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Takano et al.

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[45] **Nov. 27, 1973**

[54] **PHOTOSENSITIVE MATERIAL CONTAINING A P-PHENYLENEDIAMINE DERIVATIVE COLOR FORMER AND A HALOGENATED HYDROCARBON PHOTOACTIVATOR**

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[51] **Int. Cl.** **G03c 1/52,** G03c 5/24

[58] **Field of Search** ..... 96/90 R, 48 QP, 48

[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

A novel non-silver direct print-out photosensitive material is made from a mixture of a phenylenediamine derivative of a particular structure and an organic halide capable of discharging halogenated carbon radicals by irradiation of light. A binder and sensitizer are preferably added to this material. This photo-sensitive material is extremely excellent in resistance to oxidation and is stable before and after exposure to light. It is also excellent in resolving power, sensitivity, reproducibility of color, resistance to chemicals, etc. The present sensitive material is suitable for a photographic paper, a copying paper, a microfilm, phology, planography or relief printing.

13 Claims, No Drawings

PHOTOSENSITIVE MATERIAL CONTAINING A P-PHENYLENEDIAMINE DERIVATIVE COLOR FORMER AND A HALOGENATED HYDROCARBON PHOTOACTIVATOR

FIELD OF THE INVENTION

This invention relates to a novel non-silver direct print-out photo-sensitive material. More particularly, this invention relates to a photo-sensitive material which is oxidation resistant and excellent in stability, comprising a mixture of a phenylenediamine derivative of a particular structure and a compound capable of discharging halogenated carbon radicals by irradiation of light.

BACKGROUND OF THE INVENTION

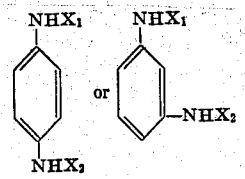
Heretofore, a photo-sensitive material comprising arylamines and organic halides has already been proposed (see U.S. Pat. Nos. 3,042,515, 3,082,086 and 3,502,476). However, the arylamines act merely as color former and their sensitivity is extremely low. Moreover, they are easily oxidized in air. The photo-sensitive products obtained therefrom, therefore, are poor in storage stability either before or after exposure. For the improvement of the storing property of these photo-sensitive products, it has been proposed to add special stabilizers thereto. This method, however, makes the procedure for producing photo-sensitive products complicated. Another proposal is to use an organic halide having a complicated structure. This method involves difficulties in the selection of solvents which highly dissolve but not decompose such organic halides, and in the exploitation of an ideal fixer which neither dissolves nor decomposes the colored images. Further drawback of this method is that the material cost becomes higher since complicated compounds are used.

SUMMARY OF THE INVENTION

The present inventors have now found that the use of a phenylenediamine derivative gives a photo-sensitive composition having an excellent resistance to oxidation and excellent in storage stability, and accomplished this invention.

In accordance with the present invention, there is provided a photo-sensitive composition, which comprises

a. a phenylenediamine derivative represented by the formula:



(A)

wherein at least one of X_1 and X_2 are phenyl or naphthyl group containing or not containing substituent groups, and the other is aliphatic hydrocarbon group, and

b. a compound capable of discharging halogenated carbon radicals by irradiation of light.

The phenylenediamine derivatives represented by the formula (A) used in the present invention are para- or meta-phenylenediamine derivatives. The substituent groups X_1 and X_2 may be both phenyl or naphthyl groups. Alternatively, either one of them may be phenyl group and the other may be naphthyl group. Further, either one of them may be a phenyl or naphthyl group and the other may be an aliphatic hydrocarbon group such as alkyl, cycloalkyl or the like. These phenyl or naphthyl groups may be in the form of mono-, di- or higher substituted derivatives, substituted, for example, with a hydroxy group, nitroso group, nitro group, amino group, alkoxy group, lower alkyl group, acetyl group, halogen atom or the like.

