United States Patent Office 3,377,167
Patented Apr. 9, 1968

3,377,167

FIXING AGENTS FOR PHOTOSENSITIVE COMPOSITIONS CONTAINING LEUCOTRIPHENYL METHANE DERIVATIVES; LEUCO XANTHENE COMPOUNDS OR LEUCO ANTHRACENE COMPOUNDS

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No Drawing. Filed Apr. 2, 1965, Ser. No. 445,273
6 Claims. (Cl. 96—48)

ABSTRACT OF THE DISCLOSURE

Fixing of photosensitive compositions by gentle heating is facilitated by the addition of suitable amounts of triaryl compounds of Sb, P, As or Bi to photosensitive compositions containing leucotriphenylmethane derivatives or leuco xanthene compounds or leuco anthracene compounds, plus an activator which enhances a color forming reaction when the leuco compound is exposed to a suitable dose of radiation.

This invention relates to the fixing of print-out images obtained directly as the result of exposure to suitable doses of radiant energy of photosensitive compositions of the types consisting essentially of the following:

(a) at least one suitable leuco compound

(b) at least one activator or sensitizer for (a)

Such photosensitive compositions have been described in a number of issued and presently pending United States Patent Applications filed on behalf of Horizons Incorporated, including the following:

United States Patents

3,113,024 issued Dec. 3, 1963 to Sprague et al.
3,121,632 issued Feb. 18, 1964 to Sprague et al.
3,121,633 issued Feb. 18, 1964 to Sprague et al.
3,140,948 issued July 14, 1964 to Stewart et al.
3,140,949 issued July 14, 1964 to Stewart et al.

Copending United States patent applications

Ser. No. 273,569 filed Apr. 17, 1963, which issued on Sept. 13, 1966, as United States Patent 3,272,635 and Ser. No. 309,407 filed Sept. 17, 1963, which issued on Nov. 8, 1966, as United States Patent 3,284,205.

As described therein, the fixing of print-out images obtained with such compositions is accomplished by removal of unreacted constituents from the composition. Two methods of fixing were described therein: fixing by heating sufficiently to remove any residual unreacted CBr_4 or other active constituent from the composition and fixing of the print-out image by solvent washing or rinsing of the same in a solvent whereby the CBr_4 or other active constituent is washed out of the exposed composition.

When a totally dry photographic system is desired only the first of these techniques is applicable and from a practical standpoint the acceptability of this method of fixing would be increased if the duration of the heating step or the intensity or temperature of the heating step could be diminished.

When photographic compositions containing leuco compounds are fixed by heating, the temperature required to drive off the volatile activator is usually high enough to cause the leuco compounds to be oxidized to their colored form and overall fog results. The overall fog is frequently high enough to completely obscure the image so that it is no longer distinguishable. This situation is observed to some extent with all leuco compounds, but it is most pronounced with those compounds which give the greatest photographic activity—in other words, the fastest.

A principal object of the present invention is to render photosensitive compositions of the type described above more amenable to fixing by gentle heating.

A principal object of the present invention is to render photosensitive compositions of the type described above more amenable to heat fixation by the addition of compounds which will prevent the oxidation of the unreacted leuco compound, i.e., that which remains after imaging takes place. Such compounds may be oxidized themselves to some colorless product—said oxidation being preferential to the oxidation of the leuco base. Such compounds may react with the unreacted leuco compound upon mild heating to form a colorless product which is no longer photographically active and which will no longer be oxidizable to form colored background fog. When volatile organic halogen compounds are used as activators these will be driven off and no longer be available for activation by light.

This and other objects of the invention are accomplished by the addition of suitable amounts of triaryl compounds of certain Group V elements of such compositions. Particularly preferred compounds for this purpose are triphenylstibine, triphenylarsine, triphenylphosphine and triphenylbismuthine.

Although the references to the above patents and literature are believed to sufficiently define the type of compositions to which the present invention applies, each of constituents will be specified in greater detail.

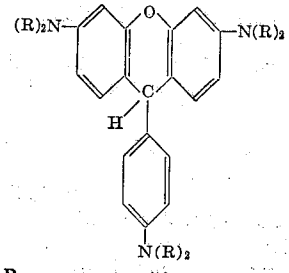
(1) The leuco compounds

Typical leuco compounds include the following:

Leuco triphenyl methane derivatives, represented by the formula

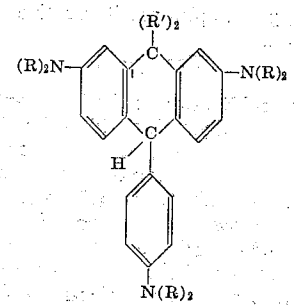
wherein each R represents either H or an alkyl or aryl group.

