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3,667,954

TRIBROMOMETHYL SULFONYL PYRIDAZINE OR PHTHALAZINE PHOTOACTIVATORS

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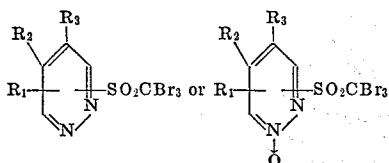
Int. Cl. G03c 1/52, 1/72

U.S. Cl. 96-90

6 Claims

ABSTRACT OF THE DISCLOSURE

A light-sensitive printing material comprising a photo-activator capable of forming a free radical by action of light and a discoloring agent showing a visible color change by action of said free radical, characterized by using as the photo-activator a pyridazine or phthalazine derivative which is represented by the general formula



wherein R₁, R₂ and R₃ are individually a hydrogen atom, a hydroxy group, a lower alkyl group, an alkylsulfonyl group, an alkoxy group or an alkoxycarbonyl group, provided that R₂ and R₃ may form a benzene ring and, in the case of an N-oxide type compound, R₃ may be a tribromomethyl sulfonyl group.

BACKGROUND OF THE INVENTION

This invention relates to a light-sensitive printing material incorporated with a photo-activator capable of forming a free radical by action of light and a discoloring agent showing a visible color change by action of said free radical, characterized in that the photo-activator is a halogenated organo-sulfone compound represented by the general formula set forth later. An object of the invention is to provide a light-sensitive printing material which is high in stability, non-toxic in handling and excellent both in light-sensitivity and gradation.

In light-sensitive printing materials of this kind, halogenated hydrocarbons have heretofore been used, in general, as photo-activators, and particularly carbon tetrabromide and aroyl trihalogenated hydrocarbons have been recommended as effective photo-activators.

However, carbon tetrabromide is extremely high in volatility and easily escapes from the light-sensitive printing materials. Accordingly, printing materials prepared by the use thereof have had such serious drawbacks that they are markedly low in stability and becomes unusable in a few days after preparation. Further, it has been known that the vapor of carbon tetrabromide is quite toxic and the toxicity thereof is about 1 p.p.m. in 3 hours. In handling carbon tetrabromide, therefore, a special attention has been required to be paid so as not to inhale the vapor thereof. Thus, carbon tetrabromide has been extremely undesirable, in practice.

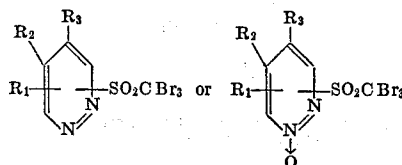
On the other hand, aroyl trihalogenated hydrocarbons are less volatile but are strongly stimulative so that in thermally fixing light-sensitive materials containing said hydrocarbons or in handling the said hydrocarbons, the skin or mucosa should have previously been covered with a rubber product or the like protector, e.g. an anti-gas mask or rubber gloves. Thus, aroyl trihalogenated hydro-

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carbons have been extremely undesirable, like the above-mentioned carbon tetrabromide.

DESCRIPTION

The present invention is characterized by using as photo-activators free from such drawbacks as mentioned above tribromomethyl sulfone derivatives having pyridazine or phthalazine nuclei which are represented by the general formula



wherein R₁, R₂ and R₃ are individually a hydrogen atom, a hydroxy group, a lower alkyl group, an alkylsulfonyl group, an alkoxy group or an alkoxycarbonyl group, provided that R₂ and R₃ may form a benzene ring and, in the case of an N-oxide type compound, R₃ may be a tribromomethyl sulfonyl group.

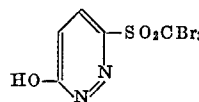
All these compounds employed in the present invention are crystalline compounds and are not volatile unlike carbon tetrabromide. Accordingly, light-sensitive printing materials prepared by the use of said compounds do not suffer from escape of the photo-activators and are quite stable. Further, the said compounds are non-toxic and odorless, and the vapors thereof are not lachrymatory, so that the handling of the compounds is extremely easy and safe and any special consideration such as aeration or the like is not required to be paid thereto.