The phenylenediamine derivatives as mentioned above may include N,N'-di-α-naphthyl-p-phenylenediamine; N-phenyl-N'-α-naphthyl-p-phenylenediamine; N,N'-di-β-naphthyl-p-phenylenediamine; N-phenyl-N'-cyclohexyl-p-phenylenediamine; N-phenyl-N'-isopropyl-p-phenylenediamine; N,N'-diphenyl-m-phenylenediamine; N,N'-diphenyl-p-phenylenediamine; N,N'-di-m-methylphenyl-p-phenylene-diamine; N,N'-di-m-chlorophenyl-m-phenylenediamine; and the like.

The organic halide used as a photo-activator component in the composition of the present invention may be any compound capable of discharging halogenated carbon radicals by irradiation of light. Usually, such compounds as represented by the following formulas may preferably be used:

1. $R - CX_3$ (wherein R represents hydrogen, halogen atom, substituted or unsubstituted alkyl, aryl or heterocyclic residual group, and X represents a halogen atom);

The organic halides represented by this general formula may include iodoform, carbon tetrabromide, pentabromo ethane, 2,2,2-tribromo ethanol, α,α,α-trichloro toluene, diphenyl-2,2,2-tribromo ethane, p-nitrobenzotrichloride, hexachloro ethane, bromal, w,w,w-tribromo quinaldine, 4-(ww,w,w-tribromomethyl) pyridine, 2,5-bis-(tribromomethyl)-3,4-dibromo thiophene, 1,1,1-tribromo-2-methyl-2-propanol, and the like; and

(2) $R'-\overset{\overset{O}{\|}}{C}-CX_3$

(wherein R' represents hydrogen, amino group or substituted or unsubstituted aryl group, and X represents a halogen atom).

The organic halides represented by this general formula may include p-nitro-α,α,α-tribromo acetophenone, α,α,α-p-tetrabromo acetophenone, tribromo acetoamide, and the like.

The photo-sensitive composition according to the present invention may also contain, other than the phenylenediamine derivatives and the organic halides as described above, binders and sensitizers as useful additives.

Substances preferably used as binders may be those having film forming property or those which promote the adhesion of the phenylenediamine derivatives and the organic halides in the composition to the flat surface of support. They may include cellulose derivatives such as nitro cellulose, acetyl cellulose, ethyl cellulose or the like; vinyl polymers such as polyvinyl chloride, polyvinyl alcohol, polyvinyl acetate, polystryrene, vinylidene chloride-vinyl chloride copolymer, polymethyl methacrylate, polyethylene, chlorinated polyethylene or the like, synthetic rubbers such as acrylonitrile-butadiene copolymer, styrene-maleic acid anhydride copolymer or the like, solid paraffinic hydrocar-

bons (represented by the general formula, C_nH_{2n+2}, wherein n is an integer from 20 to 70), and so forth. These binders may be used alone or in plural combinations thereof. By the use of these binders, the coating on the support may be applied uniformly in any desired thickness and the adhesiveness of the coated film to the surface of the support is extremely enhanced. In addition, if an organic halide having sublimating property is used, the use of a binder prevents the sublimation thereof, whereby storage property of the sensitive materials before exposure may be improved.

The sensitizers which may be used in the present invention include two different species. One is the so called color sensitizer which increases sensi-tivity of printing materials by widening the range of sensitive wavelengths to the region of visible light. The other is the true sensitizer which increases sensitivity of printing materials regardless of the range of the sensitive wavelengths thereof. The preferable dyestuffs or dyestuff bases which belong to the former are acridine dyestuff, merocyanine dyestuff, cyanine dyestuff, styryl dyestuff or the like which are conventionally used in the prior art of photography. They are, for example, Methylene Blue, Acridine Red, Acridine Orange, p-Diethylaminobenzylidene-2-pyridine, p-Dimethylaminobenzylidene-4-quinoline, and so forth. The preferable sensitizers which belong to the latter are aldehydes, pyrazoline derivatives, benzoin derivatives, benzil derivatives or the like. For example, salicyl aldehyde, benzaldehyde, ascorbic acid, 1,3-diphenyl-5-p-chlorophenyl pyrazoline, benzil, benzoin and the like may preferably be used. By the use of these sensitizers, the sensitivity of printing materials may be increased by from 2 to 15 times.