Leuco xanthene derivatives, represented by the formula



wherein each R represents either H or an alkyl or aryl group.

Leuco anthracene derivatives, represented by the formula



wherein each R represents either H or an alkyl or aryl group and each R' represents either H or an alkyl group.

(2) The activator compounds

Suitable activator compounds for the photosensitive compositions based on the combination of the above identified leuco compounds include any of the following:

(a) Sulfonyl halides and sulfenyl halides described in U.S. Patent 3,113,024;

(b) Alkyl and aryl ketones, aldehydes and esters described in U.S. Patent 3,121,632;

(c) Aliphatic and aromatic carboxylic acids and carboxylic acid anhydrides described in U.S. Patent 3,140,948 and U.S. Patent 3,140,949;

(d) Other colorless C=O containing organic compounds described in U.S. patent application Ser. No. 273,569 filed Apr. 17, 1963, the disclosure of which is incorporated herein by reference;

(e) Colorless N-containing organic compounds described in United States patent application Ser. No. 309,407 filed Sept. 17, 1963, namely triazoles and heterocyclic ketimides of the types described therein, said description being incorporated herein by reference; and

(f) Organic halogen compounds described in the above noted patents and patent applications and represented by the general formula

$$A—C—X_3$$

wherein A represents either H, Cl, Br, I, an alkyl group, a substituted alkyl group, particularly a halogen-substituted alkyl group, a substituted or an unsubstituted aryl group or an aroyl and each X represents a halogen atom which may be any of Cl, Br or I.

(3) The fixing agents of this invention

The fixing agents of this invention are the triaryl compounds of the following Group V elements: Sb, Bi, As and P, and particularly the triphenyl compounds of those elements, namely:

Triphenylphosphine
Triphenylarsine
Triphenylstibine
Triphenylbismuthine

The fixing agent may be incorporated in otherwise known compositions at the time they are prepared or it may be added to them just prior to their use, e.g. just prior to their application to a suitable support such as paper, plastic or cloth or any other base material. When applied as a coating formulation to a suitable substrate, the relative proportions of the several constituents are as follows:

Leuco compound—0.125 to 2.5% of the coating formula on a weight/volume basis
Organic halogen compounds—2.5 to 25% of the coating formula on a weight/volume basis
Or other activator or sensitizers—0.1 to 5.0% of the coating on a weight/volume basis
Fixing agent—0.5 to 4.0% of the coating mixture on a weight/volume basis
Solvent—up to 95% of the coating mixture on a weight/volume basis.

The following examples are illustrative of the practice of this invention.

Example 1

One hundred milligrams of the leuco anthracene compound 2,7-bis (dimethylamino)-10-p-dimethylaminophenyl-9,10-dihydro-9,9-dimethylanthracene and seven hundred milligrams of carbon tetrabromide were dissolved in two cc. of a 2.5% polystyrene (Dow-Styron 700) solution in benzene followed by additions of two cc. of acetone and one cc. of a 4% solution of triphenylstibene in acetone. This mixture was coated .0015 inch wet thickness on baryta paper whose surface contained a polyvinyl alcohol surface sealing layer. The coating was applied by means of a Bird applicator blade and a vacuum plate was used for holding the paper flat while the coating was applied. Photographic safelight conditions were used during the coating procedure.

After the coating was dried, the photosensitive surface was exposed to a fifteen time (15×) enlargement of a microfilm negative using a standard amateur slide projector with a 500 watt bulb. The exposure time was ten seconds which was sufficient to give a good quality print-out positive rendition of the projected negative. The exposed print was placed in an oven with moving air at 100° C. for sixty seconds after which the print was fully fixed and no longer sensitive to light.

Example 2

The same procedure as used in Example 1 except that the one cc. of 4% triphenylstibene was replaced by one cc. of 2% solution of triphenylarsine in acetone. After sixty seconds heating in moving air at 100° C., the print was fully fixed and no longer sensitive to light.

Example 3

The same procedure as used in Example 1 except that the one cc. of 4% triphenylstibene was replaced with one cc. of 1% triphenylbismuthine in acetone. After sixty seconds heating in moving air at 100° C, the print was fully fixed and no longer sensitive to light.

