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# LIGHT-SENSITIVE DIAZOTYPE MATERIAL

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U.S. Cl. 96—91 8 Claims

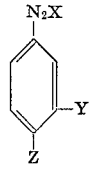
## ABSTRACT OF THE DISCLOSURE

Diazotype material having improved light-sensitivity and developing speed with good keeping and exposure properties is provided by utilizing in the light-sensitive layer a para-(tertiary) amino-2-(fluoro, chloro or bromo)-3-(fluoro, chloro or bromo)-benzenediazonium compound in which one of the tertiary amino substituents is alkyl or aralkyl and the other is alkyl, aralkyl or cyclohexyl, or in which said substituents form a heterocyclic ring with the p-amino nitrogen atom. The compound gives especially good light-sensitivity and keeping qualities when the para-amino group is acyclic.

The invention relates to light-sensitive diazonium compounds and to diazotype material sensitized therewith. The diazotype material may be so-called one-component diazotype material, which is developed with a liquid containing an azo-coupling component, so-called two-component diazotype material, which is developed with the aid of ammonia vapour, or heat-developable diaztoype material.

For sensitizing one-component diazotype material, benzene diazonium compounds having a tertiary amino group such as a diethylamino group or a N-methyl-N-cyclohexyl-amino group in the para-position and a chlorine atom in the meta-position are used on a large scale. Since diazotype materials sensitized with these diazonium compounds furnish copies the azo-dyestuff image of which has high U.V.-absorption, these diazonium compounds are chiefly used for sensitizing transparent diazotype materials for making so-called intermediate originals.

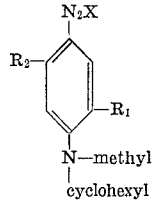
British patent specification No. 957,838 describes transparent one-component diazotype material comprising a hydrophilic film layer in which has been incorporated a diazonium compound of the general Formula I:




in which X is an anion, Y stands for a chlorine or a bromine atom, and Z for a N-alkyl-N-benzylamino, a N-alkyl-N-cyclohexylamino, or a dibenzylamino group.

This diazotype material can be developed with weakly acid phloroglucinol developers.

British patent specification No. 972,951 describes one-component diazotype material sensitized with a diazonium compound of the general Formula II:

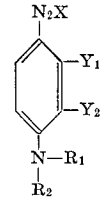





in which X is an anion, $R_1$ and $R_2$ represent chlorine or bromine atoms, and the cyclohexyl group may carry one or more methyl groups. Preferably this diazotype material is transparent diazotype material with a light-sensitive hydrophilic film layer. It has higher developing speed than material sensitized with 4-diazo-2-chloro-N-methyl-N-cyclohexylaniline. Like the last-mentioned compound, the diazonium compounds mentioned in British patent specification No. 972,951 have fair light-sensitivity.

Further compounds mentioned in the literature are the diazonium compounds 4-diazo-2,5-dichloro-N-ethyl-N-benzylaniline (see Fiat Final Report 813, page 1349) and 4-diazo-2-chloro-5-bromo-N,N-dimethylaniline (see Canadian patent specification No. 627,653).

According to the present invention, a new diazotype material is provided which comprises a support and, carried on the support, a light-sensitive layer containing one or more light-sensitive diazonium compounds of the general Formula III:




in which X is an anion, each of $Y_1$ and $Y_2$ is a fluorine, a chlorine or a bromine atom, $R_1$ is an alkyl or an aralkyl group, and $R_2$ is an alkyl, an aralkyl or a cycloalkyl group, or in which $R_1$ and $R_2$ form a saturated heterocyclic ring with the nitrogen atom to which they are attached. An alkyl group at either $R_1$ or $R_2$ may be branched or non-branched, and any of the named substitutents at $R_1$ or $R_2$ may be substituted or non-substituted.

This new diazotype material has higher light-sensitivity than diazotype material sensitized with a corresponding diazonium compound according to British patent specifications Nos. 957,838 or 972,951. Moreover, the diazotype material according to the invention has a higher developing speed and good keeping qualities, and it bleaches out clearly upon exposure.

Especially suitable diazonium compounds are those according to Formula III, in which


stands for an acyclic amino group. These diazonium compounds are more light-sensitive and have greater stability than the corresponding compounds in which


is a heterocyclic group. Consequently, diazotype material sensitized with the former is more light-sensitive and has better keeping qualities than diazotype material sensitized with the latter.

The diazotype material according to the invention is preferably one-component diazotype material. It may, however, also be two-components diazotype material or heat-developable diazotype material. (By one-component diazotype material is also to be understood a light-sensitive printing plate which has been sensitized with a diazonium compound according to Formula III, the formation of the oleophilic image being effected by azo-dyestuff formation.)

