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DIAZOTYPE REPRODUCTION MATERIAL

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6 Claims. (Cl. 96—91)

The present invention relates to a reproduction material and more particularly refers to a photosensitive diazotype reproduction material.

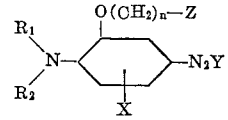
Derivatives of unilaterally diazotized p-phenylene diamine have been used as the photosensitive element in diazo reproduction materials. These diazonium compounds have a tertiary amino group of basic character and they have been used successfully for both the dry-development process and the semi-wet process.

For the dry-development process, the diazo compounds most suitable are those cantaining lower alkyl groups attached to the basic nitrogen atom, while for the semi-wet process, the best ones are those having longer hydrocarbon radicals atoms or a ring structure attached to the basic nitrogen atom.

The substituents on the basic nitrogen atom affect not only coupling speed, but they also affect the light sensitivity and keeping qualities of the diazo compound and the light sensitive layers prepared therewith.

In considerable measure the properties of the p-amino diazo compounds depend also on substituents attached to the phenylene ring. A substituent such as a methyl, methoxy, or carboxyl group in a position ortho to the diazonium group, brings about a considerable improvement in stability and at the same time a color shift toward blue. Light sensitivity is, however, lowered by these substituents. The presence of an alkoxy group in a position meta to the diazonium group makes the diazo compounds considerably more light sensitive in relation to the unsubstituted compounds, but the keeping qualities become poorer as a result. Despite their poor stability, this group of diazo compounds is nevertheless important because of their high light sensitivity and their practical use in cases where copies have to be prepared as quickly as possible.

It has now been found that the stability is improved in many compounds of the last-named type without loss of light sensitivity, and even with the improvement in light sensitivity, by the introduction of hetero-atoms in the form of ether groups into the alkoxy group. The light sensitive reproduction material contains as light sensitive substance provided by the invention at least one derivative of unilaterally diazotized p-phenylene diamine corresponding to the general formula



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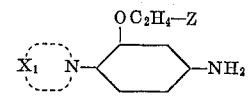
where R_1 and R_2 are members selected from the groups consisting of: Group A wherein R_1 as an alkyl group containing up to 4 carbon atoms, and R_2 is a member selected from the group consisting of alkyl groups containing up to 4 carbon atoms and aralkyl groups with up to 10 carbon atoms, and Group B wherein R_1 and R_2 are members of the same heterocyclic group; where Z is a member selected from the group consisting of alkylmercapto and



wherein R_3 is a member selected from the group consisting of alkylmercapto, hydrogen, alkyl groups containing up to 4 carbon atoms, and hydroxyalkyl groups containing up to 4 carbon atoms; R_4 is a member selected from the group consisting of alkyl containing up to 4 carbon atoms, hydroxyalkyl containing up to 4 carbon atoms, at most one of the groups R_3 and R_4 being alkyl; X is a member selected from the group consisting of hydrogen, halogen and methyl; Y is the anion of an acid; and n is an integer from 1 to 4.

The present invention is closely related to the invention described in our co-pending application Ser. No. 311,220 of Sept. 24, 1963 and should be considered in the light of the disclosure contained therein. In the co-pending application referred to above, a reproduction material is described comprising a sheet-like support and a light sensitive diazotype layer coated on said support, which layer comprises a light sensitive diazonium compound of the above formula in which Z and R_3 and R_4 are different from the definitions given above.

One kind of the light sensitive reproduction material in accordance with the present invention contains as light sensitive substance at least one derivative of unilateral diazotized p-phenylene diamine corresponding to the general formula



(II)

where X_1 represents the members required to complete the heterocyclic ring selected from the group consisting of 5-membered and 6-membered heterocyclic rings, and where Z is a member selected from the group consisting of alkylthio, alkylamino, and hydroxyalkylated amino groups.

Reproduction materials utilizing the present invention can be used both for the dry and for the semi-wet processes. According to the coupler used, dark colors such as brown or violet can be prepared with great speed.

Therefore, one object of the present invention is to provide a light sensitive diazotype reproduction material utilizing a diazonium compound which can be used for the dry and the semi-wet processes.

