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HEAT AND LIGHT STABILIZATION OF PHOTOSENSITIVE ELEMENTS CONTAINING POLYHALOGENATED HYDROCARBONS, N-VINYLCARBAZOLES AND DIFURFURYLIDENE PENTAERYTHRITOLS

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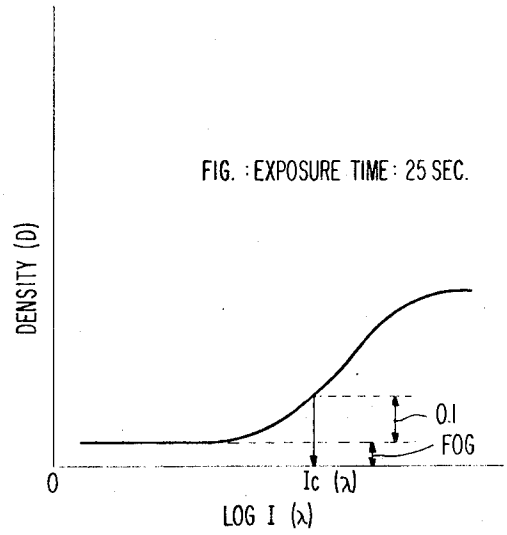

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HEAT AND LIGHT STABILIZATION OF PHOTOSENSITIVE ELEMENTS CONTAINING POLYHALOGENATED HYDROCARBONS, N-VINYLCARBAZOLES AND DIFURFURYLIDENE PENTAERYTHRITOLS

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ABSTRACT OF THE DISCLOSURE

Photosensitive elements comprising a polyhalogenated hydrocarbon, N-vinylcarbazole and difurfurylidene pentaerythritol dispersed in a water soluble binder, and, if desired, a stabilizer and a sensitizer.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a new image forming process which shows a positive response and by which stable black images are produced.

Description of the prior art

Hitherto, though many photosensitive elements comprising an organic amine and a polyhalogenated compound have been known, most of them are negative-working photosensitive elements. Examples of positive-working photosensitive elements are as follows. In U.S. Patent 3,042,519 there is disclosed a photosensitive element which comprises a polyhalogenated hydrocarbon and a N-vinyl compound dispersed in a paraffin wax which shows a positive response when it is subjected to image-wise exposure by light of 2200–2600 A. and then subjected to blanket exposure by light of 3500–4500 A. In this case, it is necessary to use ultraviolet rays of ultrashort wavelengths such as (2200–2600 A.), and consequently there is a disadvantage on practical use because the photographic film absorbs such ultraviolet rays.

In U.S. Patents 3,102,027 and 3,104,973, there is described a process which utilizes the phenomena that a system comprising a merocyanine or a cyanine dye and a halogenated hydrocarbon fades upon exposure to light. This process involves problems at fixing.

In German Patent No. 1,265,578, positive metal images are obtained by exposing a system comprising a combination of metallocene-halogenated hydrocarbon to light and then treating with a noble metal solution. This process has the disadvantage that it requires a wet treatment.

In Japanese Pat. Pub. No. Sho 44—17022, positive copies are obtained by treating with a dye solution, but this is also by a wet treatment.

In U.S. Patent 3,476,562 it is disclosed that positive images or negative images can be obtained using a combination of N-vinylcarbazole and carbon tetrabromide. The positive images are obtained by exposing to light for 2 seconds through a positive by means of a 300 W slide projector, exposing to near ultraviolet rays for 15 seconds and heating at 70° C. for 10 seconds. Though this is a skillful system which utilizes the phenomenon that N-vinylcarbazole causes a polymerization reaction in addition to a color forming reaction, complete fixing cannot be carried out because of the color forming reaction between the resulting polymer and the remaining carbon tetrabromide. Further, the images lack light fastness.

SUMMARY OF THE INVENTION

The present invention provides a positive photographic system treated by a dry treatment which is not subject to the faults of the prior art. The basic components of the photosensitive element are: (a) polyhalogenated hydrocarbon; (b) N-vinylcarbazole and (c) difurfurylidene pentaerythritol.

This photosensitive element is prepared by dispersing these components as discrete globules in a water soluble binder and applying the dispersion onto a suitable support.

