United States Patent Office

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3,533,792

DRY WORKING PHOTOGRAPHIC PROCESS UTILIZING A NON-SILVER PHOTOSENSITIVE COMPOSITION

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Int. Cl. G03c 1/00, 1/72
U.S. Cl. 96—48 17 Claims

ABSTRACT OF THE DISCLOSURE

A photographic process and composition is described in which a completely dry working photographic process utilizing a non-silver composition is used. The composition contains (a) one or more dye-forming compounds, (b) one or more organic halogen compounds in which at least three halogen atoms are attached to a terminal carbon in an alkane or aryl alkane and (c) at least one compound which forms a colored image when reacted with the compounds of group (a) and are selected from the group consisting of thiols, pyrazolones, acetoanilides and mixtures thereof.

The invention herein described was made in the course of or under a contract or subcontract thereunder, with The Systems Engineering Group, Air Force Systems Command.

This invention relates to completely dry working photography. More particularly, it relates to compositions which are sensitive to light and which are suitable for photography and photographic reproduction purposes and to the production of stable, colored, print-out, and developable-out images produced by exposing such compositions to light and/or to light and heat.

The invention relates to control of the density and contrast of the image by suitably adjusting the radiation to which the composition is exposed.

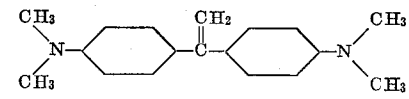
The present invention relates to the addition of one or more compounds to the compositions of the kind described in United States patent application Ser. No. 603,731 filed Dec. 22, 1966, in order to produce images of any desired color, including jet black.

A specific object of this invention is to provide a photographic composition yielding a black or near neutral image as the result of the application of heat to said composition after it has been photographically exposed.

With the exception of color photographic printing or where a specific colored image is desired for display purposes, virtually every practical application of presently known free radical photographic systems prefer a black or near black image color. Such contemplated uses include: office photocopy; microfilm retrieval systems; photographic printing, e.g., portraiture proofing; and even such military uses as the multigeneration aerial reconnaissance printing described in Photographic Science and Engineering, vol. IX, No. 2, pp. 133–137, 1965; and all such uses demand a suitable black image produced without recourse to wet processing.

Furthermore, this invention relates to the control of and the variation of the color of the image by the addition of specific chemicals to the compositions of the invention. As a result of the ability to control the color produced, a near neutral (black to blue black) image can be achieved.

Briefly it has been found that photosensitive compositions based on the single dye former 1,1-bis-(p-dimethylaminophenyl)ethylene, having the structure



such as those described in patent application Ser. No. 603,731 filed Dec. 22, 1966, can be altered by the addition of suitable color complexes so that the color normally obtained with this compound, i.e. greenish-blue, can be so altered as to form a neutral or black color.

As a consequence, it is not necessary to use a combination of dye precursors, each of which would add the appropriate absorption in the visible end of the spectrum, i.e. yellow, cyan and magenta, as to obtain total visible saturation. The main objection to the use of a combination of dye precursors is that normally it is extremely difficult to obtain dye precursors of the yellow, cyan and magenta which when activated with the appropriate organic halide will react photochemically at the same rate in order to achieve the desired total saturation in the visible. In the usual case, almost without exception, there are notable absences in the visible spectrum. In addition, when the appropriate combination of dye precursors can be found, a very delicate balance as well as a high degree of purity of these materials must be maintained in a coating mix in order to ensure the correct color balance.

The present invention eliminates many of these difficulties by the use of only one photoactive dye former in the photosensitive composition. The additives used to produce the desired color balance do not participate or influence the photochemical reaction, but become effective only when the material is being fixed. During the fixing stage the additive(s) interact with the dye salt formed during the photochemical steps to produce the desired color. It has been shown that by employing this technique that red, blue and green or any combination of these colors can be produced.