Moreover, light-sensitive printing materials in accordance with the present invention have such advantages over those of the prior art that they are higher in light-sensitivity and excellent in gradation and, even when same discoloring agents have been used, the resulting colors are brilliant and pure.

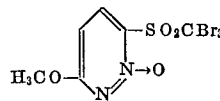
Typical examples of the compounds represented by the aforesaid general formula are as shown below, but it is needless to say that these are examples and do not limit the scope of the compounds usable in the present invention.

(1) 3-(α,α,α -tribromomethylsulfonyl)-6-hydroxypyridazine

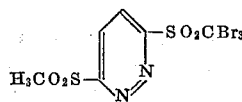
	Melting point, °C.
(1)..... 3-(α,α,α -tribromomethylsulfonyl)-6-hydroxypyridazine.	1267-268



(2)..... 3-(α,α,α -tribromomethylsulfonyl)-6-methoxyphthalazine-2-oxide.

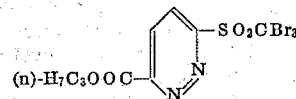
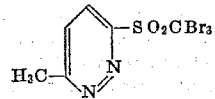
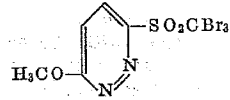
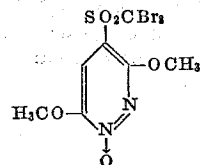
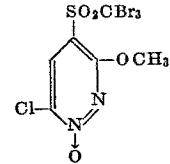
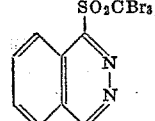
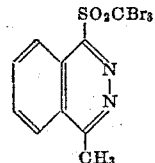
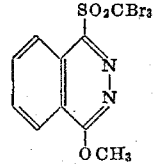


(3)..... 3-(α,α,α -tribromomethylsulfonyl)-6-methylsulfonylpyridazine.



See footnote at end of table.

TABLE—Continued

	Melting point, °C.
(4)----- <i>n</i> -Propyl-3-(α,α,α -tribromomethylsulfonyl)-pyridazine-6-carboxylate.	178-179
	
(5)----- 3-(α,α,α -tribromomethylsulfonyl)-6-methylpyridazine.	175-176
	
(6)----- 3-(α,α,α -tribromomethylsulfonyl)-6-methoxy pyridazine.	ca. 150
	
(7)----- 4-(α,α,α -tribromomethylsulfonyl)3,6-dimethoxy pyridazine-1-oxide.	> 200
	
(8)----- 4-(α,α,α -tribromomethylsulfonyl)-3-methoxy-6-chloropyridazine-1-oxide.	> 200
	
(9)----- 1-(α,α,α -tribromomethylsulfonyl)-phthalazine.	> 200
	
(10)----- 1-(α,α,α -tribromomethylsulfonyl)-4-methylphthalazine.	> 110
	
(11)----- 1-(α,α,α -tribromomethylsulfonyl)-4-methoxyphthalazine.	125 ⁴
	

⁴ Decomposition.

Generally, these compounds can be easily prepared by reacting a corresponding thio glycolic acid derivative in a sodium hypobromide solution at a temperature of 20° to 45° C.

When exposed to light, particularly ultraviolet light, the above-mentioned compounds form active free halogen groups which give a visible color change to discoloring agents. As discoloring agents showing a visible color change by action of free radicals formed from photo-activators, there are two kinds, i.e. those which originally are colorless but can be brought into a colored state by action of the free radicals and those which originally have an inherent color but the color can be changed to another color or can be decolorated to colorless. Light-sensitive materials prepared by use of the former discoloring agents which are originally colorless but form color by action of light, are used as so-called nega-posit type printing materials, while those prepared by use of the latter discoloring agents are used as posi-posit type printing materials.

Typical discoloring agents belonging to the former type are arylamines. Arylamines suitable for this purpose include not only mere arylamines such as primary and secondary aromatic amines but also so-called leuco dyes which are dyes having amino groups or reduced amino groups.

