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LIGHT-SENSITIVE REPRODUCTION MATERIAL CONTAINING UNILATERALLY DIAZOTIZED p-PHENYLENE-DIAMINE DERIVATIVES AS THE LIGHT SENSITIVE SUBSTANCE

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31 Claims. (Cl. 96—75)

The present invention relates to a reproduction material and more particularly refers to a light-sensitive diazotype reproduction material and element and to methods for preparing and using said material.

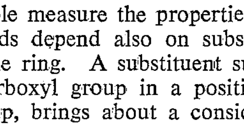
In copying papers and other copying foils that have been senstitized with diazo compounds, the derivatives of unilaterally diazotized p-phenylene-diamine have long been used as the light-senstitive substances. These diazonium salts have a tertiary amino group of basic character and they have been used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

For the dry-development process the diazo compounds which are suitable are those containing alkyl groups with few carbon atoms attached to the basic nitrogen atom, while for the semi-wet process the best suited ones are those in which the basic nitrogen atom is attached to hydrocarbon radicals with more carbon atoms or with a ring structure.

The substituents on the basic nitrogen atom affect not only coupling speed and the color of the dyestuffs obtained when coupling takes place with the couplers normally used in diazotype processes, 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 towards 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 compounds but the keeping qualities become poorer as a result of this type of substitution. Despite their poor stability, this group of diazo compounds is nevertheles important because of their 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 poor stability is 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 the form of ether groups, tertiary amino groups or carbonamide 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



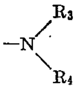
in which

R_1 is an alkyl group with up to four carbon atoms,

R_2 is a member selected from the group consisting of an alkyl group with up to four carbon atoms and an aralkyl group with up to ten carbon atoms, or

R_1 and R_2 with the nitrogen atom form a heterocyclic group which may have one or more substituents, and

Z is an alkoxy group, an arylated alkoxy group or an aryloxy group or the group



in which

R_3 and R_4 are each an alkyl group with up to four carbon atoms or together with the nitrogen atom to which they are joined form a heterocyclic group which can have one or more substituents,

X is hydrogen, halogen or a methyl group,

Y is the anion of an acid,

n is the whole number of from 1 to 4,

m is 0 to 1, and the sum of *n* and *m* is at least 2.

Reproduction materials utilizing the present invention can be used both for the dry and for the semi-wet processes. According to the coupler used, deep brown or violet copies can be prepared with great rapidity.

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 process.

Another object is to provide a light-sensitive diazotype reproduction material which is capable of producing dark colored copies with great rapidity. Other objects will become apparent during the course of the following specification.

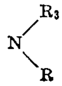
The diazo compounds used in accordance with the present invention are substituted in the basic amino group by lower alkyl groups, R_1 and R_2, having up to four carbon atoms, such as the methyl, ethyl, propyl, isopropyl and butyl groups. R_1 and R_2, together with the nitrogen atom to which they are joined, can also form a heterocyclic group, which may also be substituted, e.g., by one or more alkyl groups. Examples are the pyrrolidino, the piperazino, the morpholino, the 2-methyl-morpholino, the 2-ethyl-morpholino, the 2,3-dimethyl-morpholino, the 2,5-dimethyl-morpholino, the 2,6-dimethyl-morpholino and the 3,5-dimethyl-morpholino, the 2,6-diethyl-morpholino, the 3-methyl-5-ethyl-morpholino, the 5-methyl-2-ethyl-morpholino, the 2,3,5-trimethyl-morpholino and the thio-morpholino groups. The heterocyclic groups are suitable substituents for the —NR_3R_4 group. The benzene nucleus carrying the diazo groups in the above formula can have a halogen, particularly chlorine, or the methyl group as the substituents. The best light-sensitivity was found in diazo compounds which are substituted in the para position by a heterocyclic ring containing nitrogen and in the meta position by an alkoxy-alkyloxy group.

The diazo compounds used in accordance with the present invention are in the form of their chloride or double salts of chlorides with metal chlorides, in particular the double salts with zinc chloride or cadmium chloride. The type of the anion joined to the diazonium group does not play a critical role and many other salts can be used equally well, e.g., the bromides, sulfates or borofluorides.

The diazo compounds used in accordance with the present invention are readily obtainable in good yields by one of the processes described below.

(1) For the preparation of diazo compounds in which Z is an alkoxy group, an arylated alkoxy group, an aryloxy group or a tertiary amino group, and in which there

is no CO— group between the group Z and the $(CH_2)_n$ group, a suitable process consists of etherizing o-nitrophenol with dialkyl ethers or arylalkyl alkyl ethers or alkyl aryl ethers in which one alkyl group is terminally singly halogenated, or etherizing o-nitrophenol with omega,omega'-dihalogenoalkanes and substituting for the remaining halogen atom the above group



by a reaction with the respective secondary nitrogenic base, reducing the resultant nitro compound to the amine and doubly alkylating the amino group. The diazo group is then introduced in known manner into the position para to the resultant dialkylamino group, e.g., by treating it with a diazo compound to form an azo dyestuff and then splitting the azo dyestuff to give the amine, or by the introduction of a nitroso or a nitro group which is reduced to the amino group and then diazotized.

(2) For the preparation of compounds of the above formula in which Z forms, together with a CO— group, a carbonamide group, the following process can be followed: 2-chloro-5-nitrophenol is reacted with chloroacetic ester or chloroacetic acid to form a chloronitrophenol ether. The chlorine atom in the ring is replaced by a heterocyclic base which contains a basic nitrogen atom in its ring system, the base being used in excess to simultaneously amidate the carboxylic acid radical. The nitro group present in the reaction product is then reduced and the resultant amino group diazotized.