The neutral image, dry working characteristics of the compositions herein described are particularly important in certain of the above uses, since the use of a wet working system in high speed aircraft or space vehicles is almost inconveivable. One such use whose feasibility has been established is the preparation of multigeneration printing of aerial reconnaissance negatives as described in the above noted publication. When a military reconnaissance aircraft photographs a target, the negative resulting from that photograph is developed and reproduced through as many as four generations for determination of the intelligence revealed in the photograph. The original negative is printed only once and then is stored in the archives. All subsequent prints are made from the second generation prepared from the original negative. Conventional silver halide systems are not completely suitable for this multigeneration printing purpose, since the image is granular (particulate) and consequently each subsequent generation loses information which may be valuable in strategic decisions made from the use of these photographs. Free radical photosystems being molecular rather than granular have almost unlimited resolution particularly when coated in thin layers (about 4 to 5 microns thick), to take advantage of the geometry of present printer processors and their light sources. Free radical photographic systems have been established to be an excellent medium for these multigeneration aerial reconnaissance printing, especially photosensitive free radical compositions based on the teachings of U.S. Pat. 3,109,736 and described in Photographic Science and Engineering, vol. IX, No. 2, pp. 133–137, for March and April 1965, under the title "New Photographic Process, No. 4, The Cyanine Base Free Radical Photosystem—A Panchromatic Black Image High Resolution Printout Film." The compositions described yield excellent jet black images and

retain high latitudes multigeneration printing through four generations, with the minimum loss of intelligene. However, the compositions are not dry working, but require a solvent rinse after exposure to render the image fixed and stable to ambient light.

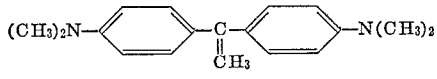
Photointerpreters who evaluate these aerial reonnaissance photographs traditionally have been schooled in the use of black image materials and are reluctant to use other colors. Hence the need for a dry working black image system to be used for aerial reconnaissance multigeneration printing.

As described in U.S. patent application Ser. No. 603,731, one preferred composition from which hand coatings were made at .0015 inch wet thickness on raw polyester film and thereafter evaluated as indicated below consisted of the following:

50 mg. 1,1-bis(p-dimethylaminophenyl)ethylene [1]
200 mg. iodoform
5 mg. 4-picoline-1-oxide
25 mg. 2,6-di-t-butyl-p-cresol
10 mg. triphenylstibine
3 cc. polystyrene 10% in benzene
1cc. acetone
1 cc. benzene

The present invention is based on the addition of one or more specific compounds from certain clases of compounds to the formulation described in the above noted application in order to produce variations in the hue or color of the final image.

The compositions described in the examples which, follow are each prepared by bringing the several constituents together in a suitable solvent system under a safelight or in total darkness and, after thoroughly mixing the composition, applying it to a solid substrate such as baryta paper or a film of polyester, glass or other suitable support.



After the composition has been laid down as a thin film, it is permitted to dry in air, in the dark, or under a safelight, and then it is photographically exposed to the equivalent of 0.01 watt second/cm.^{2}. After exposure of this material, the latent image is developed by exposing the film to radiant energy of an appropriate intensity (1.5 to 3.0 kw.) and suitable wavelength (600–800 mμ) for a period of time in the range 1 second to 40 seconds. The film sample is then heat fixed at 135° C.–150° C. in moving air for 2–5 minutes; whereby a very stable dense black image is observed in the exposed areas.

With this amount of photographic exposure, maximum density of about 1.5–2 is achieved and the heated film is completely fixed, i.e. the image and background do not change upon further exposure to light. Increasing the photographic exposure to the equivalent of 0.1 watt second/cm.^{2} and developing gave maximum densities in excess of 2.0 in the 14th step of a 21 step tablet. The density of the resulting visible image is readily varied by the dose of radiation utilized in either exposure step of the process.

In general, images having a desired color are produced by exposing photosensitive compositions of this invention to a pattern of radiant energy and then developing and intensifying the image produced as a result of said photographic exposure by exposing the entire composition to a radiant energy of between 600 and 800 mμ.

The process may include, in addition, the step of fixing the image by heating the image-containing material to between 120° C. and 160° C. for a short interval of time.