Examples of such arylamines are:

diphenylamine,
 dibenzylaniline,
 triphenylamine,
 N,N-diethylaniline,
 N,N-dimethylaniline,
 N-hydroxyethyl-N-ethylaniline,
 N,N-diethanolaniline,
 o-aminodiphenylamine,
 p-hydroxydiphenylamine,
 N-methyldiphenylamine,
 p-benzoyloxydiphenylamine,
 p-methoxydiphenylamine,
 N-vinylcarbazole,
 2-phenylindolizine,
 N,N'-diphenyl-p-phenylenediamine,
 N,N'-dihydroxyethyl-m-toluidine,
 N,N'-dihydroxyethyl-o-toluidine,
 α -phenylnaphthylamine,
 β -phenylnaphthylamine,
 3-aminoquinoline,
 indole,
 salicylidene-p-toluidine,
 salicylidene-p-chloroaniline,
 cyanomethylene-4-quinolyl-2-naphthalene,
 3-phenylindole,
 α -diethylaminopyridine,
 p,p'-methylenebis-aniline,
 p,p'-methylenebis(N,N-dimethylaniline),
 p,p'-pentylidenebis(N,N-dimethylaniline),
 p,p',p''-methylidynetris(N,N-dimethylaniline),
 p,p'-hydroxymethylenebis(N,N-diethylaniline),
 p,p'-(dimethylamino)-diphenylamine,
 p,p'-aminomethylenebis(N,N-dimethylaniline),
 p,p'-(o-chloropentylidene)-bis(N,N-dimethylaniline),
 p,p'-(p''-aminopentylidene) bis-aniline,
 p,p'-(p''-amino-m''-methylpentylidene)-bis(N-phenylaniline),
 1,1-bis(p-dimethylaminophenol)-p'-dimethylaminophthalin,
 3,6-bis(diethylamino)-spiro(phthalin-1,9'-xanthene),
 3,6-bis(diethylamino)-9-(p-dimethylaminophenol)-xanthene,
 1,1-bis(p-dimethylaminophenol)-p'-dimethylaminophthalan,
 1,1-bis(p-aminophenol)-p'-aminophenolphthalan,
 10-benzoyl-3,7-di(p-dimethylamino)-phenothiazine, and
 3-diethylamino-7-aminophloxazine.

In addition to such relatively low molecular weight amines as mentioned above, there may also be used effectively for this purpose high molecular weight arylamines such as a polymer of N-acryloyloxyethyl-N-ethyl-

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aniline, a copolymer of N-acryloyloxyethyl-N-ethylaniline and maleic anhydride, and a condensation product of a copolymer of vinyl methyl ether and maleic anhydride (which copolymer is a commercially available product having the trade name of Gantredt) with N-hydroxy-N-

As discoloring agents effective for use in nega-posit type printing materials, there may be used, in addition to those mentioned above, quaternary salts and N-oxide compounds of nitrogen-containing heterocyclic compounds, and these N-oxide compounds are effective also as the sensitizers mentioned later. Examples of the quaternary salts are 2-methylbenzothiazole-methyl iodide, 2-methylbenzothiazole-ethyl bromide, quinaldine-methyl iodide, 2,5-dimethylbenzothiazole-methyl-p-toluenesulfonate, 2,5,6-trimethylbenzothiazole-butyl iodide, etc., and examples of the N-oxide compounds are 4-methylquinoline-N-oxide, 2,2'-dipyridine-N-oxide disulfide, 4-methylpyridine-N-oxide, quinoline-N-oxide, etc.

Further, as the discoloring agents effective for use in posi-posit type printing materials which originally have an inherent color but the color is discolored or decolorated by action of free radicals, there are various dyes of the diphenylmethane, triphenylmethane, thiazine, xanthene, anthraquinone, iminonaphthoquinone and azomethine types.