Example 4

The same procedure as used in Example 1 except that the 700 milligrams of carbon tetrabromide activator is replaced by 200 milligrams of iodoform. The photosensitive material was exposed twenty seconds to the projected image described in Example 1 and after sixty seconds heating in moving air at 100° C. the print was fully fixed and no longer sensitive to light.

Example 5

The same procedure as used in Example 1 except that the leuco anthracene compound was replaced with 50 milligrams of the leuco xanthene compound 3,6-bis(dimethylamino) - 9 - (p-dimethylamino)phenylxanthene. After ten seconds exposure to the projected image described in Example 1 and sixty seconds heating in moving air at 100° C. the print was fully fixed and no longer sensitive to light.

Similar results were obtained when instead of the organic halogen compounds (CBr_4 and CHI_3) of the preceding examples considerably smaller amounts of the activators listed in sections 2(a) through 2(f) above were used.

In each instance a completely fixed print was obtained as a result of the gentle heating to temperatures between 80° C. and about 100° C.

The invention is applicable to other activators than those described in Examples 1 to 5, as shown by the following example:

Example 6

One hundred milligrams of the leuco anthracene compound 2,7 - bis(dimethylamino) - 10-p - dimethylaminophenyl-9,10-dihydro-9,9-dimethylanthracene and one hundred milligrams of p-nitrobenzenesulfonyl chloride were dissolved in two cc. of a 10% solution of polystyrene in benzene containing 10 milligrams of triphenylstibene and two cc. of acetone. The coating was applied to baryta paper in the manner described in Example 1. The dried coating was exposed to the 15× projection for 60 seconds followed by 60 seconds heating in 100° C. air. The heated print was fully fixed and no longer sensitive to light.

Having now described this invention it is not intended that it be limited except as may be required by the appended claims.

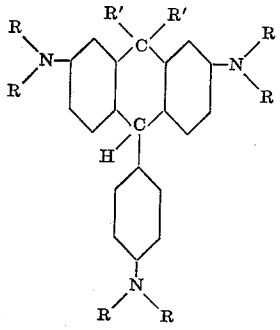
What is claimed is:

1. In a composition which prints out a visible image directly as a result of exposure to a sufficient dosage of visible radiation and which consists essentially of at least

one leuco compound selected from the group consisting of leucotriphenyl-methane compounds, leuco anthracene compounds and leuco xanthene compounds and at least one activator for said leuco compound, the improvement which consists in incorporating an amount of triaryl compound of an element selected from the group consisting of Sb, As, Bi and P sufficient to permit fixing by gently heating any visible image resulting from exposure of said composition to visible light.

2. The composition of claim 1 wherein the triaryl compound is a triphenyl compound.

3. The composition of claim 1 wherein the leuco compound is a leuco anthracene represented by the general formula



wherein each R represents a monovalent radical selected from the group consisting of H, alkyl and aryl and each R′ is a monovalent radical selected from the group consisting of H and alkyl.

4. The composition of claim 1 wherein the activator is a compound represented by the formula A—C—X_3 wherein A represents a monovalent member selected from the group consisting of H, Cl, Br, I, alkyl, aryl and aroyl and each X represents a halogen atom selected from the group consisting of Cl, Br and I.

5. The composition of claim 4 wherein the proportions are as follows:

Leuco compound—between 0.125 and 2.5% of the total on a weight/volume basis;

Fixing agent—between 0.5 and 4% of the total on a weight by volume basis; and

Activator—between 0.1 and 5% of the total on a weight by volume basis except when the activator is a colorless organic halogen compound wherein at least 3 halogen atoms are linked directly to a single carbon atom, there being between 2.5 and 25% of the total on a weight by volume basis when the activator is an organic halogen compound represented by the formula A—C—X_3 wherein A represents a member selected from the group consisting of H, Cl, Br, I, alkyl, aryl and aroyl and each X represents a member selected from the group consisting of Cl, Br and I.

6. In a method of fixing visible images printed out from a composition consisting essentially of at least one leuco compound selected from the group consisting of leucotriphenyl-methane compounds, leuco anthracene compounds and leuco xanthene compounds and at least one activator or sensitizer for said leuco compound, the improvement which comprises including a triaryl compound in said composition selected from the group consisting of triaryl compounds of P, As, Sb and Bi, exposing the composition to sufficient light of a suitable wavelength to produce a colored photoreaction production, and fixing the resulting product by heating to a temperature up to about 120° C.

References Cited

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3,275,443	9/1966	Wainer	96—90
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