United States Patent [19]

Asakawa

[11] **3,881,929**

[45] **May 6, 1975**

[54] **STABILIZING A PHOTOSENSITIVE COMPOSITION CONTAINING AN N-VINYL HETEROCYCLIC COMPOUND AND AN ORGANIC HALOGEN COMPOUND WITH AN AZABICYCLOENE COMPOUND**

[75] Inventor: **Shirow Asakawa**, Kawasaki, Japan

[73] Assignee: **Matsushita Electric Industrial Co., Ltd.**, Kadoma, Japan

[22] Filed: **May 29, 1973**

[21] Appl. No.: **364,315**

[30] **Foreign Application Priority Data**

May 31, 1972 Japan 47-54670

[52] **U.S. Cl.** ..... **96/48 R**; 96/90 R; 260/29.6 HN; 260/29.6 MN; 106/135

[51] **Int. Cl.** **G03c 5/24**

[58] **Field of Search** ..... 96/48 R, 90 R; 260/239, 260/29.6 HN, 29.6 MN; 106/135

[56] **References Cited**

UNITED STATES PATENTS

3,512,976	5/1970	Yamada et al.	96/90 R

FOREIGN PATENTS OR APPLICATIONS

1,542,058	10/1968	France	96/90 R
45-40553	12/1970	Japan	96/90 R
45-40554	12/1970	Japan	96/90 R

Primary Examiner—Won H. Louie, Jr.

[57] **ABSTRACT**

Images on photosensitive compositions made of N-vinyl heterocyclic and organic halogen compounds are stabilized in a solution of an azabicycloene compound such as 1,5-diazabicyclo [4,3,0] nonene-5 or 1,5-diazabicyclo [5,4,0] undecane-5-one. The stabilizing effect by azabicycloene can be enhanced by adding a heavy metal salt of a surface active agent to the solution.

7 Claims, No Drawings

STABILIZING A PHOTOSENSITIVE COMPOSITION CONTAINING AN N-VINYL HETEROCYCLIC COMPOUND AND AN ORGANIC HALOGEN COMPOUND WITH AN AZABICYCLOENE COMPOUND

This invention relates generally to a photographic composition. More particularly, it relates to a photographic image stabilizer used for stabilizing images obtained with organic photosensitive compositions comprising N-vinyl heterocyclic and organic halogen compounds.

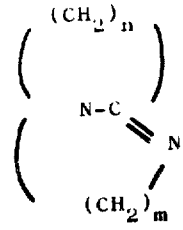
Photographic images produced in an organic photosensitive coating on baryta paper are liable to color change when subjected to daylight exposure for a period of 3 to 7 days. During this period, a yellow-to-brown color change would take place in the lightstruck areas, and a further exposure to daylight would turn the whole areas to brown. Such color change is detrimental to the preservation of photographic images for an extended period of time.

Color change may be attributable to a number of factors which include photo-oxidization of dyes produced upon exposure to light, subsequent photoreaction of the unexposed areas, and a subsequent photo-reaction of unreacted substances which may be present in the dyes. Color change may also depend on the amount of organic halogen compounds present in the light-exposed areas.

For purposes of stabilizing images, additives and stabilizers have been proposed which include peroxides (U.S. Pat. No. 3,544,320), aldehyde-$NaHSO_3$ (U.S. Pat. No. 3,503,742), Na_2SO_3 and $NaHSO_3$ (U.S. Pat. No. 3,512,976) and various mixtures thereof (U.S. Pat. No. 3,544,322). These stabilizers, however, are still unsatisfactory in terms of its quality due to inherent color change.

It is accordingly an object of the present invention to provide an improved image stabilizer which, when applied to light-exposed areas of a photosensitive film, decomposes unreacted alkylhalides which may be present in the film to render them insensitive to further exposure to light.

In accordance with a first preferred embodiment of the invention, the image stabilizer comprises as its main constituent an azabicycloene compound of a cyclic amidine expressed generally by the following formula:



where *m* and *n* are integers from 2 to 6. The image stabilizer according to the invention is obtained by dissolving 0.5 to 20% by weight of the azabicycloene compound into an aqueous solution of, for example, about 20% polyvinyl alcohol. A preferred value of the azabicycloene content in the solution is from 4 to 10% by weight. Examples of the azabicycloene compounds employed in the practice of the present invention are 1,5-diazabicyclo [5,4,0] undecane-5 ene and 1,5-diazabicyclo [4,3,0] nonene-5. These azabicycloene compounds may be dissolved either in water, in an