Examples of such dyes include: Auramine (C.I. 41000), Victoria Blue (C.I. 44045), Brilliant Lowdurine Blue R (C.I. 42565), Benzoyl Methylene Blue, Cinnamoyl Methylene Blue, p-Anisoyl Methylene Blue (C.I. 51195), Nile Blue A (C.I. 51180), Ephenew Blue (C.I. 51185), Rhodamine B (C.I. 45170), Rhodamine 3B (C.I. 45175), Rhodamine 12GM (C.I. 45310), Sudan Brau G (C.I. 61525), Sudan Blue GN (C.I. 61520), Celliton Blue (C.I. 64500),

4-p-diethylaminophenylimino-naphthoquinone, 2-carboxyanilino-4-p-diethylaminophenylimino-naphthoquinone, 2-carbostearylamino-4-p-dihydroxyethyl-aminophenylimino-naphthoquinone, p-methoxybenzoyl-p'-diethylamino-o'-methylphenylimino-acetanilide, cyano-p-diethylaminophenylimino-acetanilide, 1-phenyl-3-methyl-4-p-diethylaminophenylimino-5-pyrazolone, and 1-β-naphthyl-4-p-diethylaminophenylimino-5-pyrazolone.

The light-sensitive printing materials of the present invention are obtained by bringing the aforesaid photoactivator and discoloring agent into the form of a solution together with a suitable high molecular binder having a film-forming ability, coating the solution on a support such as a paper or film base, followed by drying. As the high molecular binders in the above case, there may be used various substances, e.g. cellulose derivatives such as acetyl cellulose, acetyl-butyril cellulose and ethyl cellulose, vinylic polymers or copolymers of vinyl chloride, vinylidene chloride, vinyl acetate, acrylates and styrol, and synthetic rubbers such as styrene-maleic anhydride copolymer, cyclic rubber, acrylic rubber and butadiene copolymer.

When the light-sensitive printing material of the present invention is exposed to light, particularly ultraviolet light, the discoloring agent brings about a visible color change by action of a free radical formed from the photoactivator, thereby giving an image. This light-sensitivity to light can further be enhanced by addition of a suitable sensitizer. As such sensitizers, there are two kinds, those belonging to so-called color sensitizers which enhance the light-sensitivity by broadening the light-sensitive wavelength area of printing material to the area of visible light, and those belonging to true sensitizers which enhance the light-sensitivity regardless of the light-sensitive wave length area.

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As the sensitizers belonging to the former, there are effectively used acridine, cyanine, merocyanine, styryl and the like dyes and dye bases which have been used as sensitizing dyes in the prior art photography.

Examples of these include: Acridine Orange, Acridine Red, Rose Bengale, Methylene Blue, pinacyanol, pinakryptol yellow,

p-dimethylaminobenzylidene-4-quinoline, p-dimethylaminobenzylidene-2-quinoline, p-diethylaminobenzylidene-4-pyridine, p-diethylaminobenzylidene-2-pyridine, 1-(3-ethyl-2-(3H)-benzothiazolidene)-4-butylidene-dibenzothiazolyl-methane, (1-ethyl-4-(1H)-quinolidene)-2-benzothiazolyl-methane, 5-2-(3-ethylbenzoxazolidene)-ethylidene-2-phenylimide-3-phenyl-4-keto-tetrahydrothiazole, 1,3-diethylthia-4'-carbocyanine iodide, 1,3'-dimethyloxa-2'-carbocyanine-p-toluene-sulfonate, and 5-1-methyl-2-(1H)-quinolidene-2-butylidene-3-ethyl-2-thio-2,4-oxazolinedione.

As the true sensitizers belonging to the latter, there are effectively used the aforesaid heterocyclic N-oxides and such aldehydes and pyrazoline derivatives as exemplified below.

Examples of aldehydes include benzaldehyde, dimethylaminobenzaldehyde, o-phthalaldehyde, salicylaldehyde, thiosalicylaldehyde, anisaldehyde, vanillin, phenylacetaldehyde, ascorbic acid, and benzaldehydecaboxylic acid, and examples of pyrazoline derivatives include

1,3-diphenyl-5-p-methoxy-phenylpyrazoline, 1,3-diphenyl-5-p-dimethylaminophenylpyrazoline, 1-phenyl-3-diphenyl-5-p-dimethylaminophenylpyrazoline and 1-phenyl-3-diphenyl-5-p-chlorophenylpyrazoline.