The following is a list, though not a complete one, of diazonium compounds which can be used with good results in diazotype material according to the invention:

4-diazo-2,3-difluoro-N,N-dimethylaniline
4-diazo-2,3-dibromo-N,N-dimethylaniline
4-diazo-2,3-dichloro-N,N-dimethylaniline
4-diazo-2,3-dichloro-N,N-diethylaniline
4-diazo-2,3-dichloro-N,N-di-n-propylaniline
4-diazo-2,3-dichloro-N,N-di-n-butylaniline
4-diazo-2,3-dichloro-N,N-di-n-pentylaniline
4-diazo-2,3-dichloro-N,N-di-n-hexylaniline
4-diazo-2,3-dichloro-N-methyl-N-isobutylaniline
4-diazo-2,3-dichloro-N-ethyl-N-2'-hydroxyethylaniline
4-diazo-2,3-dichloro-N-ethyl-N-2'-chloroethylaniline
4-diazo-2,3-dichloro-N,N-bis(2'-hydroxyethyl)aniline
4-diazo-2,3-dichloro-N-methyl-N-benzylaniline
4-diazo-2,3-dichloro-N-ethyl-N-benzylaniline
4-diazo-2,3-dichloro-N-n-propyl-N-benzylaniline
4-diazo-2,3-dichloro-N-n-butyl-N-benzylaniline
4-diazo-2,3-dichloro-N-methyl-N-3',4'-dichlorobenzylaniline
4-diazo-2,3-dichloro-N-methyl-N-cyclohexylaniline
4-diazo-2,3-dichloro-N-methyl-N-4'-methylcyclohexylaniline
4-diazo-2,3-dichloro-N-isobutyl-N-benzylaniline
4-diazo-2,3-dichloro-N,N-diisobutylaniline
4-diazo-2,3-dichloro-N-benzyl-N-cyclohexylaniline
4-diazo-2,3-dichloro-N-methyl-N-pentylaniline
4-diazo-3-bromo-2-chloro-N,N-dimethylaniline
4-diazo-2-chloro-3-bromo-N,N-dimethylaniline
4-diazo-3-chloro-2-fluoro-N,N-dimethylaniline
4-diazo-3-fluoro-2-chloro-N,N-dimethylaniline
4-diazo-3-fluoro-2-bromo-N,N-dimethylaniline
4-diazo-3-bromo-2-fluoro-N,N-dimethylaniline
N-(4-diazo-2,3-dichlorophenyl)morpholine
N-(4-diazo-2,3-dichlorophenyl)piperidine
N-(4-diazo-2,3-dichlorophenyl)pyrrolidine
N-(4-diazo-2,3-dichlorophenyl)-N'-acetylpiperazine(1,4).

The diazonium compounds can be used as diazonium salts, e.g. as diazonium chloride, nitrate, sulfate, hydrogen sulfate or phosphate, or as diazonium metal chloride double salt, such as chlorozincate, chloromanganate, or chlorostannate, as diazonium borofluoride or as a diazonium aryl sulfonate.

They can be applied in the diazotype material individually, mixed together, or in admixture with diazonium compounds of other types. Accordingly as the diazotype material according to the invention has a higher content of another diazonium compound it will present the specific advantages of the diazonium compounds according to the invention to a lesser degree.

Using the diazonium compounds according to the invention, the conventional supports, such as paper, tracing paper, printing-plate paper, tracing linen, opaque linen, synthetic paper, metal foils, glass fibre, polyester film and the like, can be sensitized. The diazonium compound may or may not be incorporated in a hydrophilic or hydrophobic film layer, which, if desired, has been anchored to the support with the aid of one or more intermediate layers.

In the diazotype material according to the invention the conventional auxiliary agents can be used, e.g. acids, such as citric acid, tartaric acid, boric acid, and phosphoric acid; stabilizers, such as benzene and naphthalene sulfonic acids, p-phenolsulfonic acid, and their water-soluble salts; metal salts, such as zinc chloride, magnesium chloride, nickel sulfate, and alum; substances which serve to enhance the developing speed, such as glycerol, polyethylene glycol, urea, thiosinamine, and the like; surface-improving substances, such as finely divided silicium dioxide (colloidal or non-colloidal), aluminium oxide, barium sulfate, rice starch, etc.; binders, such as gelatin, gum arabic, cellulose ethers, starch derivatives, polyvinyl alcohol; dispersions of synthetic resins, such as dispersions of cationic, nonionic, and anionic polyvinyl acetate.