The ratio of the amount of the phenylenediamine derivative to that of the organic halide in the photosensitive composition according to the present invention is 50 : 1 to 1 : 40, preferably from 25 : 1 to 1 : 20, in terms of the molar ratio. The amount of the binders which may be added to the composition of the present invention is from 0.02 to 50, preferably from 0.1 to 10, parts by weight per one part by weight of the total amount of the phenylenediamine derivative and the organic halide. The amount of the sensitizers is preferably 0.05 part by weight or less per one part by weight of the total amount of the phenylenediamine derivative and the organic halide.

A photosensitive printing material may easily be produced from the composition of the present invention according to the procedure which comprises dissolving or dispersing the aforesaid phenylenediamine derivative and organic halide, preferably together with a binder and a sensitizer, into a suitable solvent, coating the thus obtained solutions or dispersions onto the surface of a support or alternatively immersing the support into siad solutions or dispersions, and drying the support through evaporation of solvents. Evaporation may be conducted by drying in air when volatile solvents are used. On the other hand, it may be conducted by heating in a drier at 50°C to 80°C when non-volatile solvents are used.

The support which may be used for the production of the photosensitive material may be any solid material which is capable of supporting the aforesaid phenylenediamine derivative and the organic halide as a uniform mixture thereof either in the form of surface coating or in the form of an internal dispersion or immersion. For example, various synthetic resin films, woven fabrics, earthen-wares, papers, metal plates, metal foils, glasses, woods or the like may preferably be used as supports.

As for the solvents used in the preparation of the sensitive materials, it is necessary to select those solvents which are good solvents or good dispersing agents for the phenylenediamine derivative, the organic halide, the binder and the sensitizer. They may include, for example, toluene, benzene, tetrahydrofuran, dioxane, ethyl acetate, a mixed solvent of benzene with acetone, a mixed solvent of acetone with tetrahydrofuran, etc.

The method for image formation is a direct printing procedure, comprising placing a negative film or a negative manuscript in contact with the surface of the printing material prepared according to the procedure as described above and irradiating the photosensitive system by a light emitted at a certain distance from a light source such as a xenon lamp, a mercury lamp or the sunlight. The color of the image may vary according to the phenylenediamine derivative used, e.g. blue, green, violet, brown, black, etc.

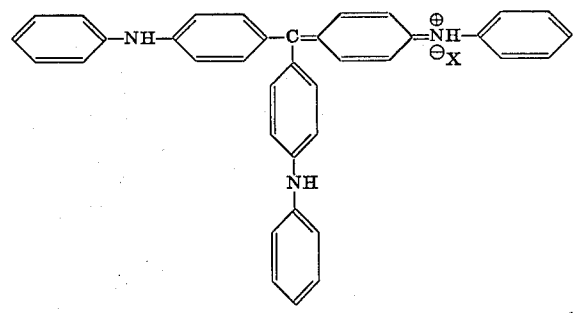
The method for fixing after the image formation may be either a dry system (heating method) in which the residual organic halides are deactivated or gasified by heating or a wet system (solvent method) in which both unreacted phenylenediamine derivatives and organic halides or only unreacted organic halides are removed through dissolution by using suitable solvents. In the dry system, heating may be conducted for from 0.5 to 5 minutes so that the temperature of the surface of the sensitive material may become from 80° to 150°C by the use of an infrared-ray lamp, a heating plate or a heating roll. In the wet fixing system, the exposed sensitive material may be treated for from 0.5 to 5 minutes by the use of suitable solvents which removes residual unreacted substances through dissolution without dissolving the dyestuff formed by the exposure, and more preferably, without dissolving the binder. Thus, a stable image may be obtained. Suitable solvents for the solvent fixing may include benzene, ethylether, acetone, cyclohexane, a mixed solvent of cyclohexane with ethyl acetate or the like.