When these sensitizers are suitably used, the light-sensitivities of printing materials can be increased to 2 to 20 times.

As components which are preferable to be used in combination with the sensitizers, there are color tonemodifiers.

The light-sensitive printing materials of the present invention are exposed and then fixed by treatment with a solvent or a reducing agent, whereby final images are obtained. However, when the present printing materials have previously been incorporated with certain additives and are then exposed, images markedly different in color tone can be obtained. For example, organic compounds having mercapto groups in the molecules, e.g. 4-phenylmercaptotetrazole, 2-methylmercaptobenzothiazole, thioglycolic acid anilide, thiourea, phenylthiourea and diphenylthiourea, are effective for browning the color tones of color images obtained from the arylamines and the photoactivators.

The light-sensitive printing material of the present invention is obtained by dissolving the aforesaid various components in a binder solution and coating the resulting solution on a suitable support according to a known procedure. In this case, preferable quantitative proportions of the components are as follows:

	Parts by weight
Solvent	500-1000
Film-forming binder	10-100
Photo-activator	1-50
Discoloring agent	10-100
Color tone modifier (optional)	1-10
Sensitizer (optional)	1-5

¹ Provided that the amount of the binder is at most 10% based on the weight of the solvent.

As the support, there may be used any of papers, plastic film bases, glass plates and metal sheets. Gen-

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erally, however, the use of photographic papers and plastic-coated papers makes it possible to obtain high density, clear images with good resolution. Alternatively, the use of a photographic film gives a clear, transparent image.

The optimum thickness of the light-sensitive layer to be coated on the support is about 2 to 3 μ , in general, though high sensitivity and density can be attained with increasing thickness of the light-sensitive layer.

When the present light-sensitive printing material obtained in the above manner is superposed on an original and then printed by application of light, a color is immediately formed or the dye is discolored or decolorated to give a clear image. The present printing material has several to several ten times the sensitivity of a commercially available diazotype positive light-sensitive paper. If necessary, the printing material may be subjected to a suitable enlarging device to obtain an enlarged image. The image formed by printing is stable but is not storable in a bright place, unless the image is freed from the light-sensitivity of unexposed portion, and hence should be subjected to fixation. This fixation can be accomplished simply by treating the printed material with a suitable solvent to remove residual components or by reducing the active components with a suitable reducing agent, so that the material shows no activity to light any more.

In the solvent fixation, there is used a suitable solvent capable of dissolving off the photo-activator without dissolving a dye formed by exposure or the dye left undecolored or un-decolored. For example, in the case of a nega-positi type light-sensitive printing material prepared by using the previously exemplified compound (1) as the photo-activator and diphenylamine as the discoloring agent, an equal amount mixture of ethyl acetate and cyclohexane was most preferable, and such a solvent as trichlene, methanol or acetone dissolved out the dye formed and was not usable. Thus, for the solvent fixation, it is essential that a suitable solvent should be selected according to the components of the printing material used.

Alternatively, a reducing agent solution, such as an aqueous solution of sodium sulfite, acid sodium sulfite or a ketone or aldehyde addition product thereof, or an acid solution of stannous chloride, is simply kiss-coated on the light-sensitive printing material after exposure, or the material is immersed in said solution, whereby a sufficiently stable image storable in a bright place can be obtained with a treating time of about 0.5 to 2 minutes, like in the case of the solvent fixation.

The present invention is illustrated in detail below with reference to examples, but it is needless to say that the invention is not limited only to these examples but various modifications are possible within the scope of the invention.

PREFERRED EMBODIMENTS

Example 1

A photographic paper was subjected to surface treatment by application of 1-1.5 g./mm.² of polyvinyl alcohol having a polymerization degree of about 600. On this photographic paper was coated under a yellow safety lamp 20 cc./mm.² of a light-sensitive liquid of the composition shown below, followed by drying to prepare a light-sensitive printing material.