With exposures of at least about 1 watt second per square centimeter, a direct printout image is obtained. With exposures of substantially less than 1 watt second per square centimeter, a latent image is produce which is

[1] Structure

then developed by a subsequent exposure to a suitable dose of radiation.

The following examples will serves to further illustrate the invention, the compounds being listed in the order in which they are added to the formulation, in a solution of suitable solvents.

EXAMPLE 1

By using a compound containing an —SH group, attached to an alkyl, aryl, aralkyl or other monovalent group of the type hereinafter described, a blue image is obtained. One preferred formulation is as follows:

100 mg. 1,1-bis-p-dimethylaminophenyl ethylene
50 mg. 2,6-di-t-butyl-p-cresol
10 mg. 2-mercaptoacetanilide
5 mg. 4-picoline-N-oxide
10 mg. triphenylstibine
200 mg. iodoform
3cc. 10% polystyrene in benzene

Other formulations yielding a blue image are those in which the mercaptoacetanilide utilized by way of example in the above formulation was replaced with similar amounts of any of the following R—SH compounds in which R is shown to be an alkyl, aryl, or hetero group which may be substituted or unsubstituted.

4-acetamidothiophenol
Allyl mercaptan
Benzyl mercaptan
4-bromothiophenol
1,2-butanedithiol
1,4-butanedithiol
2-naphtholenethiol
n-butylmercaptan
4-tert-butylthiophenol
4-chlorobenzylmercaptan
p-chlorothiophenol
Cyclohexylmercaptan
1-decanethiol
2,2-dichloro-1-ethanethiol
2,3-dimercapto-1-propanol
3,4-dimercaptolotoluene
Lauryl mercaptan
1,2-ethanedithiol
Furfuryl mercaptan
1-heptanethiol
2-mercaptobenzimidazole
2-mercaptoethanol

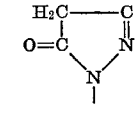
or other aryl, alkyl, etc. compounds with an —SH group.

EXAMPLE 2

By utilizing a pyrazolone instead of the mercapto compound of Example 1, a red to violet image was obtained with the following formulation:

100 mg. 1,1-bis-p-dimethylaminophenyl ethylene
5–10 mg. 1-phenyl-3-amino pyrazol-5-one
50 mg. 2,6-di-t-butyl-p-cresol
5 mg. 4-picoline-N-oxide
10 mg. triphenylstibine
200 mg. iodoform
3 cc. 10% polystyrene in benzene

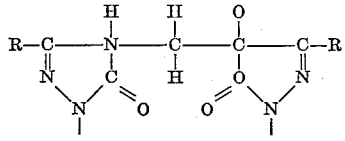
Red to violet images were obtained with similar formulations in which the following compounds containing the ring



were used in place of the 1-phenyl-3-amino-pyrazol-5-one:

3-methyl-5-pyrazolone
1-(3'-amino benzene)-3-methyl-5-pyrazolone
1-(4'-amino benzene)-3-methyl-5-pyrazolone

1-(2'-chloro benzene)-3-methyl-5-pyrazolone
1-(3'-chloro benzene)-3-methyl-5-pyrazolone
1-(4'-chloro benzene)-3-methyl-5-pyrazolone
1-(2',5'-dichlorobenzene)-3-methyl-5-pyrazolone
1,3-diphenyl-5-pyrazolone
1-(4'-methylbenzene)-3-methyl-5-pyrazolone
1-phenyl-3-methyl-5-pyrazolone
Bis-pyrazolone of the structure



EXAMPLE 3

The following formulation produces a green image when processed in the previously described manner.