The photo-sensitive material according to the present invention possesses many improved characteristics as photosensitive printing materials as well as excellent physical properties. It also includes various advantages in the process for production thereof. That is, the image formed is excellent in resolving power (the resolving power is 1,000 lines/mm or more) and in stability. The sensitivity of this printing material is higher as compared with the formerly proposed non-silver photo-system printing material. For example, as compared with the commercially available diazo photographic paper, the sensitivity of the present photosensitive material is from twice to 10 times as much. Further, the image formed is beautifully reproduced in half-tone. The dyestuffs formed by exposure are excellent in resistance to chemicals, particularly, to acids. The direct print-out system makes the sunlight available as a light source. Simple developing and fixing procedures may be employed and even a fixing procedure may be omitted in some particular purpose of uses. Even in such a case, an image stable for a long time may be formed. The phenylenediamine derivatives are cheap and may easily be supplied or produced.

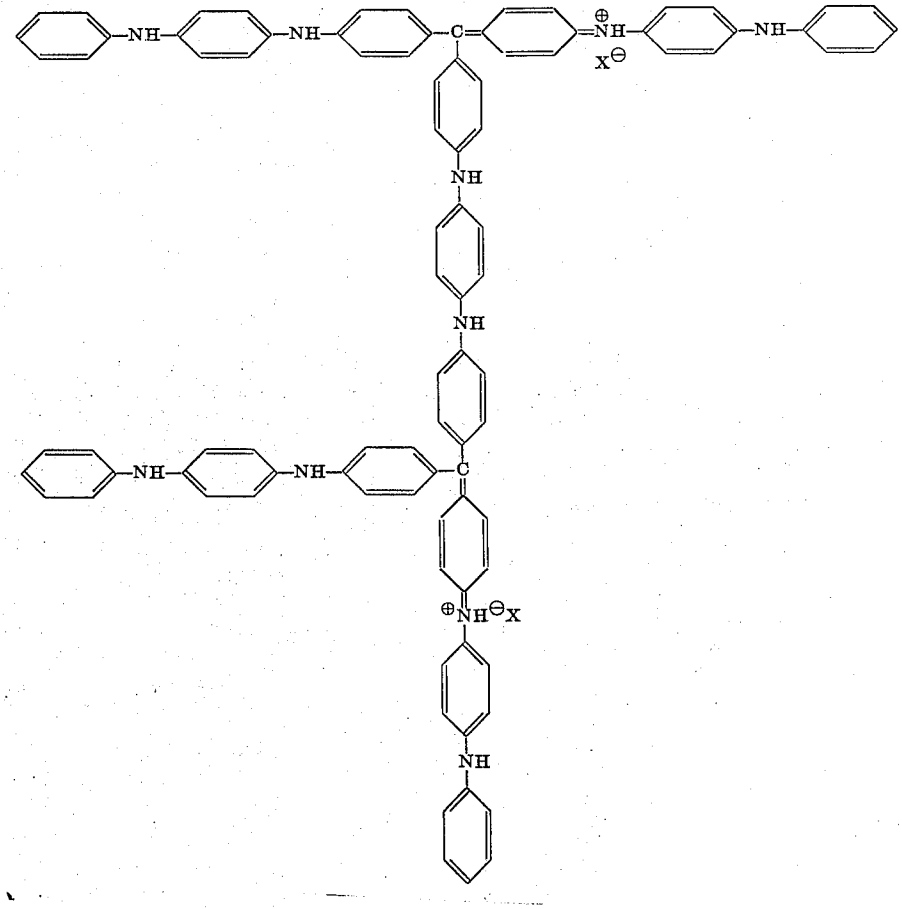
The remarkable fact in the photo-sensitive material according to the present invention is that the phenyl-

enediamine derivative used is a peculiar unique compound having the functions of a colour former, a photo-activator and an antioxidant. In the photo-sensitive material formerly proposed as mentioned above, which contains aryl amines and organic halides, only organic halides are photo-activated by the action of light to form halogenated carbon radicals. These free radicals react with aryl amines, whereby visible color changes of aryl amines are effected. In such a mechanism of color change reaction, only organic halides are photo-activated and aryl amines merely function as colour formers (see R.H. Sprague, Phot. Sci. Eng., 5, No. 2, 98 (1961), 8, No. 2, 91 and (1964) 8, No. 2, 95 (1964)). However, the photosensitive material of the present invention containing the phenylenediamine derivative exhibits a mechanism of color change reaction substantially different from those of the formerly proposed photosensitive materials. That is, in the photosensitive material of the present invention, the phenylenediamine derivative component functions not only as a colour former, but also as a photo-activator. By the action of light, the phenylenediamine derivative is activated at the same time with the organic halide to form free radicals, so that the color change reaction may proceed according to a mechanism wherein the free radicals thus formed react with each other through chain reaction to form stable dyestuffs at a high speed.