aqueous solution containing a water-soluble resin or a polymer dissolving organic solvent organic. The light-exposed film may be dipped into the solution or it may be sprayed or wiped with the solution and the solvent is then removed by drying the film in the ambient atmosphere. These azabicycloene compounds are strongly alkaline and therefore they serve to decompose organic halogen compounds present in the light-exposed areas as intermediates of a photo-reaction to thereby stabilize the images formed. The desensitizing compounds would allow the whiteness of background areas to increase, which would otherwise turn to light yellow-green. This could result in an increase in the image contrast. These azabicycloene compounds also have a desensitizing effect on this background areas by increasing their whiteness while penetrating deeply into the photosensitive composition with the aid of a heavy metal salt of a surface active agent which will be described hereinbelow. The desensitizing effect is enhanced by heating the film at a temperature of about 50°C for a period of about 30 seconds.

The aforementioned water soluble resin may be natural high polymers such as gelation and agar-agar, or polyvinyl alcohol, polyethylene glycol, polyacrylamide, polyvinylpyrrolidone and polyacryl acid. The organic solvent may be, for example, alcohol, acetone, tetrahydrofuran, dimethylformamide, etc. As polymers dissolved in one of the above-stated organic solvents, such substances as polyacrylate, polyvinyl compounds, polycondensated compounds including polyamid derivatives may be used.

In a second preferred embodiment, the present invention contemplates the use of other compounds as additives to the azabicycloene compounds such as a heavy metal salt of a surface active agent such as sulfate, sulfonate, or phosphate. The surface active agent (usually a sodium salt) enhances the desensitizing effect when added to the image stabilizer of a photosensitive composition containing a water-soluble resin such as gelatin, because the surface active agent serves to swell the gelatin, thus allowing the azabicycloene compound to penetrate deep into the composition. The desensitizing effect can be further enhanced by the use of a heavy metal salt such as, for example, a zinc, tin or an iron salt. In the practice of the invention, the additive to the azabicycloene compounds may preferably be heavy metal laurylsulfate, oleylsulfate, stearylsulfate, laurylsulfonate, dibutylnaphtalenesulfonate, dodecylbenzenesulfonate, oleyletherphosphate and laurylphosphate. More preferably, the additive may be Zn-dibutyl-naphthalenesulfonate or stannous sulfonate. These additives are used in a concentration of about 0.5 to 20 weight percent in the solvent. Synthesis of the azabicycloene compounds suitable for the invention is known as briefly described hereinafter, and the above-mentioned preferred two azabicycloene compounds are disclosed by Aldrich Co. W. Reppe et al in "Annalen de Chemie," Vol. 596, p. 210(1950) and by H. Oediger et al in "Chemische Berichte," Vol. 99, p. 2012 (1966) where the synthesis of azabicycloene compounds is reported. For example, 1,5-diazabicyclo(4,3,0)nonene-5 is prepared from pyrrolidone. In the first place, pyrrolidone is reacted with acrylonitrile by heating in the presence of potassium hydroxide and hydroquinone. The product is acidified with hydrochloric acid and then concentrated under a reduced pressure to give 1-(2-cyanoethyl)-pyrrolidone. The thus ob-

tained nitrile is dissolved in a mixture of methanol and ammonia and subjected to catalytic reduction by the use of a Ni—Al catalyst, followed by filtration, vacuum concentration and vacuum distillation. The distilled product, which is 1-(3-aminopropyl)-pyrrolidone, is then dissolved in xylol and admixed with p-toluenesulfonic acid, followed by reflux for a dehydration reaction. The final reaction product is subjected to filtration and vacuum distillation.

All the above sulfates, sulfonates and phosphates are well known and are commercially available surface active agents as their respective sodium salts. The heavy metal salts for the stabilizer of the invention are known and can be easily obtained by usual replacement reactions of such sodium salts with, e.g., chlorides of the preferred heavy metals, which reactions require no detailed description for one skilled in general chemistry.

The invention will be described in detail by way of examples.

EXAMPLE 1

First, a photosensitive composition was prepared by mixing and thoroughly stirring the following constituents at high speed:

N-vinylcarbazol	10g.
4-p-dimethylaminostylquinoline	6mg.
Carbon tetrabromide	4g.
Water	80mg.

A sheet of baryta paper was coated with the thus obtained composition.

The photosensitive film thus formed on the baryta paper had a wet thickness of 20 microns. After the coated sheet had been dried, it was subjected to an imagewise exposure by a 250 watt xenon lamp from a distance of about 1 meter for 1 second through a suitable image pattern placed in an intermediate position between the lamp and the film. A second exposure was made by subjecting the film to light of wavelengths above 5300 A from a 100 watt tungsten lamp through an optical filter for a period of 5 seconds. A negative image was produced in the film when it was left under the influence of ambient light radiation.