100 mg. 1,1-bis-p-dimethylaminophenyl ethylene
50 mg. acetoacetanilide
50 mg. 2,6-di-t-butyl-p-cresol
10 mg. triphenylstibine
5 mg. 4-picoline-N-oxide
200 mg. iodoform
3 cc. 10% polystyrene

Other compounds which have been found to produce a green image when used in place of the acetoanilide in example include the following anilides:

Acetoacet-2,5-dichloroanilide
Acetoacet-2,5-diethoxy-4-chloroanilide
Acetoacet-2,4-dimethoxy-5-chloroanilide
Acetoacet-2-methyl-3-chloroanilide
Acetoacet-2-methyl-4-chloroanilide

Although the exact mechanism is not known whereby the additions of the several classes of compounds produces a change in the color of the image, it appears possible that the dimethylaminophenyl substituted ethylene contributes to the formation of a black or near neutral image when acted on by the products which result when the iodoform and acetanilide and/or pyrazolone are exposed to a suitable dose of radiant energy.

Instead of the vinyl $>C{=}CH_2$ group in this compound, compounds in which one or both of the hydrogens are replaced by an alkyl or aryl group could be utilized.

It will be evident that other compounds may be used in place of each of the several constituents in the formula without departing from the invention, especially since the equivalency of these are described in a number of issued patents already issued to applicants' assignee.

For example, triphenylstibine may be replaced with triphenylbismuthine, triphenylphosphine or triphenylarsine; polystyrene may be replaced with polycarbonates or other synthetic film-forming resins; and the iodoform may be replaced by other compounds in which at least three halogen atoms are attached to a single terminal carbon atom in an organic compound. Such organic halogen compounds are represented by the general formula $A{-}C{-}Q_3$ wherein each Q represents a halogen atom selected from the group consisting of Cl, Br and I and A represents a monovalent member selected from the group consisting of H, Cl, Br, I, alkyl, substituted alkyl, particularly halogen substituted alkyl, aryl, aroyl and substituted aryl.

It is also possible to include *both* an acetanilide and a pyrazol-5-one in the same formulation, as shown by the following example.

EXAMPLE 4

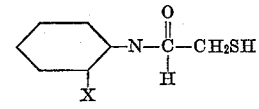
A typical formulation producing a near neutral image is:

100 mg. 1,1-bis-p-dimethylaminophenyl ethylene
50 mg. 2,6-di-t-butyl-p-cresol
10 mg. 1-phenyl-3-amine-pyrazol-5-one

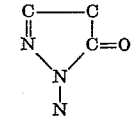
10 mg. 2-mercaptoacetanilide
5 mg. 4-picoline-N-oxide
10 mg. triphenylstibine
200 mg. iodoform
3 cc. 10% polystyrene in benzene

Although only a few of the many color-forming additives found to produce blue, red to violet or green colored images are listed above, the following general formulas describe classes of compounds which produce the indicated colored image when processed as in the preceding examples and which do not diffuse appreciably through the sensitive film.

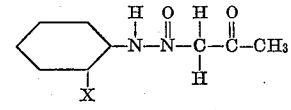
Blue image



Red to violet image



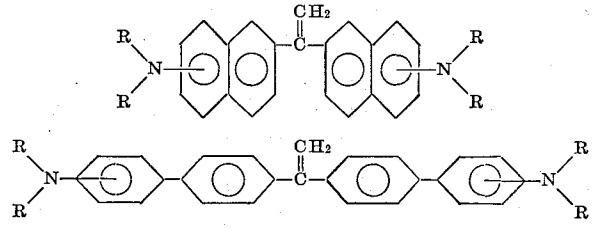
Green image



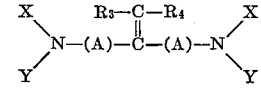
X is a long chain alkyl, such as octadecyl or heptadecyl.

The photosensitive compositions above described may produce either a direct printout image or a latent image depending on the amount of energy utilized in the exposure step. A latent image is produced by an exposure of approximately 0.1 watt second per square centimeter. When approximately ten times as much energy, i.e. about 1 watt second per square centimeter, is utilized in the exposure step, a direct printout image results. It has been observed that the color of the final image produced as a direct printout is not always the same as that which results when the latent image is later developed from an otherwise similar composition.

Other compounds having a vinyl group may be utilized in place of the 1,1-bis(p-dimethylaminophenyl)ethylene. For example, each of the following has been found to be suitable in the present invention:



These compounds and the preferred compound may be represented by the general formula:



in which A represents benzyl; naphthyl or diphenyl; X and Y are each H or alkyl (particularly methyl or ethyl); and R_3 and R_4 are each H, alkyl or aryl.

It should also be understood that by the use of mixtures of the color forming constituents it is possible to obtain a black image instead of the colors previously described.

The compositions may include, as additional constituents which enhance the formation of the desired image, any one or more of the following: picoline-1-

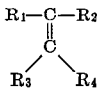
oxides; triaryl compounds of P, Sb, As or Bi; and cresols such as 2,6-di-tert-butyl-cresol.

Having now described the invention in general terms, it is not intended that it be limited except by the claims which follow.

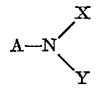
We claim:

1. A photosensitive composition consisting essentially of the following:

(a) one or more dye-forming compounds represented by the general formula



wherein R_1 and R_2 are each a monovalent radical represented by the formula



in which A is selected from the group consisting of benzyl, naphthyl and diphenyl, and in which X and Y are each selected from the group consisting of H and alkyl and wherein R_3 and R_4 are each selected from the group consisting of H, alkyl and aryl;

(b) one or more organic halogen compounds in which at least three halogen atoms selected from the group consisting of Cl, Br and I are attached to a terminal carbon in an alkane or aryl alkane compound represented by the general formula A—C—Q_3 wherein Q represents a halogen selected from the group consisting of Cl, Br and I and A represents a monovalent member of the group selected from H, Cl, Br, I, alkyl, substituted alkyl, aryl, aroyl, and substituted aryl; and

(c) at least one compound which forms a colored image when reacted with the compounds of group (a) above, said colored image forming compounds being selected from the group consisting of thiols, pyrazolones and acetoanilides and mixtures of said compounds.

2. The composition of claim 1 including at least one additional compound which enhances the formation of the desired image and which is selected from the group consisting of picoline-1-oxides; triaryl compounds of P, Sb, As or Bi; and tertiary cresols.

3. The composition of claim 1 wherein the dye forming compound is 1,1-bis-dimethylaminophenyl ethylene.

4. The composition of claim 1 wherein the organic halogen compound is iodoform.

5. A composition according to claim 1 wherein the image which prints out is blue and the thiol is a mercapto compound represented by the formula R—SH wherein R represents alkyl, aryl or hetero groups, substituted or unsubstituted.

6. A composition according to claim 1 wherein the image which prints out is red to violet and the composition contains 1-phenyl-3-amino-pyrazol-5-one.

7. A composition according to claim 1 in which both an acetanilide and a pyrazolone are present, whereby a near neutral image is obtained.

8. A composition according to claim 1 containing in addition a film-forming resinous binder for the constituents of the composition so that it may exist as a thin film.

9. A composition according to claim 1 comprising 1,1-bis-p-dimethylaminophenyl ethylene; 2,6-di-t-butyl-p-cresol; 2-mercaptoacetanilide; 4-picoline-N-oxide; triphenylstibine; and iodoform.

10. A composition according to claim 1 comprising 1,1-bis-p-dimethylaminophenyl ethylene; 1-phenyl-3-amino pyrazol-5-one; 2,6-di-t-butyl-p-cresol; 4-picoline-N-oxide; triphenylstibine; and iodoform.

11. A composition according to claim 1 comprising 1,1-bis-p-dimethylaminophenyl ethylene; acetoacetanilide; 2,6-di-t-butyl-p-cresol; triphenylstibine; 4-picoline-N-oxide; and iodoform.

12. A composition according to claim 1 comprising 1,1-bis-p-dimethylaminophenyl ethylene; 2,6-di-t-butyl-p-cresol; 1-phenyl-3-amino-pyrazol-5-one; 2-mercaptoacetanilide; 4-picoline-N-oxide; triphenylstibine; and iodoform in a film forming binder.

13. A composition according to claim 1 in which a mixture of compounds under (c) is utilized to produce a black image.

14. A process for producing an image having a desired color which comprises exposing a photosensitive composition according to claim 1 to a pattern of radiant energy and then developing and intensifying the image produced as a result of said photographic exposure by exposing the entire composition to radiant energy of between 600 and 800 mμ.

15. Process of claim 14 including in addition, the step of fixing the image by heating the image containing composition to between 120° C. and 160° C. for a short interval of time.

16. A process according to claim 14 in which the exposure is at least about 1 watt second per square centimeter whereby a direct printout image is obtained.

17. A process according to claim 14 wherein the exposure is substantially less than 1 watt second per square centimeter and a latent image is produced which is then developed by a subsequent exposure to a suitable dose of radiation.

References Cited

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WILLIAM D. MARTIN, Primary Examiner

W. R. TRENOR, Assistant Examiner

U.S. Cl. X.R.

96—88, 90, 115

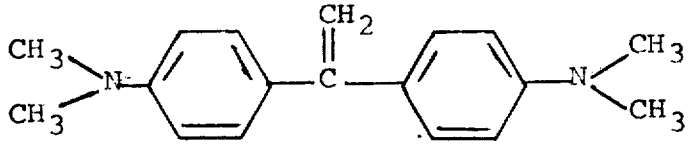
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,533,792 Dated Oct. 13, 1970

Inventor(s) Victor P. Petro et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, lines 1-4; correct the structural formula to read:

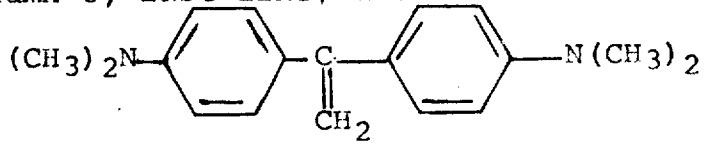


Column 3, line 1; after "latitudes" insert --for--

Column 3, line 2; correct --intelligence--

Column 3, lines 37-41; delete the strucutral formula

Column 3, last line; after "structure" insert



Column 4, line 12; insert parenthesis to read: 1,1-bis-(p-dimethylaminophenyl)ethylene

Column 4, line 25; after "unsubstituted" insert a colon (:)

Column 4, line 55; insert parenthesis to read: 1,1-bis-(p-dimethylaminophenyl)ethylene

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334

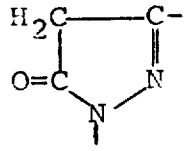
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,533,792 Dated October 13, 1970

Inventor(s) Victor P. Petro et al PAGE - 2

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 65; correct the formula to read:

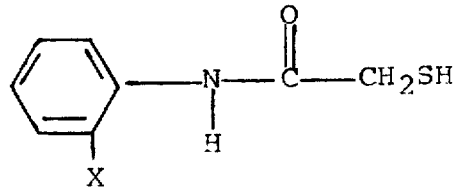


Column 5, line 14; after the structural formula; insert --of the type described in United States Patent 2,294,909.--

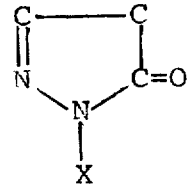
Column 5, line 25; after "polystyrene" insert --in benzene--

Column 5, line 73; insert parenthesis to read:
1,1-bis(p-dimethylaminophenyl)ethylene

Column 6, lines 15-19, correct the formula to read:



Column 6, lines 21-25, correct the formula to read:



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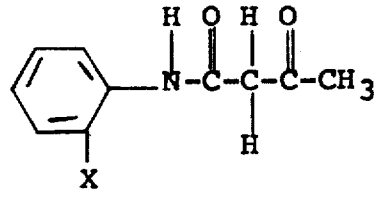
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,533,792 Dated Oct. 13, 1970

Inventor(s) Victor P. Petro et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, lines 27-31, correct the formula to read:



In line 2 of claims 3, 9, 10, 11 and 12, insert parenthesis to read --1,1-bis(dimethylaminophenyl)ethylene--

Signed and sealed this 6th day of April 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents

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