The diazonium compounds according to the invention may be prepared as follows:

2,3,4-tri(fluoro, chloro, bromo) nitrobenzene is converted into 3,4-di(fluoro, chloro or bromo) 2-aminonitrobenzene with ammonia in an autoclave. The halogen atom in para-position to the nitro group is then replaced by a tertiary amino group by reaction with an amine, the amino group in ortho-position to the nitro group is diazotized, and then the diazonium group is replaced by a fluoride, a chlorine or a bromine atom according to the Sandmeyer reaction. The 4-tert.amino-3-(fluoro, chloro or bromo)-2-(fluoro, chloro or bromo) nitrobenzene thus prepared is converted into a diazonium compound by reduction and diazotization.

Several compounds according to the invention can also be prepared starting from 2,3-di(fluoro, chloro or bromo)-aniline. This product is tosylated and then nitrated to 4-nitro-2,3-di-(fluoro, chloro or bromo)-N-tosylaniline, which is alkylated, saponified, and alkylated again. Thus 4-dialkylamino-2,3-di-(fluoro, chloro or bromo) nitrobenzene is obtained, from which the diazonium salt can be prepared by reduction and diazotization.

The phloroglucinol developers which are used in the one-component diazotype process often vary as to their composition and acidity. Below, two weakly acidic phloroglucinol developers and one weakly alkaline phloroglucinol developer are described which are employed in practice and are used for development in a number of the following examples.

Developer A is a solution of

4 g. of phloroglucinol
0.1 g. of acetoacetanilide
3 ml. of an aqueous solution of 38% by weight of sodium 2-ethylhexyl sulfate
15 g. of beet sugar
2.5 g. of benzoic acid
14 g. of sodium benzoate
135 g. of sodium formate

in 1000 ml. of water.

The pH of this liquid is approximately 5.8.

Developer B is a solution of

6.5 g. of phloroglucinol
4 g. of resorcinol
10 g. of thiourea
2 g. of sodium dibutylnaphthalene sulfonate
14 g. of sodium formate
22 g. of sodium benzoate
49 g. of trisodium citrate (2 aq.)
1.2 g. of citric acid

in 1000 ml. of water.

The pH of this liquid is approximately 6.5.

Developer C is a solution of

30 g. of thiourea
5.4 g. of phloroglucinol
6.5 g. of resorcinol
1 g. of potassium hydroquinone monosulfonate
5 g. of sorbitol
15 g. of beet sugar
50 g. of potassium tetraborate (5 aq.)
1.5 g. of sodium isopropylnaphthalene sulfonate

in 1000 ml. of water.

The pH of this liquid is approximately 9.

## EXAMPLE I

White base paper for the diazotype process of weight 80 g./m.$^2$ is sensitized with a solution containing

13 g. of 4-dimethylamino-3,3-dichlorobenzene diazonium chloride, zinc chloride double salt
50 g. of tartaric acid
10 g. of thiourea
10 g. of 7'-hydroxy-1',2',4,5-naphthimidazole
10 ml. of hydrochloric acid (s.g. 1.19)
0.2 g. of saponine

in 1000 ml. of water and dried.

A sheet of the diazotype material thus obtained is imagewise exposed underneath an ink drawing on tracing paper until the diazonium compound underneath the image-free portions has completely bleached out, and is then developed in ammonia vapour. The copy thus obtained shows an orange-red image on a white background.

The diazonium compound used according to the example can be prepared as follows:

2,3-dichloroaniline is tosylated, nitrated, and then brought into reaction with dimethyl sulfate. The 4-nitro-2,3 - dichloro-N-methyl - N - tosylaniline thus obtained is saponified to 4-nitro-2,3-dichloro-N-methylaniline, which is then alkylated to 4-dimethylamino-2,3-dichloronitrobenzene, which melts at 80° C. From this compound the above-mentioned diazonium salt is obtained by reduction and diazotization.

## EXAMPLE II

(a) A sheet of white base paper for the diazotype process of weight 80 g./m.² is sensitized with a solution containing

30 g. of 4-N-methyl-N-cyclohexylamino-2,3-dichlorobenzene diazonium chloride, stannic chloride double salt
5 g. of tartaric acid
30 ml. of aqueous polyvinyl acetate dispersion Vinnapas H.60 (from Wacker-Chemie G.m.b.H., Munich, Germany)

in 1000 ml. of water and dried.

