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3,432,301

REPRODUCTION MATERIAL

Herbert Rauhut and Oskar Süss, Wiesbaden-Biebrich, Germany, assignors, by mesne assignments, to Keuffel & Esser Company, Hoboken, N.J.

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K 51,880

The portion of the term of the patent subsequent

to Sept. 13, 1983, has been disclaimed

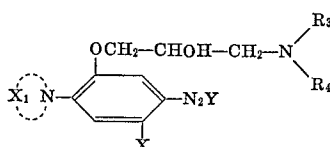
U.S. Cl. 96-91

7 Claims

Int. Cl. G03c 1/54; C07c 113/04

ABSTRACT OF THE DISCLOSURE

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



in which X_1 represents the members required to complete a heterocyclic ring selected from the group consisting of 5-membered and 6-membered heterocyclic rings, X is selected from the group consisting of hydrogen and alkyl, R_3 and R_4 are members of one of the groups selected from Group A in which R_3 is alkyl up to 4 carbon atoms and hydroxyalkyl with up to 4 carbon atoms, and R_4 is hydrogen, alkyl up to 4 carbon atoms, and hydroxyalkyl with up to 4 carbon atoms; and Group B in which R_3 and R_4 are members of the same 5- or 6-membered heterocyclic ring, and Y is the anion of an acid.

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

In copying papers and other copying foils that have been sensitized with diazo compounds, the derivatives of unilaterally diazotized p-phenylene diamine have been used as the photosensitive elements. These diazonium compounds have a tertiary amino group of basic character and they have been used successfully for both the dry process and the semi-wet process.

For the dry process the diazo compounds which are most suitable are those containing lower alkyl groups attached to the basic nitrogen atom, while for the semi-wet process the best ones are those in which the basic nitrogen atom is attached to higher hydrocarbon radicals or a ring structure.

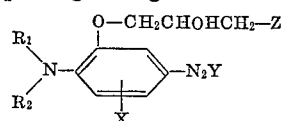
The substituents on the basic nitrogen atom affect not only coupling speed, but they also affect the light-sensitivity and keeping qualities of the diazo compounds and the light-sensitive layers prepared therewith.

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 compound considerably more light-sensitive in relation to the unsubstituted compound, but the keeping qualities become poorer as a result. Despite their poor stability, this type

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of diazo compound is nevertheless important because of its high light-sensitivity and they find practical use in cases where copies have to be prepared as quickly as possible.

It has now been found that the stability can be improved in many compounds of the last-named type without loss of light-sensitivity, and even with improvement in light-sensitivity by the introduction of hetero-atoms in form of hydroxyl and amino 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:



(I)

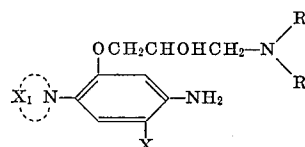
where R_1 and R_2 are members selected from the groups consisting of: group A wherein R_1 is an alkyl group containing up to 4 carbon atoms, and R_2 is a member selected from the group consisting of alkyl groups containing up to 4 carbon atoms and aralkyl groups with up to 10 carbon atoms; and group 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 alkoxy, arylated alkoxy, aryloxy, alkylthio and the group



wherein R_3 and R_4 are members selected from the groups consisting of: group C wherein R_3 is selected from the group consisting of hydrogen, alkyl groups containing up to 4 carbon atoms, hydroxy alkyl groups having up to 4 carbon atoms and R_4 is a member selected from the group consisting of alkyl groups containing up to 4 carbon atoms, hydroxy alkyl groups containing up to 4 carbon atoms and aralkyl groups with up to 10 carbon atoms; and group D wherein R_3 and R_4 are members of the same heterocyclic group; X is a member selected from the group consisting of hydrogen, halogen and methyl; and Y is the anion of an acid.

The present invention is closely related to the invention described in our co-pending application Ser. No. 311,220 filed Sept. 24, 1963, now U.S. Patent 3,272,630, issued Sept. 13, 1966 and should be considered in the light of the disclosure contained therein. In our co-pending application referred to, a reproduction material had been 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 nearly the above formula.

