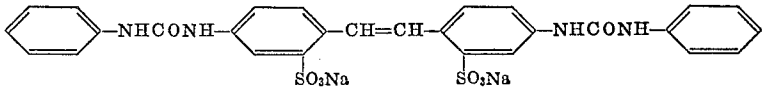
1. In a method of producing color photographic images in a silver halide color material containing a color coupler by exposing the material and color developing the same with a primary aromatic amino developing agent, the improvement which comprises avoiding fading or discoloration due to ultraviolet radiation and the formation of color stains after exposing and color development by contacting the material, after exposure and development, with a processing solution containing at least one ultraviolet absorbent selected from the group consisting of:



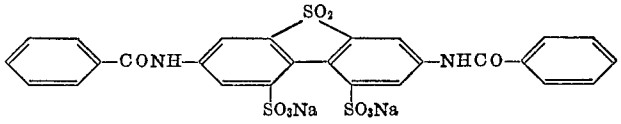
and



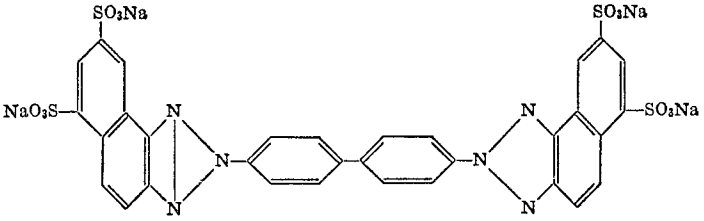
2. The method of claim 1 wherein the absorbent is



3. The method of claim 1 wherein the absorbent is



4. The method of claim 1 wherein the absorbent is



5. The method of claim 1 wherein said processing solution further contains an inorganic salt.

6. The method of claim 5 wherein the inorganic salt is sodium thiosulfate.

7. The method of claim 5 wherein the inorganic salt is borax.

8. The method of claim 1 wherein the amount of absorbent in the processing solution is from about 0.5 to 10 grams per liter of the processing solution.

9. The method of claim 1 wherein the processing solution is an aqueous solution.

10. The method of claim 6 wherein the processing solution is aqueous and is a secondary fixing solution.

11. The method as claimed in claim 1 wherein said color photographic light sensitive material is processed in an aqueous solution containing said ultraviolet absorbent after the completion of the color photographic processing steps.

12. The method as claimed in claim 1 wherein said color photographic light sensitive material is a color photographic light sensitive film.

13. The method as claimed in claim 1 wherein said color photographic light sensitive material is a color photographic paper.

References Cited

UNITED STATES PATENTS

2,483,971	10/1949	Harsh et al.	96—56
2,487,569	11/1949	Mackey	96—56
2,515,122	7/1950	Harsh et al.	96—56
2,647,057	7/1953	Seary et al.	96—56
3,047,390	7/1962	Koerber et al.	96—82

FOREIGN PATENTS

706,792	4/1954	Great Britain	96—22

J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

96—22, 55, 61, 82