Additionally, hydroquinone or resorcinol derivatives may be used in order to improve shelf-life, and sensitizers such as ferrocene and anthraquinone derivatives may be added.

Positive images can be obtained by treating the photosensitive element having such composition by three steps: (1) image-wise exposure; (2) heating; and (3) blanket exposure. For example, when the sensitive element is exposed to light for 5 seconds through a positive at a distance of 30 cm. from a 250 w. high pressure mercury arc lamp, heated at 100° C. for 10 seconds and exposed again to light for 10 seconds by a mercury arc lamp, positive images having a black color on a yellow background are obtained.

The light strength needed varies with kinds of light wavelengths and cannot clearly be defined. The light-sensitive material of the present invention largely depends on the light strength and does not form color unless the light strength is higher, even though the exposure time is prolonged.

The critical intensity (Ic) is determined on the light-strength needed to show the density of Fog +0.1 when exposed for a certain period of time, e.g., 25 seconds, by varying the light wave lengths and the light-strength as shown in the attached figure. Ic is a minimum light-strength and varies somewhat with the wave lengths employed.

Ic ranges from 0.1×10^4 erg/cm.^{2} sec to 1×10^5 erg/cm.^{2} sec and is sufficient so long as it is more than the above range, for example, at least 10^3 erg/cm.^{2} sec is necessary on the light of the wave length having the highest sensitivity. The strength of the first and second exposure is within the above range.

The short heating time is desirable, although the heating temperature is high.

The above range is included within the conditions as described in U.S.P. 3,476,562 (70–90° C.; 10 seconds; 176–176'° C. (375° F.); 107° C., 5 seconds; 107° C., 2–5 seconds). It is used for fixing heating in the present

invention, while it is used for developing heating in U.S.P. 3,476,562, as is clear from the description on column 8, lines 23 to 27, "which . . . during such heating" or column 9, lines 13 to 14, "by heating . . . development exposure."

The resulting images hardly change even though left in a light room. The "light room" is used for investigating the change of the photo-sensitive element after treatment by the scattered light from the sun in a room. Such a positive response is obtained when difurfurylidene pentaerythritol is used together with a water soluble binder.

This invention provides a black image obtained by positive working, which is a simplified dry process using heat and light.

DETAILED DESCRIPTION OF THE INVENTION

As the polyhalogenated hydrocarbon, there are compounds represented by the following formula:

$$R—C(H)_{3-m}X_m$$

wherein

R is H, X, COOR' or $—C(H)_{3-n}X_n$,
R' is H, CH_3 or C_2H_5
X is Cl, Br or I
m and *n* are 2 or 3

The polyhalogenated hydrocarbon is selected from the group of the compounds which produce free radicals or ions upon exposure to light of a suitable wavelength.

Additional examples of the polyhalogenated hydrocarbon are carbon tetrabromide (CBr_4), hexachloroethane (C_2Cl_6) and iodoform (CHI_3).

As the binder, there are water soluble substances such as gelatin, polyvinyl alcohol, casein, starch, hydroxyethyl cellulose, carboxymethyl cellulose, polyvinyl pyrrodidone and polyethyleneglycol. The molecular weight for the binder is thousands to hundred thousands, preferably 20,000 to 100,000.

The composition of the mandatory materials are as follows:

The ratio of the N-vinylcarbazole/polyhalogenated hydrocarbon is 50/1 to 1/5, preferably 5/1 to 1/5.

The ratio of the N-vinylcarbazole/difurfurylidene pentaerythritol is 100/1 to 1/10, preferably 10/1 to 1/2.

The ratio of the binder/light-sensitive material is 1/100 to 20/1, preferably 1/10 to 5/1.

The following examples are offered to explain the present invention in great detail. The treatment of the photosensitive element, exposure and heating were carried out under a photographic red safety lamp.

Example 1

An acetone solution of 5 g. of N-vinylcarbazole was added to 50 ml. of a 16% aqueous gelatin solution. The mixture was stirred at 70° C. for 2 minutes with a homomixer to finely disperse the N-vinylcarbazole in the gelatin. After adding 4 g. of carbon tetrabromide and a dichloroethane solution of 0.5 g. difurfurylidene pentraerythritol, the mixture was similarly dispersed. The amount of acetone 5 ml., and the amount of dichloroethane is 5 ml. The resulting dispersion was applied to baryta paper to provide a photosensitive element after drying.