Second, a stabilizer was prepared by mixing the following constituents and the image produced on the baryta paper was coated with the mixture:

1,5-diazabicyclo [5,4,0] undecane-5-ene	4g.
Polyvinylalcohol	20g.
Water	100ml.

The stabilizer coated film was heated to, and kept at 50°C for 30 seconds. For purposes of comparison, a separate negative image without the stabilizer coating was also produced in the same manner as described above and exposed to the radiation of a 40 watt fluorescent light from a distance of 30cm. The light-exposed areas started to change their color to yellow in 3 days and turned totally brown within one week. In contrast, the stabilizer-coated image did not appreciably change in color even after a one-week exposure to the same fluorescent radiation.

EXAMPLE 2

First, a photosensitive composition was prepared by mixing and thoroughly stirring the following constituents:

N-vinylcarbazol	10g.
Tetrabromoethane	4g.
4-p-dimethylaminostyrylquinoline	6mg.
Gelatin	20g.
Water	8ml.

A sheet of baryta paper was coated with the thus obtained composition. The photosensitive film was subjected to light exposures as described in Example 1 to develop a negative image.

Second, a stabilizer was prepared by mixing the following constituents and the image produced on the baryta paper was coated with the mixture:

1,5-diazabicyclo [4,3,0] nonene-5	8g.
Polyvinylalcohol	20g.
Water	100ml.

A similar desensitizing effect was observed as in Example 1 when the film was subjected to a one-week exposure to the 40 watt fluorescent light.

EXAMPLE 3

The same procedures as in Example 1 were repeated except that the components of the stabilizer were replaced by the following constituents:

1,5-diazabicyclo [4,3,0] nonene	2g.
Zn-dibutyl-naphtalenesulfonate	2g.
Polyvinylalcohol	20g.
Water	40ml.

No appreciable color change was observed after a one-week exposure to the 40 watt fluorescent radiation.

EXAMPLE 4

The same procedures as in Example 2 were repeated except that the components of the stabilizer were replaced by the following constituents:

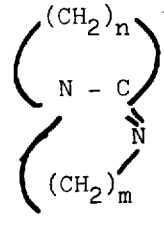
1,5-diazabicyclo [5,4,0] undecane-5-ene	3g.
Stannous sulfosuccinate	3g.
Polyvinylalcohol	5g.
Water	50ml.

No noticeable color change took place after a one-week exposure to the 40 watt fluorescent radiation.

What is claimed is:

1. A process of stabilizing image and background areas produced by exposure to light of a photosensitive composition containing an N-vinyl heterocyclic compound and an organic halogen compound, the process comprising the steps of:

wetting the image and background areas with an aqueous solution of 0.5 to 20% weight of an azabicycloene compound of a cyclic amidine represented by the formula



where *m* and *n* are each an integer ranging from 2 to 6; and drying the wet image and background areas at a temperature ranging from room temperature to 50°C.

2. A process as claimed in claim **1**, wherein said aqueous solution further contains up to 50% by weight of a water-soluble resin selected from the group consisting of gelatin, agar-agar, polyvinyl alcohol, polyethylene glycol, polyacrylamide, polyvinylpyrrolidone and polyacryl acid.

3. A process as claimed in claim **2**, wherein said aqueous solution further contains 0.5 to 20% by weight of a heavy metal salt of a surface active agent selected from the group consisting of a sulfate, sulfonate and phosphate, said heavy metal being selected from the group consisting of zinc, tin and iron.

4. A process as claimed in claim **1**, wherein said azabicycloene compound is selected from the group consisting of 1,5-diazabicyclo(4,3,0)nonene-5 and 1,5-diazabicyclo(5,4,0)undecane-5-ene.

5. A process as claimed in claim **3** wherein said sulfate is selected from the group consisting of laurylsulfates, oleylsulfates and stearylsulfates, said sulfonate is selected from the group consisting of laurylsulfonate, dibutylnaphthalenesulfonates and dodecylbenzenesulfonates, and said phosphate is selected from the group consisting of oleyletherphosphates and laurylphosphates.

6. A process as claimed in claim **3** wherein said heavy metal sulfonate is Zn-dibutylnaphthalenesulfonate, the concentration of which in said solvent is about 5% by weight.

7. A process as claimed in claim **3** wherein said heavy metal sulfonate is stannous sulfosuccinate, the concentration of which in said solvent is about 6% by weight.

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