Another object is to provide a light sensitive diazotype reproduction material which has improved photosensitivity and stability.

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

The diazo compounds are generally used as diazonium chlorides in the form of double salt containing metal halides such as zinc chloride or cadmium chloride. Other forms such as sulfates, phosphates or borofluorides may also be used.

The diazo compounds are simply obtained according to methods known in the art particularly if the desired compounds contain a heterocyclic ring in the para position to the diazo group. In such a case, for example, 2-chloro-5-nitrophenol is reacted with omega-bromo-dialkylthioether in the presence of an alkali, the chlorine atom of the resulting thioether is replaced by a heterocyclic base containing a secondary nitrogen atom, the nitro group is reduced, and then the product is diazotized.

It should be understood that the products obtained according to the present process may also be obtained according to different reaction sequences.

A detailed description of the properties and the production of various compounds is given by the examples where one part per volume may be considered one cubic centimeter and one part by weight is considered one gram. The formulas of some of the new diazonium salts used according to the present invention are inserted in the table. The melting points of the nitro compounds (nitro group

in para position to the —NR_1R_2— group) which are the basic materials for these diazonium salts are:

(1) 81° C.
(2) 42° C.
(3) 54° C.
(5) 117° C.
(6) 92° C.

The FIGURES 1 to 6 correspond to the figures of the annexed formulae. The nitro compound relating to No. 4 represents an oil.

Example 1

A diazotype base paper which has on one side a precoat of colloidal silicic acid and polyvinyl acetate, is coated on this precoated surface with a solution which contains in 100 parts by volume of water

3.5 parts by weight of citric acid
3.5 parts by weight of boric acid
5.0 parts by weight of thiourea
1.2 parts by weight of 3,5-dihydroxy-4-bromobenzoic acid amide
2.3 parts by weight of the diazo compound from 1-amino-4-pyrrolidino-3-[(β-ethylamino)-ethoxy]-benzene (in the form of the hydrochloride zinc chloride double salt) (Formula 1)

After drying, the sensitized base paper, which has an excellent shelf life, is exposed image-wise under a transparent original and developed with ammonia. A red image on a white background is obtained.

The diazo compound of Formula 1 is prepared as follows:

A solution of 260 parts by weight of 2-chloro-5-nitrophenol in 150 parts by volume of NaOH (40%), 350 parts by volume of water, and 550 parts by volume of glycol monomethyl ether is added, dropwise, at boiling temperature and with stirring, to a mixture of 560 parts by weight of ethylene bromide and 200 parts by volume of glycol monomethyl ether over a period of one hour. The mixture is kept boiling for one hour, with stirring, evaporated to dryness in vacuo and the residue is treated with water, filtered under suction and recrystallized from methanol. 232 parts by weight of 2-choloro-5-nitrophenyl-β-bromoethyl ether having a melting point of 77–78° C. are obtained. 120 parts by weight of this compound are dissolved in 250 parts by volume of dioxane, and with ice cooling, added dropwise to 360 parts by volume of ethylamine solution (40%, aqueous) and 150 parts by volume of dioxane over three hours, and stirring continued overnight at room temperature. The solution is then strongly acidified with hydrochloric acid, separated from undissolved matter, concentrated in vacuo, rendered alkaline with NaOH and extracted with ether. The ether solution is dried and the ether evaporated. After recrystallization from petroleum ether 65 parts by weight of 2-chloro-5-nitro-phenyl-β-ethylaminoethyl ether having a melting point of 64° C. are obtained.

65 parts by volume of pyrrolidine and 13 parts by volume of water are added to 65 parts by weight of the last-mentioned compound, heated at boiling point for 3 hours under reflux, and, after cooling, poured into water. The residue is filtered under suction, washed with water, and recrystallized from methanol. The yield is 60 parts by weight of 5-nitro-2-pyrrolidinophenyl-β-ethylaminoethyl-ether having a melting point of 81° C. 60 parts by weight of the compound so prepared are dissolved in 200 ml. of hydrochloric acid (concentrated), reduced with zinc dust, made up to 800 parts by volume with ice water, and diazotized with 38 parts by volume of sodium nitrite solution (40%) at a temperature between 0° and 5° C.