A black image on a light yellow background was obtained by exposing this photosensitive element to light for 10 seconds through a positive at a distance of 30 cm. from a 250 w. super high pressure mercury arc lamp, heating at 100° C. for 10 seconds and exposing further for 10 seconds by a mercury arc lamp. Similarly, a black image on a yellow background could be obtained by leaving the element in a light room and omitting the last exposure by the mercury arc lamp. The resulting images hardly changed in a light room.

On the other hand, the photosensitive element was treated by the method described in U.S. Patent 3,476,562, i.e., a black image on a yellow background could be obtained by exposing for 10 seconds through a photographic positive at a distance of 35 cm. from a 300 w. incandescent electric lamp. But the yellow background changed into brown color in a light room, which meant the fixing had not been carried out completely.

Example 2

	G.
N-vinylcarbazole	5
Carbon tetrabromide	4
Difurfurylidene pentaerythritol	0.5
p-Bis(2-tetrahydropyranyloxy) benzene	0.25

A photosensitive element was produced by dispersing the abovementioned components in an aqueous gelatin solution by the same procedure as in Example 1.

When the sensitive element was exposed to light for 10 seconds through a photographic positive at a distance of 30 cm. from a 250 w. mercury arc lamp, heated at 80° C. for one minute and then exposed further for 10 seconds by a mercury lamp, a black image which was identical to that of the original was produced on a light yelow background. This image hardly changed in a light room.

Example 3

A photosensitive element was produced substituting polyvinyl alcohol for the gelatin in Example 2. By carrying out the same exposing and heating treatments as in Example 2, a black image on a light yellow background was obtained.

Example 4

The same result as in Example 1 was obtained when iodoform was used instead of carbon tetrabromide in Example 1.

Example 5

	G.
N-vinylcarbazole	5
Carbon tetrabromide	2
Hexachloroethane	1
Difurfurylidene pentaerythritol	0.5

A stable positive image which hardly changed in a light room was obtained by treating a photosensitive element prepared by dispersing the abovementioned components in an aqueous solution of polyvinyl alcohol and thereafter heating and exposing as in Example 1.

The most important commercial embodiments are as follows. Duplicating by micro-film image or slide-film image. Duplication can be carried out on both of a positive and negative image, and generally on the positive image. The binders are gelatin, polyvinyl alcohol, gum arabic, polyvinylpyrrolidone, etc. The globule size is 0.1 to 30μ, preferably 0.5 to 10μ.

While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. In an image forming process by dry treatment which comprises imagewise exposing a photosensitive element comprising a support having thereon a polyhalogenated hydrocarbon and N-vinylcarbazole dispersed as discrete globules in a water-soluble binder to ultraviolet rays or visible rays and heating, the improvement comprising said photosensitive element containing difurfurylidene pentaerythritol and the improvement further comprising exposing uniformly said imagewise exposed element to ultraviolet rays or visible rays after the heating thereof, by which a black positive image is obtained; said polyhalogenated hydrocarbon having the following general formula;

$$R—C(H)_{3-m}x_m$$

wherein R is a hydrogen atom, X, COOR' or

$$-C(H)_{3-n}X_n$$

R' is H, CH_3 or C_2H_5; X is Cl, Br or I; and *m* and *n* are an integer of 2 or 3.

2. An image forming process as claimed in claim 1 wherein said water soluble binder is selected from the group consisting of casein, starch, hydroxyethyl cellulose, carboxymethyl cellulose, polyethylene glycol, gelatin, polyvinyl alcohol, gum arabic, and polyvinylpyrrolidone.

3. An image forming process as claimed in claim 1 wherein said weight ratio of the N-vinylcarbazole to polyhalogenated hydrocarbon is 50/1 to 1/5.

4. An image forming process as claimed in claim 1 wherein said weight ratio of the N-vinylcarbazole/difurfurylidene pentaerythritol is 100/1 to 1/10.

5. An image forming process as claimed in claim 1 wherein said globules range from 0.1μ to 30μ in size.

6. An image forming process as claimed in claim 1 wherein said heating is 40° C. to 230° C. of temperature range, and 0.5 sec. to 10 min. of time range.

References Cited

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