One kind of the light-sensitive reproduction material in accordance with the present invention contains as light-sensitive substance a diazonium compound of the following formula:



(II)

in which X_1 represents the members required to complete a heterocyclic ring selected from the group consisting of 5-membered and 6-membered heterocyclic rings, X is selected from the group consisting of hydrogen and alkyl, and R_3 and R_4 are members of one of the groups selected from Group A in which R_3 and R_4 are selected from the group consisting of hydrogen, alkyl up to 4 carbon atoms,

and hydroxy alkyl with up to 4 carbon atoms, and Group B in which R_3 and R_4 are members of the same heterocyclic ring.

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 deep 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 for the semi-wet processes.

Another object is to provide a light-sensitive, diazotype reproduction material which has excellent photosensitivity, good stability, and good compatibility with additives and stabilizers.

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

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

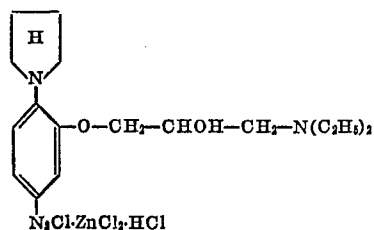
The diazo compounds were simply obtained according to methods known in the literature particularly where the compounds contain a heterocyclic ring in the para position to the diazo group. In such a case 2-chloro-5-nitrophenol e.g. was etherified with epichlorhydrin in the presence of an alkali, and the epoxide ring in the ether side chain was split and substituted by suitable agents. Subsequently the nuclear chlorine atom was replaced by a heterocyclic base containing a secondary nitrogen atom, the nitro compound reduced, and the product diazotized.

If the diazo compound used is a p-dialkylamino-benzenediazonium compound, the starting material may be o-nitrophenol which is etherified in the above explained manner. The nitro compound thus obtained is reduced and dialkylated according to one of the methods which are commonly known for reducing and dialkylating respectively. The substitution of an amino group in the para position of the dialkylamino group is achieved by coupling with a diazo compound to form an azo dyestuff and subsequent reductive splitting of the azo group of the dyestuff; instead of coupling, a nitroso or a nitro group may be substituted to the benzene nucleus by a known method with subsequent reduction of the nitroso or nitro group. The amino group is finally converted into the diazo group by the application of nitrous acid.

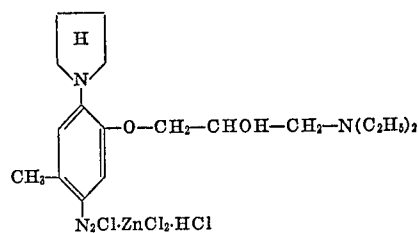
It should be understood that the products obtained according to the present process may also be obtained according to different reaction sequences.

Detailed descriptions of the properties and of the production of various compounds are given by the examples wherein the volume unit is milliliters and the weight unit is 1 gram. The formulas of some of the new diazonium compounds according to the present invention are in the table. The melting points in degrees centigrade of the nitro compounds (nitro group in the p-position to the $-NR_1R_2$ group) which are the basic materials for these diazonium salts are: (1) 94°C ., (2) 92°C ., (3) 92°C ., (4) 198°C ., (5) $108-109^\circ\text{C}$., (6) 131°C ., (7) $78-79^\circ\text{C}$., (8) 101°C . The figures 1 to 8 correspond to the figures of the formulas in the table.

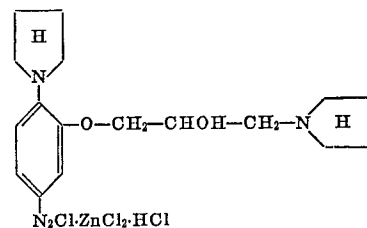
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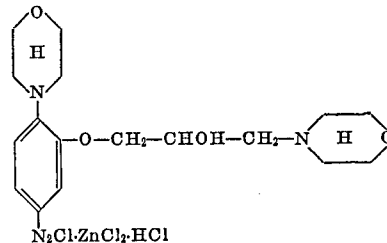
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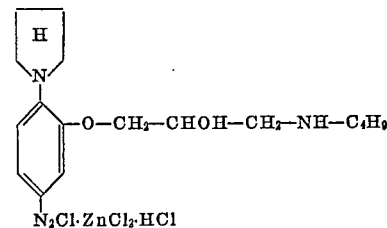
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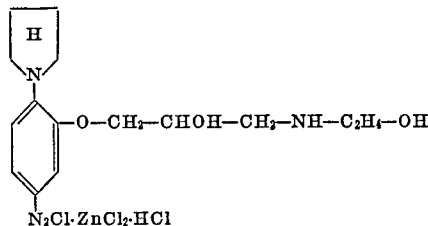
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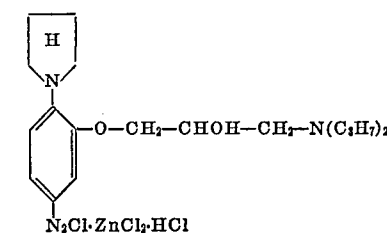
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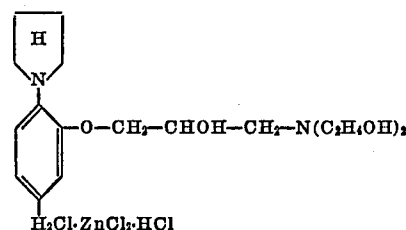
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Example 1

A reproduction paper base conventionally used for diazotype materials having a coating of colloidal silica and polyvinyl acetate was coated on the precoated surface with a solution containing:

	Parts by weight
Citric acid	4.0
Thiourea	5.0
Aluminium sulfate	3.0
1,3,6-naphthalene trisulfonic acid sodium salt	3.5
2,7-dihydroxy naphthalene-3,6-disulfonic acid sodium salt	2.4
Zinc chloride	1.0
Diazo product of 1-amino-4-pyrrolidino-3-(gamma-hydroxy ethyl-amino-beta-hydroxy-propoxy)-benzene in the form of its zinc chloride double salt of hydrochloric acid (Formula 6)	2.3

per 100 parts by volume of water. After drying the sensitized raw paper was exposed behind a transparent master and developed with ammonia. Blue images on a white background were obtained. The reproduction paper had an excellent shelf life.

The diazo compound employed was obtained by the following procedure. 173 parts by weight of 2-chloro-5-nitrophenol were dissolved in 250 parts by volume of methyl glycol, 176 parts by weight of epichlorhydrin were added and heated nearly to the boiling point. Then 100 parts by volume of 40% soda were gradually dropped into the solution without further heating. After addition of the soda, the mixture was refluxed for one hour. Then the warm solution was filtered, 100 parts by volume of water were added, cooled and the residue was drawn off. The latter was dried and recrystallized from methanol. The yield was 183 parts by weight melting at 93° C.

45 parts by volume of 2-chloro-5-nitro-phenyl glycidyl ether in 100 parts by volume of dioxane were dropped while cooling with ice into a solution of 120 parts by weight of ethanolamine in 100 parts by volume of dioxane under agitation within two hours. Then the solution was maintained fifteen hours at room temperature, poured on water, the residue drawn off and dried. The crude yield was 55 parts by weight of 1-nitro-4-chloro-3-(gamma-hydroxy ethyl-amino-beta-hydroxy-propoxy)-benzene melting at 132-133° C.

55 parts by weight of this intermediate product were heated to boiling temperature with 70 parts by volume of pyrrolidine and 10 parts by volume of water during three hours, poured on water, drawn off and recrystallized from methanol. The yield was 40 parts by weight of 1-nitro-4-pyrrolidino-3-(gamma-hydroxy ethylamino-beta-hydroxy-propoxy)-benzene melting at 131° C.

40 parts by weight of 1-nitro-4-pyrrolidino-3-(gamma-hydroxy-ethylamino-beta-hydroxy-propoxy)-benzene in 86 parts by volume of concentrated hydrochloric acid and 40 parts by volume of water were reduced while cooled with ice with zinc dust to 1-amino-4-pyrrolidino-3-(gamma-hydroxyethylamino-beta-hydroxy-propoxy)-benzene. The filtered solution was added to 37 parts by volume of hydrochloric acid and diazotized with 62 parts by volume of 2 N sodium nitrite solution under cooling with ice. The precipitated diazo compound was reprecipitated from a mixture of water and sodium chloride. The yield was 50 parts by weight.

Example 2

A reproduction paper conventionally used for diazotype purposes having on one side a precoat of colloidal silica and polyvinyl acetate was coated on the pretreated surface with a solution containing:

	Parts by weight
Citric acid	3.5
Boric acid	3.5
Thiourea	5.0

3,5-dihydroxy-4-bromo-benzoic-2-diethylamino

anilide	1.2
Zinc chloride	1.0
Diazo compound of 1-amino-4-pyrrolidino-3-(gamma-di-n-propylamino-beta-hydroxy-propoxy)-benzene in the form of its zinc chloride double salt of hydrochloric acid (Formula 7)	2.2

per 100 parts by volume of water. The process according to Example 1 was followed and red images on a white background were obtained.

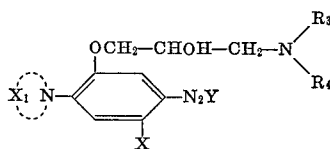
The diazo compound was obtained by the following procedure. 45 parts by weight of 2-chloro-5-nitrophenylglycidylether were heated with 60 parts by volume of di-n-propylamine during three hours on a steam bath. Then ice water was added and the precipitated product was drawn off and dried. The crude yield was 55 parts by weight melting at 41-42° C. Further processing was effected with good yields analogous to the method described in Example 1.

Similar results were obtained if the compounds of the Formulas 1-5 and 8 were used which may be obtained analogously to the compound of Formula 6. In Formula 5, the N-n-butyl compound and in Formula 7 the N-di-n-propyl compound were used.

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



in which X₁ represents the members required to complete a heterocyclic ring selected from the group consisting of 5-membered and 6-membered heterocyclic rings, X is selected from the group consisting of hydrogen and alkyl, R₃ and R₄ are members of one of the groups selected from: Group A in which R₃ is alkyl up to 4 carbon atoms and hydroxyalkyl with up to 4 carbon atoms, and R₄ is hydrogen, alkyl up to 4 carbon atoms, and hydroxyalkyl with up to 4 carbon atoms; and Group B in which R₃ and R₄ are members of the same 5- or 6-membered heterocyclic ring, and Y is the anion of an acid.

2. A diazotype reproduction material which comprises a support and a photosensitive layer coated on said support, said layer comprising a diazonium compound selected from the group consisting of:

- 4-pyrrolidino-3-(gamma-diethyl-amino-beta-hydroxy-propoxy)-benzene diazonium chloride;
- 6-methyl-4-pyrrolidino-3-(gamma-diethylamino-beta-hydroxy-propoxy)-benzene diazonium chloride;
- 4-pyrrolidino-3-(gamma-pyrrolidino-beta-hydroxy-propoxy)-benzene diazonium chloride;
- 4-morpholino-3-(gamma-morpholino-beta-hydroxy-propoxy)-benzene diazonium chloride;
- 4-pyrrolidino-3-(gamma-n-butylamino-beta-hydroxy-propoxy)-benzene diazonium chloride;
- 4-pyrrolidino-3-(gamma-hydroxyethylamino-beta-hydroxy-propoxy)-benzene diazonium chloride;
- 4-pyrrolidino-3-(gamma-di-n-propylamino-beta-hydroxy-propoxy)-benzene diazonium chloride; and
- 4-pyrrolidino-3-(gamma-di-hydroxyethylamino-beta-hydroxy-propoxy)-benzene diazonium chloride.

3. A material in accordance with claim 1 in which said diazonium compound is 4-pyrrolidino-3-(gamma-di-ethyl-

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amino-beta-hydroxy-propoxy)-benzene diazonium chloride.

4. A material in accordance with claim 1 in which said diazonium compound is 4-pyrrolidino-3-(gamma-n-butyl-amino-beta-hydroxy-propoxy)-benzene diazonium chloride.

5. A material in accordance with claim 1 in which said diazonium compound is 4-pyrrolidino-3-(gamma-dihydroxyethylamino-beta-hydroxy-propoxy)-benzene diazonium chloride.

6. A material in accordance with claim 1 in which said diazonium compound is 4-pyrrolidino-3-(gamma-hydroxyethylamino-beta-hydroxy-propoxy)-benzene diazonium chloride.

7. A material in accordance with claim 1 in which said

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diazonium compound is 4-pyrrolidino-3-(gamma-di-n-propylamino-beta-hydroxy-propoxy)-benzene diazonium chloride.

References Cited

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10 J. TRAVIS BROWN, *Primary Examiner*.

C. BOWERS, *Assistant Examiner*.

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