35 parts by weight of the resulting diazo compound, which crystallizes very well, are isolated in the form of its hydrochloride zinc chloride double salt.

Example 2

A paper base conventionally used for diazotype purposes was coated with a solution containing:

0.4 part by weight of tartaric acid
0.4 part by weight of aluminum sulfate
2.2 parts by weight of the diazo compound of 1-amino-4-piperdino-3-[(β-ethylmercapto)-ethoxy]-benzene (in the form of the zinc chloride double salt) (Formula 4)

per 100 parts by volume of water. After drying, the sensitized paper was exposed behind a transparent master and developed with a solution containing:

2.5 parts by weight of borax
3.0 parts by weight of soda
2.0 parts by weight of sodium chloride
5.0 parts by weight of thiourea
0.1 part by weight of sodium isopropyl naphthalene sulfonate
0.6 part by weight of phloroglucinol
0.6 part by weight of resorcinol

per 100 parts by volume of water.

Equally good results were obtained if the diazo compound corresponding to Formula 3 was used instead of the diazo compound corresponding to Formula 4.

The diazo compound of Formula 4 was obtained by the following procedure:

To 125 grams of 2-chloro-5-nitrophenol in 400 ml. of methyl glycol were added 28 parts by weight of sodium hydroxide in 75 parts by volume of water and 122 parts by weight of 2-ethylmercapto-1-bromoethane. This was refluxed for three hours under agitation. After cooling, the solution was poured on ice water, the residue was drawn off and dried. 148 parts by weight were produced. The melting point of the resulting 2-chloro-5-nitrophenol-β-ethyl-mercapto-ethylether was 52° C.

48 parts by weight of this compound were covered with 80 parts by volume of piperidine and 10 parts by volume of water, and refluxed 24 hours with agitation. After cooling, the mixture was poured on ice water, shaken with ether, separated from water, and the ether was evaporated. The product obtained from the oily residue was purified by means of hydrochloric acid and sodium hydroxide. 38 parts by weight were obtained. The diazo compound was obtained from the nitro compound by conventional reduction and diazotization.

If morpholine was used instead of piperidine, the compound corresponding to Formula 3 was obtained.

Example 3

A reproduction paper base conventionally used for diazotype purposes was coated with the following solution:

4.0 parts by weight of citric acid
5.0 parts by weight of thiourea
3.0 parts by weight of aluminum sulfate
3.5 parts by weight of naphthalene-1,3,6-trisulfonic acid sodium salt
2.0 parts by weight of 2-hydroxy-3-naphthoic acid-β-amino-ethylamide (in the form of its hydrochloric acid salt)
2.5 parts by weight of the diazo compound from 1-amino-4-pyrrolidino-3-β-(bis-hydroxyethylamino)-ethoxy-benzene (in the form of the hydrochloride zinc chloride double salt) (Formula 5)

per 100 parts by volume of water.

Using the procedure described in Example 1, blue images on a white background were obtained.

If the diazo compound corresponding to Formula 5 was replaced by the diazo compound of Formula 2 or the diazo compound of Formula 6, a material was obtained which yielded copies with particularly good contrast.

The diazo compound corresponding to Formula 5 was prepared as follows:

115 parts by weight of 2-chloro-5-nitrophenyl-β-bromo-

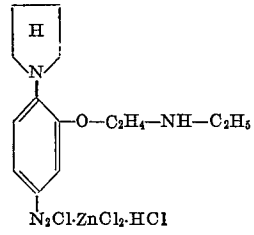
ethylether were heated with 130 parts by weight of diethanolamine and 40 parts by volume of water for three hours on a steam bath with stirring, diluted with water, drawn off, washed with water, and recrystallized from dilute alcohol. 78 grams of a material melting at 113° C. were obtained. 61 parts by weight of 2-chloro-5-nitrophenyl-β-dihydroxy-ethylamino ethylether were refluxed for three hours in 80 parts by volume of pyrrolidine and 10 parts by volume of water, poured on ice water, drawn off, washed with water, and recrystallized from methanol. The yield was 67 grams of a material melting at 117° C.

38 parts by weight of the diazo compound were obtained from 32 parts by weight of 5-nitro-2-pyrrolidinophenyl-β-dihydroxy ethylamino ethylether after reduction with zinc dust in hydrochloric acid by diazotization under conventional conditions.

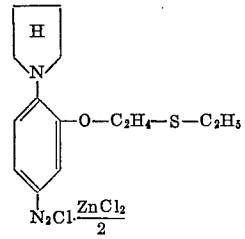
The compound corresponding to Formula 6 was prepared in analogy to the procedure described above for the preparation of the compound of Formula 5, using the diisopropanol amine instead of the diethanol amine. The compound of Formula 2 was prepared by the method described in Example 2 for the preparation of the compound corresponding to Formula 4; using pyrrolidine instead of piperdine.

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.

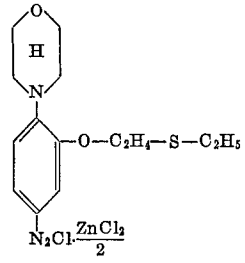
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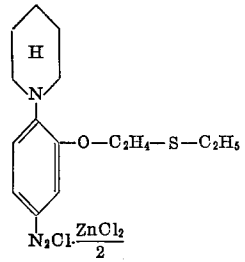
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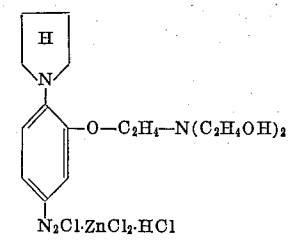
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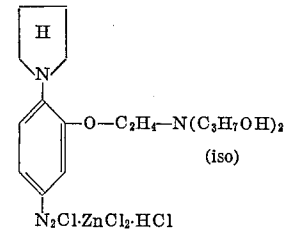
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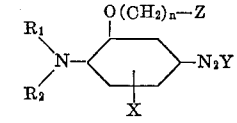


(6)



What is claimed is:

1. A diazotype reproduction material which comprises a support and a photosensitive layer coated on said support, said layer comprising a photosensitive diazonium compound having the formula

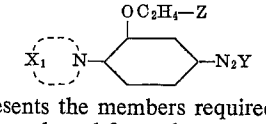


where R_1 and R_2 are members selected from the groups consisting of: Group A wherein R_1 is an alkyl group containing up to 4 carbon atoms and R_2 is a member selected from the group consisting of alkyl groups containing up to 4 carbon atoms and aralkyl groups with up to 10 carbon atoms, and Group B wherein R_1 and R_2 are members of the same heterocyclic group; where Z is a member selected from the group consisting of alkylmercapto and



wherein R_3 is a member selected from the group consisting of alkylmercapto, hydrogen, alkyl groups containing up to 4 carbon atoms, and hydroxyalkyl groups containing up to 4 carbon atoms; R_4 is a member selected from the group consisting of alkyl containing up to 4 carbon atoms, hydroxyalkyl containing up to 4 carbon atoms, at most one of the groups R_3 and R_4 being alkyl; X is a member selected from the group consisting of hydrogen, halogen and methyl; Y is the anion of an acid; and *n* is an integer from 1 to 4.

2. A diazotype reproduction material which comprises a support and a photosensitive layer coated on said support, said layer comprising a photosensitive diazonium compound having the formula



where X_1 represents the members required to complete a heterocyclic ring selected from the group consisting of 5-membered and 6-membered heterocyclic rings, and where Z is a member selected from the group consisting of alkylthio, alkylamino and hydroxyalkylated amino groups, and Y is the anion of an acid.

3. A material in accordance with claim **2** in which said diazonium compound is 3-(ethylthio-ethoxy)-4-pyrrolidino-benzene diazonium chloride.

4. A material in accordance with claim **2** in which said diazonium compound is 3-(ethylamino-ethoxy)-4-pyrrolidino-benzene diazonium chloride.

5. A material in accordance with claim 2 in which said diazonium compound is 3-[di-(2-methyl-2-hydroxy-ethyl)-amino-epoxy]-4-pyrrolidino-benzene diazonium chloride.

6. A material in accordance with claim 2 in which said diazonium compound is 3-(di-hydroxyethylamino-ethoxy)-4-pyrrolidino-benzene diazonium chloride.

No references cited.

NORMAN G. TORCHIN, *Primary Examiner.*
ALEXANDER D. RICCI, *Examiner.*