3-(α,α,α -tribromomethylsulfonyl)-6-methylpyridazine: 5 g.
Diphenylamine: 10 g.
Acetyl cellulose: 10 g.
Acetone: 30 cc.
Benzene: 70 cc.

The thus prepared printing material was placed on a photographic negative and exposed for 5 seconds to an 800 w. mercury lamp at a distance of 5 cm., whereby a deep blue positive image on a white background was immediately obtained. Subsequently, the printing mate-

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rial bearing the said image was subjected to solvent fixation by immersing for 1 minute in an equal amount mixture of ethyl acetate and cyclohexane, whereby the image could be made stable. This light-sensitive printing material had about 2 times the light-sensitivity of a commercially available diazotype positive light-sensitive paper and was excellent in resolution and clear in color tone.

Example 2

A light-sensitive printing material was prepared in the same manner as in Example 1, except that in place of the diphenylamine was used the same amount of Leuco-crystal Violet. When treated in the same manner as in Example 1, the thus prepared printing material gave a clear, deep purple image on a white background. This printing material is nega-positi type, and hence gives a positive image if a negative is used as an original and gives a negative image if a positive is used as an original.

Example 3

1-(α,α,α -tribromomethylsulfonyl)-4-methoxyphthalazine: 5 g.
N,N-diethanolaniline: 10 g.
1-phenyl-3-diphenyl-5-chlorophenylpyrazoline: 0.5 g.
Cellulose acetate butyrate: 10 g.
Acetone: 30 cc.
Benzene: 70 cc.

A light-sensitive liquid comprising the above-mentioned components was coated according to a known procedure in a proportion of 20 cc./mm.² under a yellow lamp on a photographic cellulose triacetate film base of 0.14 mm. in thickness, followed by drying in a dark place at below 60° C. to prepare a light-sensitive printing material. When this printing material was exposed for 2 seconds to the same light source as in Example 1, there was obtained an image which was sufficiently high in density and clear in color tone.

Example 4

On a 150 g. baryta paper was coated 23 cc./mm.² of a light-sensitive liquid of the composition shown below, followed by drying to prepare a light-sensitive printing material.

3-(α,α,α -tribromomethylsulfonyl)-6-methoxypyridazine-2-oxide: 3 g.
N,N-diethanolaniline: 10 g.
Diphenylthiourea: 0.3 g.
Vinyl methyl ether-maleic anhydride copolymer: 2 g.
Acetone: 50 cc.
Methyl ethyl ketone: 25 cc.
Methanol: 25 cc.

The thus prepared printing material was exposed to the same mercury lamp as in Example 1 to obtain a clear, bluish brown image on a white background. This image was fixed by immersing the material for 5-30 seconds in a fixing solution of the following composition:

Stannous chloride: 20 g.
Hydrochloric acid: 4 cc.
Water: 100 cc.
Activator (5% aqueous solution): 4 cc.

As the result, the image became a completely fixed stable image showing no change even when exposed to strong ultraviolet light.

Example 5

In a 150 g. baryta paper was coated 20 cc./mm.² of a light-sensitive liquid of the composition shown below to prepare a light-sensitive photographic material.

3-(α,α,α -tribromomethylsulfonyl)-6-hydroxypyridazine: 5 g.
N-vinylcarbazole: 10 g.
p-(N,N-dimethylamino)-pentylidene- γ -pyridine: 0.5 g.
Vinyl methyl ether-maleic anhydride copolymer: 2 g.

Acetone: 50 cc.
Methyl ethyl ketone: 25 cc.
Methanol: 25 cc.

The thus prepared printing material had been incorporated with a dye base and hence was sensitized to a visible light area. Accordingly, the light-sensitivity of this printing material was far more excellent than that of the printing material prepared in Example 1.