(b) A sheet of white base paper for the diazotype process of weight 80 g./m.² is sensitized with a solution containing

30 g. of 4-N-methyl-N-cyclohexylamino-2,5-dichlorobenzene diazonium chloride, zinc chloride double salt
5 g. of tartaric acid
30 ml. of aqueous polyvinyl acetate dispersion Vinnapas H.60

in 1000 ml. of water and dried.

(c) A sheet of white base paper for the diazotype process of weight 80 g./m.² is sensitized with a solution containing

21 g. of 4-N-methyl-N-cyclohexylamino-3-chlorobenzene diazonium chloride, zinc chloride double salt
5 g. of tartaric acid
30 ml. of aqueous polyvinyl acetate dispersion Vinnapas H.60

in 1000 ml. of water and dried.

From each sheet a strip is cut. The strips are placed side by side in a step wedge and exposed until, underneath the step with the highest light-transmission, the diazonium compound on the strip having the lowest light-sensitivity has just bleached out. Then the strips are developed with developer C. The test shows that strip *a* has the highest light-sensitivity, strip *c* has the lowest light-sensitivity.

A second strip of each sheet is exposed underneath an original having large black well-masking areas, until the diazonium compound underneath the image-free portions of the original has completely bleached out, and is then developed with developer B. The strips *a* and *b* have an approximately equal developing speed; strip *c* clearly shows a lower developing speed.

The diazonium compound used according to the Example II(a) can be prepared as follows:

2,3,4 - trichloronitrobenzene is brought into reaction with ammonia in an autoclave and then converted with N-methylcyclohexylamine into 4-N-methyl-N-cyclohexylamino-3-chloro-2-aminonitrobenzene, which compound is converted, by diazotization and the Sandmeyer reaction, into 4-N-methyl-N-cyclohexylamino-2,3-dichloronitrobenzene, which melts at 78° C. From this compound the above-mentioned diazonium salt is obtained by reduction and diazotization.



## EXAMPLE III

Tracing linen of weight 80 g./m.² is sensitized with a solution containing

45 g. of 4-di-n-butylamino-2,3-dichlorobenzene diazonium chloride, stannic chloride double salt
5 g. of tartaric acid
300 ml. of ethanol (96%)
700 ml. of water

and dried.

A sheet of the transparent diazotype paper thus obtained is imagewise exposed underneath a pencil drawing on tracing paper until underneath the image-free portions of the drawing the diazonium compound has largely bleached out, and is then developed with developer B.

The copy shows a dark image on a foggy brown-grey background. It may be used as an intermediate original for further copying on diazotype material.

The diazonium compound used according to the example can be prepared as follows:

3,4-dichloro-2-aminonitrobenzene is reacted with dibutylamine and then diazotized and treated by the Sandmeyer reaction to give 4-di-n-butylamino-2,3-dichloronitrobenzene. From this compound the above-mentioned diazonium salt is obtained by reduction and diazotization.

## EXAMPLE IV

White base paper for the diazotype process of weight 80 g./m.² is sensitized with a solution containing

28 g. of 4-N-methyl-N-benzylamino-2,3-dichlorobenzene diazonium chloride, stannic chloride double salt
5 g. of citric acid
30 ml. of Vinnapas H.60

in 1000 ml. of water and dried.

A sheet of the diazotype paper thus obtained is imagewise exposed as in Example III and developed with developer A.

The copy shows a dark violet-brown image on a foggy background.

The diazonium compound used according to the example can be prepared as follows:

3,4-dichloro-2-aminonitrobenzene is brought into reaction with N-methylbenzylamine and then diazotized and treated by the Sandmeyer reaction to give 4-N-methyl-N-benzylamino-2,3-dichloronitrobenzene, which melts at 65–66° C. From this compound the above-mentioned diazonium salt is prepared by reduction and diazotization.

## EXAMPLE V

Sized natural tracing paper of weight 80 g./m.² is sensitized with a solution containing

27 g. of 4-morpholino-2,3-dichlorobenzene diazonium chloride, zinc chloride double salt
30 g. of sodium naphthalene-1,3,6-trisulfonate
5 g. of tartaric acid
100 ml. of ethanol (96%)
900 ml. of water

and dried.

A sheet of the transparent diazotype paper thus obtained is imagewise exposed and developed as in Example III. The copy shows a red-brown azo-dyestuff image on a foggy background. The copy can be used as an intermediate original for making further copies on diazotype material.

The diazonium compound used according to the example can be prepared as follows:

3,4-dichloro-2-aminonitrobenzene is brought into reaction with morpholine and then diazotized and by the Sandmeyer reaction converted to 4-morpholino-2,3-dichloronitrobenzene, which melts at 95° C. From this compound the above-mentioned diazonium salt is prepared by reduction and diazotization.

## EXAMPLE VI

A planographic paper printing plate of the type Rotaprint C3 is sensitized with a solution containing

30 g. of 4-N-methyl-N-benzylamino-2,3-dichlorobenzene diazonium chloride, zinc chloride double salt
200 ml. of ethanol (96%)
800 ml. of water

and dried.

The light-sensitive printing plate has good keeping qualities. It is imagewise exposed underneath a transparent ink drawing until the diazonium compound underneath the image-free portions of the drawing has completely bleached out. The image on the printing plate is developed by moistening the image side of the plate with a solution of

12 g. of phloroglucinol
11 g. of citric acid
87 g. of disodium phosphate 2 aq.

in 1000 ml. of water.

Then the plate is sponged down with water.

The plate shows a black image, which absorbs ink quite selectively. From the plate 50 good offset prints can be made.

## EXAMPLE VII

White base paper for the diazotype process of weight 80 g./m.$^2$ is sensitized with a solution containing

20 g. of 4-dimethylamino-3-fluoro-2-chlorobenzene diazonium chloride, stannic chloride double salt
5 g. of citric acid
30 ml. of Vinnapas H.60

in 1000 ml. of water and dried.

A sheet of the diazotype paper thus obtained is imagewise exposed as in Example III and developed with developer C.

The copy shows a brown image on a foggy background.

The diazonium compound used according to the example can be prepared as follows:

3-chloro-2-fluoro-1-nitrobenzene is reduced to 3-chloro-2-fluoroaniline. This product is tosylated. The tosylamino compound is nitrated, methylated and saponified. The 4-methylamino-3-fluoro-2-chloro-1-nitrobenzene thus obtained is methylated. From the nitro compound thus produced (M.P. 102° C.) the above diazonium salt is obtained by reduction and diazotization.

## EXAMPLE VIII

White base paper for the diazotype process of weight 80 g./m.$^2$ is sensitized with a solution containing

22 g. of 4-dimethylamino-3-bromo-2-chlorobenzene diazonium chloride, stannic chloride double salt
5 g. of citric acid
30 ml. of Vinnapas H.60

in 1000 ml. of water and dried.

A sheet of the diazotype paper thus obtained is imagewise exposed as in Example III and developed with developer C.

The copy shows a brown image on a foggy background.

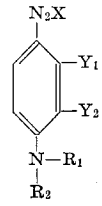
The diazonium compound used according to the example can be prepared as follows:



2,3-dichloro-1-nitrobenzene is converted with ammonia in an autoclave into 3-chloro-2-aminonitrobenzene. This product is diazotized and by the Sandmeyer reaction converted into 3-chloro-2-bromo-1-nitrobenzene. This product is reduced to 3-chloro-2-bromoaniline which is tosylated. The tosylamino compound is nitrated, methylated and saponified. The 4-methyl-3-bromo-2-chloro-1-nitrobenzene thus obtained is methylated. From the nitro compound thus produced (M.P. 212° C.) the above diazonium salt is obtained by reduction and diazotization.

What is claimed is:

**1.** A light-sensitive diazonium compound of the formula




wherein: X is an anion; $Y_1$ is a fluorine, chlorine or bromine atom; $Y_2$ is a fluorine, chlorine or bromine atom; $R_1$ is an alkyl or aralkyl group; and $R_2$ is an alkyl, aralkyl or cycloaikyl group; or $R_1$ and $R_2$ together form a saturated five- or six-membered heterocyclic ring with the notrogen atom to which they are attached.

**2.** Diazotype material which comprises a support and, carried thereon, a light-sensitive layer containing a light-sensitive diazonium compound as defined in claim **1.**

**3.** Diazotype material according to claim **2**, wherein $R_1$ is an alkyl or aralkyl group and $R_2$ is an alkyl, aralkyl or cycloalkyl group.

**4.** Diazotype material according to claim **2**, wherein one of $R_1$ and $R_2$ is a cyclohexyl group.

**5.** Diazotype material according to claim **2**, wherein said diazo compound is a 4-N-alkyl-N-cyclohexylamino-2,3-dichlorobenzene diazonium salt.

**6.** A process for the production of a diazotype record which comprises imagewise exposing a diazotype material as defined in claim **1** and developing the product with a phloroglucinol developer.

**7.** A process for the production of a diazotype record which comprises imagewise exposing a diazotype material as defined in claim **2** and developing the product with a phloroglucinol developer.

**8.** A light-sensitive diazonium compound according to claim **1**, namely, a 4-N-alkyl-N-cyclohexylamino - 2,3-dichlorobenzene diazonium salt.

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