In the preent invention, the dyestuff structure formed is also substantially different from that of the formerly proposed sensitive material. The dyestuff formed in the conventional photosensitive system may, for example, be represented by the following formula (wherein diphenyl amine is used as a component):



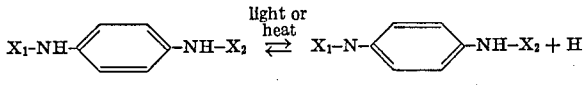
This is a low molecular weight structure wherein only one triarylmethane type dyestuff unit is contained in one dyestuff molecule. In contrast thereto, the dyestuff formed in the present invention may, for example, be represented by the following formula (wherein N,N'-diphenyl-p-phenylenediamine is used):



The results of elemental analysis, ultra-violet and visible-ray absorption and other measurements show that the dyestuff has a high molecular weight structure where-in plural triarylmethane type dyestuff units are contained in one dyestuff molecule. In case of the dye-

stuff having the former structure, the image may sometimes be blurred with smudges in the solvent fixing. The dyestuff of the present invention having the latter structure, which is insoluble, is free from such defect.

In addition, the phenylenediamine derivative used in the present invention is advantageous in that it also functions as an antioxidant to give a photo-sensitive composition and a photosensitive material excellent in storage stability. For example, N,N'-di-β-naphthyl-p-phenylenediamine, N-phenyl-N'-cyclohexyl-p-phenylenediamine, N-phenyl-N'-isopropyl-p-phenylenediamine are conventionally used as antioxidants for plastics or synthetic rubbers. As is confirmed by electron spin resonance absorption measurement, these compounds generate hydrogen radicals to form stable diarylamine radicals when they are heated or irradiated by ultra-violet ray in the state of powders or solutions in non-polar solvents. The p-phenylenediamine derivative and the free radicals formed by decomposition thereof are thereby in an equilibrium state as follows:



The generated hydrogen radicals prevent thermal oxidation or photooxidation. Other phenylenediamine derivatives may also behave similarly. Therefore, in accordance with the present invention, there is provided a photo-sensitive material excellent in storage stability without particular addition of stabilizers. The storage stability of the photosensitive system before exposure to light is also excellent since the phenylenediamine derivative prevents the degradation of the supports for the composition such as solid paraffinic hydrocarbons, woven fabrics, synthetic resins, papers, etc. Further, after exposure to light, if the phenylenediamine derivative remains after the removal of unreacted organic halides alone in the heating fixing method or in the solvent fixing method as described above, the decoloration and the fog of the colored image as well as the degradation of support are prevented. It should further be noticed that in the photo-sensitive system according to the present invention the photo-synthesized dyestuff is resistant against oxidation to improve the storing property of the image.

The photo-sensitive material according to the present invention is higher in sensitivity as compared with other non-silver photo-sensitive system, excellent in resolving power and easy of handling. The dyestuff formed is resistant to chemicals and lipophilic. These features of the present composition makes extensive uses possible. For example, the present material is suitable as a photo-sensitive material for photographic paper, copying paper, planography, relief printing, a microfilm, photography and the like.

The present invention will now be further explained by referring to the following examples, wherein all 'parts' and '%' are by weight.

EXAMPLE 1

A photo-sensitive liquid was prepared by mixing N,N'-di-α-naphthyl-p-phenylenediamine with hexachloro ethane (CCl_6) in tetrahydrofuran to a concentration of 0.05 mol/l of each substance. Into this liquid was immersed for one minute a spot film for thin layer chromatography the surface of which is coated with cellulose. Then, after the withdrawal of the film out of the liquid, the solvent on the surface of the film was immediately evaporated. A 36 mm negative film was placed on the surface of this spot film and then exposure was conducted by the daylight of mid-summer for 5 minutes. Subsequently, after the removal of the negative film, the exposed spot film was irradiated by a 175 W reflex-type infrared-ray lamp at a distance so that the temperature of the surface thereof may become about 130°C. A green image was obtained.