This printing material was exposed for 15-20 seconds at a distance of 30 cm. to a slide projector having a tungsten lamp as a light source in which had been inserted a photographic negative, whereby a sufficiently readable blue image was obtained. This image was further heated at 100° C. for 5-10 seconds to obtain a deep bluish brown, high density image. Subsequently, the image was subjected to fixation by immersing the printing material in gasoline, whereby the image could be made stable.

Example 6

A solution of the composition shown below was coated by means of a rotary coater on a zinc plate, followed by drying to prepare a pre-sensitized plate.

Methacrylic acid - N - ethyl - N - phenylaminoethyl methacrylate copolymer (6:4): 0.6 g.
1 - (α,α,α - tribromomethylsulfonyl) - phthalazine: 0.4 g.
Dioxane: 10 cc.

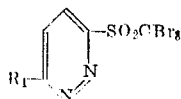
The thus prepared plate was closely adhered to a negative, set to a printing machine and exposed for 5 minutes to a 500 w. tungsten lamp at a distance of 30 cm. to obtain a blue, clear image. The zinc plate bearing the said image was developed with a 0.05% aqueous caustic soda solution, slightly dried and then etched with a Dow etching machine to obtain a relief printing plate excellent in resolution.

On the other hand, the above-mentioned light-sensitive solution was coated on a grained aluminum plate, exposed and developed in the same manner as above and then coated with rubber to obtain an offset printing aluminum plate bearing a blue image.

What is claimed:

1. Light-sensitive imaging material comprising a support and a coating thereon of a light-sensitive composition comprising an organic compound reactive in the presence of a free radical to yield a visible color change and a photo-activator capable of forming said free radical upon exposure to light, said photo-activator being selected from the group consisting of:

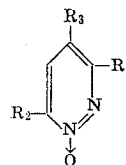
(a) pyridazine derivatives of the formula:



wherein

R₁ is hydrogen, hydroxy, lower alkyl, alkylsulfonyl, alkoxy, or alkoxy carbonyl;

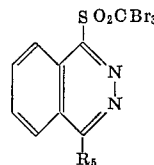
(b) phthalazine derivatives of the formula:



wherein

R₂ is hydrogen, hydroxy, lower alkyl, alkylsulfonyl, alkoxy, or alkoxy carbonyl, or tribromomethyl sulfonyl, R₃ is hydrogen or tribromomethyl sulfonyl, at least one of R₂ and R₃ being tribromomethyl sulfonyl, and R₄ is hydrogen, hydroxy, lower alkyl, alkylsulfonyl, alkoxy, or alkoxy carbonyl; and

(c) phthalazine derivatives of the formula:



wherein R₅ is hydrogen, hydroxy, lower alkyl, alkylsulfonyl, alkoxy, or alkoxy carbonyl.

2. Material according to claim 1 wherein said photo-activator is 3 - (α,α,α - tribromomethylsulfonyl) - 6-methylpyridazine.

3. Material according to claim 1 wherein said photo-activator is 1 - (α,α,α - tribromomethylsulfonyl) - 4-methoxyphthalazine.

4. Material according to claim 1 wherein said photo-activator is 3 - (α,α,α - tribromomethylsulfonyl) - 6-methoxy pyridazine-2-oxide.

5. Material according to claim 1 wherein said photo-activator is 3 - (α,α,α - tribromomethylsulfonyl) - 6-hydroxypyridazine.

activator is 1 - (α,α,α - tribromomethylsulfonyl) - phthalazine.
activator is 1 - (α,α,α - tribromomethylsulfonyl) - phthalazine.

References Cited

UNITED STATES PATENTS

3,502,476 3/1970 Itano et al. ----- 96-90

NORMAN G. TORCHIN, Primary Examiner

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96-89; 260-250

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,667,954 Dated 6 June 1972

Inventor(s) Kohei Itano, Masashi Nakano, and Mitsuru Hashimoto

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

Col. 10, line 4, "(b) phthalazine derivatives" should read -- (b) pyridazine derivatives--.

Col. 10, line 43, should read "6. Material according to claim 1 wherein said photo-".

Signed and sealed this 12th day of September 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents