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DIAZOTYPE REPRODUCTION MATERIAL

Oskar Süs, Wiesbaden-Biebrich, and Heinz Schäfer, Wiesbaden-Sonnenberg, Germany, assignors, by mesne assignments, to Kenffel & Esser Company, Hoboken, N.J.,

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16 Claims. (Cl. 96—91)

ABSTRACT OF THE DISCLOSURE

Greater stability without loss of light-sensitivity can be obtained in p-amino diazo compound having a meta-alkoxy group by the introduction of an alkyl, alkoxy or halogen in the ortho-position located next to the alkoxy group in the diazo molecule.

The present invention relates to reproduction materials, more particularly referring to the diazotype reproduction materials and diazonium compounds for use thereon.

In the diazotype are, derivatives of the unilaterally diazotized p-phenylene diamine are used among other basic diazo compounds as light-sensitive substances for the preparation of reproduction coatings. These diazo compounds have attained great technical importance for the so-called dry-development process, as well as for the so-called semi-dry process. Generally speaking, diazo compounds containing alkyl groups with a low number of carbon atoms on the basic nitrogen atom are particularly well-suited for the dry-development process, whereas the compounds having groups with long-chain or cyclic hydrocarbon radicals on the nitrogen atom are suitable for the semi-dry process. Apart from the coupling speed, the hue of the dyestuff obtainable through coupling with the azo components known for diazotype processes is influenced through substitution on the nitrogen atom. The light sensitivity and stability of the diazo compounds or rather of the light-sensitive coatings prepared therefrom can also be influenced by variation of the substituents on the nitrogen atom.

The above-mentioned properties of the p-amino-diazo compounds can be influenced to an even stronger degree through substituents in the benzene ring carrying the diazo group. A substituent in ortho position to the diazo group, such as a methyl, methoxy, or carboxylic acid group causes a considerable increase in stability, and also a shift in hue toward the blue, whereas the light-sensitive property is decreased. If an alkoxy group is introduced in meta-position to the diazo group, the diazo compound is substantially more light sensitive as compared with the unsubstituted compound, but the stability is decreased. Despite the loss of stability, this group of diazo compounds has a cetrain technical importance in view of its high light sensitivity, for example, for producing quick copies of letter originals merely for information purposes.

It has been found that the stability of the diazo molecules can be improved by introducing a substituent, such as alkyl, alkoxy, or halogen, in the ortho-position to the alkoxy group which in turn is in the meta-position in relation to the diazo group, and that the high light sensitivity of the type of p-amino diazo compound characterized by an alkoxy group in the meta-position is not essentially affected.

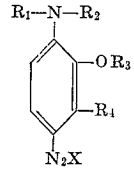
Therefore, one object of the present invention is to provide diazonium compounds having improved light sensitivity and improved stability.

Another object is to provide methods for preparing diazonium compounds having improved light sensitivity and improved stability.

Another object is to provide a diazotype reproduction material having thereon a diazonium compound of improved light sensitivity and improved stability.

Other objects will become apparent in the course of the following specification.

Diazotype reproduction materials according to the present invention comprise a support, such as paper, other cellulose material, cellulose derivatives, or plastic material, having as the light-sensitive substance a diazonium salt according to the general formula:



where R_1 and R_2 are members selected from one of the two groups consisting of:

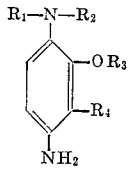
group A in which R_1 and R_2 are alkyl groups, and
group B in which R_1 and R_2 are members of the same heterocyclic ring,

R_3 and R_4 are members selected from one of the two groups consisting of:

group C where R_3 is alkyl and R_4 is a member selected from the group consisting of alkyl, alkoxy, and halogen, and
group D where R_3 and R_4 are members of the same heterocyclic ring, and
X is the anion of the diazonium salt.

The diazonium salts are also used as double salts, for example, with zinc, tin, or cadmium salts. As alkyl and alkoxy groups, preferably those groups are used which have a low number of carbon atoms, for example, the methyl, ethyl, and propyl groups, or the methoxy, ethoxy, and propoxy groups.

The diazo compounds of the present invention have not been previously known in the art. They were obtained by diazotizing 2,3-substituted para-amino compounds of the formula:

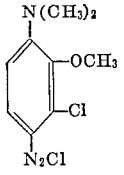


wherein R_1, R_2, R_3, and R_4 represent the above mentioned groups, in acid solution with nitrous acid and precipitating them as salts, or, if desired, as double salts with the aid of a salt of a heavy metal.

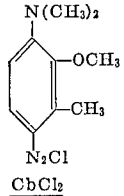
The above mentioned 2,3-substituted para-aminodiazo compounds in which R_1 and R_2 are alkyl groups, R_3 is an alkyl group and R_4 is an alkoxy group, alkyl group, or a halogen, may be prepared from 6-amino-1-alkoxy-benzene, which is substituted in the 2-position by an alkoxy- alkyl, or halogen group by di-alkylating the amino group, for example, with dimethyl sulphate, then by providing the obtained tertiary amino compound with an azo group in the para-position to the tertiary amino group by coupling with a diazo compound, then by finally changing this into an amino group by reduction.

Further details concerning the preparation of the diazo compounds to be used according to the present invention are given in the following examples. The formulae of the diazo compounds mentioned in the examples are listed below.

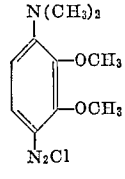
Formula 1



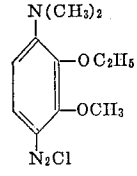
Formula 2



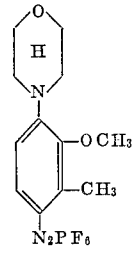
Formula 3



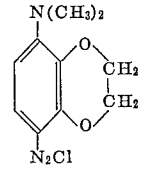
Formula 4



Formula 5



Formula 6



Example 1

A commonly-used photocopying base paper (80 g./s.m.) was coated with the following solution:

Tartaric acid	grams	0.4
Aluminum sulphate	do	0.4
1 - methoxy - 2-chloro-6-dimethylaminobenzene-3-diazonium chloride (as cadmium chloride double salt)	grams	2.0
Water	milliliters	100.0

After the coating was dried, the sensitized paper was exposed imagewise and developed according to the semi-dry process, using the following developer:

Sodium borate	grams	2.5
Sodium carbonate	do	3.0
Sodium chloride	do	2.0
Thiourea	do	5.0
Sodium-iso-propyl-naphthalene-sulfonate	do	0.1
Phloroglucinol	do	0.6
Resorcinol	do	0.6
Water	milliliters	100.0

Strongly-colored, reddish-brown images on a white background were obtained.

The diazo compound according to Formula 1, 1-methoxy - 2 - chloro-6-dimethylamino-benzene-3-diazonium chloride (as cadmium chloride double salt) was prepared as follows:

Following the directions given by S. Hünig in Berichte Der Deutschen Chemischen Gesellschaft 85 (1952) 1056, 2-chloro-6-amino-anisole (J. Am. Chem. Soc. 68 (1946) 1268-1269) was converted into 2-chloro-6-dimethylamino-anisole by dialkylating it with dimethyl sulphate in the presence of sodium bicarbonate in a methanol-water mixture between 0–10° C. The base thus obtained was liquid at room temperature and boiled at 103° C. at 5.0 torr.

By coupling the base with diazotized p-nitroaniline in the presence of pyridine, the dyestuff 2-chloro-3-(4'-nitrophenyl)-azo-6-dimethylamino-anisole was obtained. The hydrochloride of the dye melted at 147–149° C.

The reduction of the free dyestuff to an amine was effected catalytically. After evaporation of the solvent, the oily residue was agitated with water, whereby separation of the by-product p-phenylene diamine was easily accomplished. 2-chloro-3-amino-6-dimethylamino-anisole, a water-insoluble oil remained. Boiling point: 168–171° C. at 15.0 torr.

To diazotize the amine, it was dissolved in 16% hydrochloric acid, to which a 2 N sodium nitrite solution was slowly added. The diazo compound was precipitated as a double salt of cadmium chloride. It crystallized with one half mol of cadmium chloride and had a decomposition point of 119° C.

Example 2

A photocopying base paper (80 g./s.m.) was coated with the following solution:

Citric acid	grams	3.5
Boric acid	do	3.5
Thiourea	do	3.0
3,5 - dihydroxy - 4 - bromo - benzoic acid-2'-diethylamino-anilide	grams	1.2
1 - methoxy - 2 - methyl-6-dimethylamino-benzene-3-diazonium chloride (cadmium chloride double salt)	grams	1.8
Water	milliliters	100.0

After exposure and development with ammonia vapor, copies with red lines on a white background were obtained.

An equally good result was obtained when the compound according to Formula 5, that is, 1-methyl-2-methoxy - 3 - morpholino-benzene-6-diazonium-hexafluorophosphate was used.

The diazo compound according to Formula 2, 1-methoxy - 2 - methyl-6-dimethylamino-benzene-3-diazonium chloride (cadmium chloride double salt), was prepared as follows:

2 - methyl - 6 - amino-anisole (J. Chem. Soc. London, 1933, 2 p. 1377) was converted into 2-methyl-6-dimethylamino-anisole by dialkylating it with dimethyl sulphate in the presence of sodium hydrogen carbonate in a methanol-water mixture between 5–10° C. The base thus obtained was liquid at room temperature and boiled at 101–103° C. at 18 torr. By coupling the base with diazotized p-nitroaniline in the presence of pyridine, a dyestuff, 2-methyl - 3 - (4'-nitrophenyl-azo)-6-dimethylamino-anisole was obtained.

The reduction of the dyestuff to the amine was effected catalytically with the aid of nickel. After evaporation of the solvent, the oily residue was agitated with water, thereby dissolving the separated p-phenylene-diamine. The 2-methyl-3-amino-6-dimethylamino-anisole remained as a water insoluble oil. Its boiling point was 153–155° C. at 15 torr.

The amine was diazotized in hydrochloric acid with a 2 N sodium nitrite solution. The diazo compound was precipitated as a cadmium chloride double salt. It crystallized with one half mol of cadmium chloride. Its decomposition point was 126° C.

The diazo compound according to Formula 5, the 1-methyl - 2 - methoxy-3-morpholino-benzene-6-diazonium-hexafluoro-phosphate, was prepared as follows:

3 - chloro - 6 - nitro-2-hydroxy-toluene (Annalen der Chemie 417, 240) was etherified in an aqueous alkaline solution with dimethyl sulphate. The 3-chloro-6-nitro-2-methoxy-toluene had a boiling point of 136–137° C. at 7 torr. Its melting point was 38–39° C.

While refluxing the above intermediate product with morpholine to replace the chlorine with morpholine, the methoxy groups were hydrolyzed to a considerable extent. Apart from chloro-nitro-cresol formed due to hydrolysis of the methoxy groups, a poor yield of 3-morpholino-6-nitro-2-methoxy-toluene was produced. This was isolated by adding a dilute solution of caustic soda to the reaction mixture and extracting it with methylene chloride. After

evaporation of the methylene chloride, an oily residue remained. This was extracted several times with hot, dilute (approximately 16%) hydrochloric acid. Pouring the hydrochloric acid solution into water, the free base of the nitro compound was precipitated, due to hydrolysis. The base melted at 119° C.

Through catalytic reduction, the base was converted into 3-morpholino-1-amino-2-methoxy-toluene having a melting point of 130° C.

Diazotization was carried out conventionally in a hydrochloric solution. The diazo compound was precipitated as a salt of the hexahydrofluorophosphoric acid. It melted and decomposed at 129° C.

Example 3

The following solution was applied to paper and dried.

Citric acid	grams	4.0
Boric acid	do	1.0
Aluminum sulfate	do	1.0
Thiourea	do	2.5
Cresylglutaric acid	do	2.0
1,2 - dimethoxy - 3 - dimethylamino - benzene - 6 - diazonium chloride (stannic chloride double salt)	grams	3.2
Propanol	milliliters	15.0
Water	do	85.0

After exposure and development with ammonia vapor, copies with a yellow tone were obtained. Because of their high-covering power in the violet and neighboring ultraviolet region, these copies were particularly suitable for use as intermediates.

The diazo compound according to Formula 3, 1,2-dimethoxy-3-dimethylamino-benzene-6-diazonium chloride (stannic chloride double salt), was prepared as follows:

3-aminoveratrole was converted into 3-dimethylaminoveratrole by dialkylation with dimethyl sulphate in the presence of sodium bicarbonate in a methanol-water mixture between 2–10° C. The base thus obtained was an oil with a boiling point of 107–109° C. at 9 torr.

As in the previous example, the azo dyestuff 6-(4'-nitrophenyl-azo)-3-dimethylaminoveratrole was produced by coupling the base with diazotized p-nitroaniline. The dyestuff melted at 120–121° C.

The reduction of the dye to the amine was effected catalytically with the aid of nickel in a solvent. After evaporation of the solvent, the oily residue was agitated with water. The 6-amino-3-dimethylaminoveratrole remained as a water-insoluble oil. It boiled at 161° C. under a pressure of 14 torr.

Diazotization was carried out conventionally in hydrochloric acid with a 2 N sodium nitrite solution. The diazo compound was precipitated as a tin tetrachloride double salt. It crystallized with one half mol stannic chloride. Decomposition point: 139° C.

Example 4

A photocopying base paper was provided with a light-sensitive coating prepared according to the following formula:

Citric acid	grams	5.0
Boric acid	do	3.0
Thiourea	do	4.0
Sulphosalicyclic acid sodium salt	do	2.0
Resorcinol	do	1.2
1 - ethoxy - 2 - methoxy - 6 - dimethylamino - benzene-3-diazonium chloride (tin tetrachloride double salt)	grams	2.0
Water	milliliters	100.0

Photocopies having brown lines on a pure white background were obtained by dry development.

The diazo compound according to Formula 4, the 1-ethoxy - 2 - methoxy - 6 - dimethylamino - benzene - 3-diazonium chloride (tin tetrachloride double salt), was prepared as follows:

3-nitro-2-hydroxy-anisole was ethylated to 3-nitro-2 ethoxyanisole with diethyl sulfate in alkaline solution. I was obtained as a yellow oil with a boiling point of 162-164° C. (10 torr). It was converted into 3-amino-2 ethoxy-anisole by catalytic reduction. Boiling point: 134-136° C. (9 torr).

This base was dimethylated with dimethyl sulfate ir the presence of sodium hydrogen carbonate in a methanol-water mixture between 4–20° C. The 3-dimethyl amino-2-ethoxy-anisole boiled at 120° C. (8 mm.).

By coupling the base with diazotized p-nitroaniline ir the presence of pyridine, the dyestuff 6-(4'-nitrophenyl) azo-3-dimethylamino-2-ethoxy-anisole was obtained. Its melting point was 112–114° C.

The reduction of the dyestuff and further treatment of the base were carried out as in the previous example. The 6-amino-3-dimethylamino-2-ethoxy-anisole which was obtained in the form of an oil boiled at 145–147° C. (8 torr).

Diazotization was carried out conventionally in the hydrochloric acid with a 40% sodium nitrite solution. The diazo compound crystallized with one half mol stannic chloride. Its decomposition point was 140° C.

Example 5

A photocopying base paper was coated with the following solution:

Citric acid	grams	4.0
Aluminum sulfate	do	2.0
Thiourea	do	4.0
1,3,6-naphthalene trisulfonic acid sodium salt	grams	3.0
2,7 - dihydroxy - naphthalene - 3,6 - disulfonic acid sodium salt	grams	2.0
5 - dimethylamino - benzodioxane - 8 - diazonium chloride (cadmium chloride double salt)	grams	2.1
Water	milliliters	100.0

After exposure and development with ammonia vapor, copies having blue lines on a white background were obtained.

The diazo compound according to Formula 6, the 5 - dimethylamino-benzodioxane - 8 - diazonium chloride (cadmium chloride double salt) was prepared as follows:

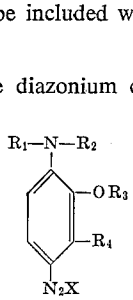
5-amino-8-acetylamino-benzodioxane (J. Chem. Soc. London (1954) page 20) which was suspended in water was converted into 5-dimethylamino-8-acetylamino-benzodioxane using dimethyl sulfate in the presence of sodium bicarbonate. Subsequently, the acetylamino group of said compound was hydrolyzed by heating with a dilute solution of caustic soda, whereby 5-dimethylamino-8-amino-benzodioxane was obtained. Its melting point was 98°–100° C.

The obtained amino compound was diazotized in hydrochloric acid solution with a 40% sodium nitrite solution. The diazo compound was precipitated from the solution as the cadmium chloride double salt. It crystallized with one half mol cadmium chloride. It decomposition point was 155° C.

It is apparent that the described examples are capable of many variations and modifications. All such variations and modifications are to be included within the scope of the present invention.

What is claimed is:

1. A photosensitive diazonium compound having the general formula:



where R_1 and R_2 are lower alkyl groups, or are members of the same morpholino heterocyclic ring; R_3 is a lower alkyl; R_4 is a lower alkyl, lower alkoxy, or halogen, or R_3 and R_4 are members of the same dioxane ring, and X is the anion of the diazonium salt.

2. A photosensitive diazonium compound selected from the group consisting of:

1-methoxy-2-chloro-6-dimethylamino-benzene-3-diazonium chloride;
1-methoxy-2-methyl-6-dimethylamino-benzene-3-diazonium chloride;
1,2-dimethoxy-3-dimethylamino-benzene-6-diazonium chloride;
1-ethoxy-2-methoxy-6-dimethylamino-benzene-3-diazonium chloride;
1-methyl-2-methoxy-3-morpholino-benzene-6- diazonium-hexafluorophosphate; and
5-dimethylamino-benzodioxane-8-diazonium-chloride

3. 1 - methoxy - 2 - chloro - 6 - dimethylamino - benzene-3-diazonium-chloride, cadmium chloride double salt.

4. 1 - methoxy - 2 - methyl - 6 - dimethylamino - benzene-3-diazonium chloride, cadmium chloride double salt.

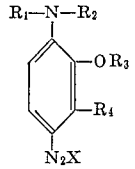
5. 1,2 - dimethoxy - 3 - dimethylamino - benzene - 6 - diazonium chloride, stannic chloride double salt.

6. 1 - ethoxy - 2 - methoxy - 6 - dimethylamino - benzene-3-diazonium chloride, tin tetrachloride double salt.

7. 1 - methyl - 2 - methoxy - 3 - morpholino - benzene-6-diazonium hexafluorophosphate.

8. 5 - dimethylamino - benzodioxane - 8 - diazonium chloride, cadmium chloride double salt.

9. A diazotype reproduction material comprising a support and a photosensitive diazonium compound having the general formula:



where R_1 and R_2 are lower alkyl groups, or members of the same morpholino heterocyclic ring; R_3 is a lower alkyl; R_4 is a lower alkyl, lower alkoxy, or halogen, or R_3 and R_4 are members of the same dioxane ring; and X is the anion of the diazonium salt.

10. A diazotype reproduction material comprising a support having a layer containing a photosensitive diazonium compound selected from the group consisting of:

1-methoxy-2-chloro-6-dimethylamino-benzene-3-diazonium chloride;
1-methoxy-2-methyl-6-dimethylamino-benzene-3-diazonium chloride;
1,2-dimethoxy-3-dimethylamino-benzene-6-diazonium chloride;
1-ethoxy-2-methoxy-6-dimethylamino-benzene-3-diazonium chloride;
1-methyl-2-methoxy-3-morpholino-benzene-6-diazonium-hexafluorophosphate; and
5-dimethylamino-benzodioxane-8-diazonium chloride.

11. A diazotype reproduction material comprising a support having a layer containing the photosensitive diazo compound 1-methoxy-2-chloro-6-dimethylamino-benzene-3-diazonium chloride, cadmium chloride double salt.

12. A diazotype reproduction material comprising the support having a layer containing a photosensitive diazonium compound 1-methoxy-2-methyl-6-dimethylamino-benzene-3-diazonium chloride, cadmium chloride double salt.

13. A diazotype reproduction material comprising a support having a layer containing the photosensitive diazonium compound 1,2-dimethoxy-3-dimethylamino-benzene-6-diazonium chloride, stannic chloride double salt.

14. A diazotype reproduction material comprising a support having a layer containing the photosensitive diazonium compound 1-ethoxy-2-methoxy-6-dimethylamino-benzene-3-diazonium chloride, tin tetrachloride double salt.

15. A diazotype reproduction material comprising the support having a layer containing a photosensitive diazonium compound 1-methyl-2-methoxy-3-morpholino-benzene-6-diazonium-hexafluorophosphate.

16. A diazotype reproduction material comprising a support having a layer containing the photosensitive diazonium compound 5-dimethylamino-benzodioxane-8-diazonium chloride, cadmium chloride double salt.

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NORMAN G. TORCHIN, *Primary Examiner.*

C. L. BOWERS, JR., *Assistant Examiner.*

U.S. Cl. X.R.

260—141, 142