EXAMPLE 2

Fifty ml of 5 percent acetone solution of nitrocellulose containing 0.5 g N,N'-di-β-naphthyl-p-phenylenediamine and 0.5 g carbon tetrabromide (CBr_4) was prepared. This solution was coated on an offset paper under a yellow safety lamp and dried. A negative film for a scanning-type electron microscope was placed on this offset paper and then exposure was conducted at a distance of 30 cm by a USHIO 500 W mercury lamp (Lamphouse No., UI501, super high pressure mercury lamp No. USH 500). After the removal of the negative film, the exposed offset paper was irradiated by a 175 W reflex-type infrared-ray lamp for 5 minutes at an adequate distance to give a stable brown image excellent in resolving power.

EXAMPLE 3

Into the mixed solvent made from 9 parts of warmed benzene and 1 part of warmed acetone was dissolved 0.5 part of wax (m.p.=110°C) and 0.05 part of styrene, Then, 0.1 part of acetylcellulose and 0.2 part of N,N'-diphenyl-m-phenylenediamine were dissolved into the mixture. Further, 0.4 part of pentabromo ethane were added to the mixture to prepare a photo-sensitive liquid. This photosensitive liquid was coated on a sheet of polyester film to obtain a coated film of about 2 mils in thickness after removal of the mixed solvent through vaporization. A negative film was placed on this film and then exposure was conducted by a 500 W mercury lamp for 10 seconds. Immediately after the exposure, the negative film was taken off from the polyester film and the whole surface of the exposed film was heated for 5 minutes with a 175 W infrared-ray lamp at a distance of 15 cm. Then, the printed polyester film was immersed in ethylether for 5 minutes for fixing and dried. A stable blue image was obtained.

EXAMPLE 4

Into 10 parts of warmed benzene solvent were added 0.5 part of eicosane and 0.05 part of polystryrene were added. After further addition of 0.2 part of N,N'-diphenyl-m-phenylenediamine and 0.3 part of carbon tetrabromide to the solution, the solution thus prepared was stored in a brown bottle. Then, this liquid was coated on the surface of a support of a zinc plate to an adequate thickness and benzene was evaporated. A negative film was laid on such treated surface of a zinc plate and a blue image was printed thereon by irradiation effected for 10 seconds by a 500 W mercury lamp. Immediately after the exposure, the printed image was stabilized by irradiating the image by means of a 175 W reflex-type infrared-ray lamp for 5 minutes at a distance of 5 cm and then washed with benzene. The surface of this plate was subsequently subjected to a corrosive treatment in 6% nitric acid aqueous solution, whereby the non-light struck area of the surface of a zinc plate

was removed through dissolution to obtain a relief image.

EXAMPLE 5

A photo-sensitive liquid was prepared by mixing N,N'-diphenyl-p-phenylenediamine and carbon tetrabromide in benzene to a concentration of 0.07 mol/l of each substance. Into this liquid was immersed for one minute a spot film for thin layer chromatography the surface of which was coated with cellulose. Then, after the withdrawal of the film out of the liquid, benzene was evaporated therefrom. A 36 mm negative film was placed on this spot film and exposure was conducted by means of a USHIO 500 W mercury lamp at a distance of 30 cm for 5 seconds to obtain a blue image. After the exposure, the film was stored for one week without fixing, with the result of little fog and decoloration of the image.

EXAMPLE 6

A photo-sensitive liquid having the following composition was prepared and coated under a yellow safety lamp on a photographic baryta paper to a thickness of about 2 mils and dried to prepare a photo-sensitive printing material.

N-isopropyl-N'-phenyl-p-phenylenediamine — 2.5 g.
hexabromo ethane — 2.0 g
polystyrene — 10 g
benzene — 90 cc
acetone — 10 cc

A 36 mm negative film for X-ray was placed on the printing material and exposure was conducted by means of a USHIO 500 W mercury lamp at a distance of 30 cm for 5 seconds. A blue image was immediately formed which was excellent in resolving power. Then, the developed printing material was immersed in a fixer of ethylether for 1 minute. The printing obtained was entirely stable to light.

EXAMPLE 7

Example 6 was repeated except that the same amount of N-phenyl-N'-cyclohexyl-p-phenylenediamine was used in place of the N-isopropyl-N'-phenyl-p-phenylene-diamine to produce a sensitive printing material. After exposure and fixing, a sharp blue image was formed against a white basic paper.

EXAMPLE 8

A photo-sensitive liquid having the following composition was prepared and coated under a yellow safety lamp on a baryta paper and dried to produce a photo-sensitive printing material.

N-phenyl-N'-cyclohexyl-p-phenylenediamine — 2.0 g
α,α,α-tribromo acetophenone — 2.5 g
benzoin — 0.1 g
acetylcellulose — 8 g
acetone — 50 cc
benzene — 50 cc

A 36 mm negative film was placed on this sensitive material and exposure was effected by means of a USHIO 500 W mercury lamp at a distance of 30 cm for 5 seconds. Then the negative film was taken off and the exposed paper was solvent fixed by dipping into benzene for one minute and dried. A stable blue image was formed against the white basic paper.

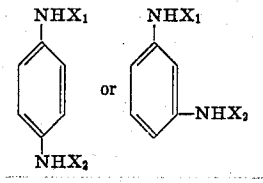
COMPARATIVE EXAMPLE

A photo-sensitive liquid was prepared by mixing diphenylamine and carbon tetrabromide in benzene to a concentration of 0.07 mol/l of each substance. Then, according to the same procedure as described in Example 5 except that exposure was continued for 40 seconds, printing was carried out. The image formed thereby was similarly stored for 1 week without fixing. After the storage, a high degree of fog and decoloration of the image was observed.

We claim:

1. A photo-sensitive composition, which comprises

a. a phenylenediamine derivative represented by the formula:



wherein at least one of X_1 and X_2 is a phenyl or naphthyl group or a phenyl or naphthyl group with a substituent selected from the group consisting of hydroxyl, nitroso, nitro, amino, alkoxy, lower alkyl, acetyl and halogen, and the remainder is an alkyl or cycloalkyl group, and

b. a compound capable of discharging halogenated carbon radicals by irradiation of light.

2. The photo-sensitive composition according to claim **1**, wherein a binder and a sensitizer are contained.

3. The photo-sensitive composition according to claim **2**, wherein the binder is nitrocellulose, acetylcellulose, polyvinyl chloride, polyvinyl alcohol, polystyrene, vinylidene chloride-vinyl chloride copolymer, polymethyl methacrylate, polyethylene, chlorinated polyethylene, acrylonitrile-butadiene copolymer, or n-eicosane.

4. The photo-sensitive composition according to claim **2**, wherein the sensitizer is Methylene Blue, Acridine Red, Acridine Orange, p-Dimethylaminobenzylidene-4-quinoline, p-Diethylaminobenzylidene-2-pyridine, salicyl aldehyde, benzaldehyde, benzil, benzoin, or 1,3-diphenyl-5-p-chlorophenyl pyrazoline.

5. The photo-sensitive composition according to claim **1**, wherein the molar ratio of at least one phenylenediamine derivative of the formula to the organic halide is from 50 : 1 to 1 : 40.

6. The photo-sensitive composition according to claim **2**, wherein from 0.02 to 50 parts by weight of a binder and 0.05 part or less by weight of a sensitizer is added per one part by weight of the total amount of the phenylenediamine derivative and the organic halide.

7. A process for forming an image by direct printing-out, which comprises placing a negative film or a negative manuscript on the photo-sensitive material as produced in claim **1**, and irradiating light thereover by means of a xenone lamp, a mercury lamp or a sunlight.

8. A dry system fixing method applied to the photo-sensitive material after image formation in claim **7**, which comprises heating the surface of the sensitive material to a temperature of from 80° to 150°C by means of an infrared-ray lamp, a heating plate or a heating roll in order to evaporate or deactivate the unreacted organic halide.

9. A wet system fixing method applied to the photo-

sensitive material after the image formation in claim **7**, which comprises removing through dissolution only unreacted organic halides or both unreacted organic halides and phenylenediamine derivatives by the use of benzene, ethyl ether, cyclohexane, a mixed solvent of cyclohexane with ethyl acetate, or ethanol.

10. The photo-sensitive composition according to claim **1**, wherein the phenylenediamine derivative represented by the formula is N,N′-di-α-naphthyl-p-phenylene-diamine, N,N′-di-β-naphthyl-p-phenylenediamine, N-phenyl-N′-α-naphthyl-p-phenylenediamine, N-phenyl-N′-cyclohexyl-p-phenylenediamine, N-phenyl-N′-isopropyl-p-p-phenylenediamine,N,N′-diphenyl-m-phenylenediamine, N,N′-diphenyl-p-phenylenediamine, N,N′-di-m-methylphenyl-p-phenylenediamine or N,N′-di-m-chlorophenyl-m-phenylenediamine.

11. The photo-sensitive composition according to claim **1**, wherein the organic halide is carbon tetrabromide, hexabromo ethane, hexachloro ethane, pentabromo ethane, α,α,α-tribromo toluene, bromal, w,w,w-tribromo quinaldine, 4-(w,w,w-tribromo methyl)-pyridine, α,α,α-tetrabromo acetophenone, α,α,α-tribromo acetophenone, p-nitro-α,αα-tribomo acetophenone, or tribromo acetoamide.

12. The photo-sensitive composition according to claim **2**, wherein the phenylenediamine derivative is N-,N′-di-α-naphthyl-p-phenylenediamine, N,N′-di-β-naphthyl-p-phenylenediamine, N-phenyl-N′-cyclohexyl-p-phenylenediamine, N,N′-diphenyl-m-phenylenediamine, N,N′-diphenyl-p-phenylenediamine, or N-phenyl-N′-isopropyl-phenylene-diamine, the organic halide is carbon tetrabromide, hexabromo ethane, hexachloro ethane, pentabromo ethane, w,w,w-tribromo quinaldine, or α,α,α-tribromo acetophenone, the binder is polystyrene, polyvinyl chloride, n-eicosane, nitrocellulose, acetylcellulose, ethylcellulose, or vinylidene chloride-vinyl chloride copolymer, and the sensitizer is benzil, benzoin, Acridine Orange, benzaldehyde, 1,3-diphenyl-5-p-chlorophenyl pyrazoline, p-dimethylaminobenzylidene-4-quinoline, the molar ratio of the phenylenediamine to the organic halide being from 25 : 1 to 1 : 20, and the amount of the binder and the sensitizer being from 0.1 to 10 and 0.05 part or less parts by weight, respectively, per one part by weight of the total amount of the phenylenediamine derivative and the organic halide.

13. An article comprising the composition of claim **1** as a coating on a solid supporting surface.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,775,123 Dated November 27, 1973

Inventor(s) HIROSHI TAKANO 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, line 3: replace "4-(ww, w, w" with ---4-(w, w, w--- .

Column 3, line 14: replace "sensi-tivity" with ---sensitivity--- .

Column 5, line 13: replace "91 and (1964)" with ---91(1964) and--- .

Column 6, line 67: replace "where-in" with ---wherein--- .

Column 10, Claim 7 should read as follows:

---7. A process for forming an image by direct printing-out, which comprises placing a negative film or a negative manuscript on a photo-sensitive material, and irradiating light thereover by means of a Xenon lamp, a mercury lamp or sunlight, said photo-sensitive material being prepared by dissolving or dispersing (a) and (b) as defined in Claim 1 together with or without a binder and a sensitizer into a solvent, coating the solution on the surface of a support or immersing a support into the solution, and evaporating the solvent.--- .

Column 11, Claim 10, line 7: replace "isopropyl-p-p-" with ---isopropyl-p- --- .

Signed and sealed this 23rd day of July 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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