(3) Many of the diazo compounds used in accordance with the invention can be prepared as follows:

2-chloro-5-nitrophenol is reacted with dialkyl ethers or arylalkyl alkyl ethers or alkyl aryl ethers terminally singly halogenated in one alkyl group or with an omega-chloro-omega-dialkylamino-alkane, e.g., with 1-chloro-2-diethylamino-ethane, the phenolic hydroxyl group being etherified by the reaction, the aromatic chlorine is then replaced by a secondary nitrogenic base group, in particular by a heterocyclic nitrogenic base group which has a basic nitrogen atom in the ring system, by a reaction with the respective base, the nitro group in the 5-position reduced to the amino group, and diazotization then carried out in known manner.

Detailed descriptions of the preparation of the compounds are found in some of the following examples.

Structural formulas are given in Table 1.

The following examples further illustrate the present invention and are not intended to limit the scope of the present invention.

EXAMPLE 1

A conventional diazotype base paper was coated with a solution containing in 100 cc. water:

	G.
Citric acid	6
Thiourea	4
Naphthalene-1,3,6-trisulfonic acid sodium salt	3
2,3-dihydroxynaphthalene-6-sulfonic acid sodium salt	2
Diazo compound from 1-amino-4-pyrrolidino-3-(beta-ethoxy)-ethoxy-benzene (in the form of the zinc chloride double salt) (Formula 1)	1.8

After drying, the sensitized paper was exposed under a transparent master and developed with ammonia. Blue images were obtained on a white ground. The reproduction papers had excellent keeping qualities.

The diazo compound was obtained as follows: 35 g.-2-chloro-5-nitrophenol were dissolved in 110 cc. glycol monomethyl ether. A solution of 8 g. NaOH in 10 cc. water was added with stirring. After the addition of 31 g. beta-bromoethyl-ethyl ether, the mixture was heated to boiling for three hours with stirring. After cooling, twice the volume of water was added and the precipitate was filtered off with suction, washed with water and dried. 45 g. crude product was obtained which after recrystallization from methanol had a melting point of 58° C.

35 g. of the resultant 2-chloro-5-nitro-phenyl-beta-ethoxy-ethyl ether were heated to boiling for two hours with 35 cc. pyrrolidine and 2.5 cc. water. The mixture was then poured into water, filtered off with suction, washed with water and recrystallized from methanol. 28 g. of 5-nitro-2-pyrrolidinophenyl-beta-ethoxy-ethyl ether with a melting point of 73° C. were obtained. 90 cc. concentrated hydrochloric acid were poured thereover and reduction was carried out with 24 g. zinc dust. The precipitate was filtered off with suction, cooled and diazotized at 0 to 5° C. with 17.5 cc. 40% $NaNO_2$ solution. Twice the quantity of water was added followed by 200 g. sodium chloride. The precipitated diazo compound was purified by recrystallization from aqueous sodium chloride solution. The yield was 26.5 grams.

EXAMPLE 2

A conventional diazotype base paper with a precoat of colloidal silica and polyvinyl acetate was coated on the precoated surface with a solution containing in 100 cc. water:

3.5 grams citric acid
3.5 grams boric acid
5.0 grams thiourea
1.2 grams 3,5-dihydroxy-4-bromo-benzoic-acid-2'-diethylamino anilide
2.4 grams of diazo compound from 1-amino-4-diethylamino-3-(beta-phenoxy)-ethoxy-6-methyl benzene (in the form of the zinc chloride double salt) (Formula 2)

The process described in Example 1 was followed and red images on a white ground were obtained.

The diazo compound was obtained as follows: 100 grams 3-nitro-4-hydroxy-toluene were dissolved in 330 cc. glycol monomethyl ether. 26 grams NaOH in 40 cc. water and 130 grams beta-bromoethylphenyl ether were added with stirring and boiled for five hours. After cooling, the same quantity of water was added and the precipitate was filtered off, washed with water, dried and recrystallized from acetone. 135 grams light yellow crystals with a melting point of 90° C. were obtained.

100 grams of 4-methyl-2-nitrophenyl-beta-phenoxy-ethyl ether thus obtained were heated under reflux for 30 hours with 185 grams of sodium sulfide, 24 grams of flowers of sulfur, 280 cc. commercial ethyl alcohol and 280 cc. water. After cooling, an equal volume of water was added, filtered by suction, thoroughly washed with water, dried, and recrystallized from methanol. The precipitated white flakes (67 grams) had a melting point of 99° C.

60.7 grams of 2-amino-4-methyl-phenyl-beta-phenoxy-ethyl ether were stirred for four days with 74 grams sodium bicarbonate, 500 cc. water, 100 cc. benzene, and 81 cc. diethyl sulfate. From this mixture colorless crystals precipitated out. They were recrystallized from methanol. Their melting point was 64° C. and the yield was 43 grams. The product was 2-diethyl-amino-4-methyl-phenyl-beta-phenoxy ethyl ether. 30 grams were dissolved in 200 cc. 70% acetic acid; 52 cc. 40% sodium nitrite solution were added at 0 to 5° C. and the mixture was stirred for three hours at room temperature. The resultant yellow precipitate was filtered off with suction, washed with water, dried and recrystallized from methanol. Its melting point was 103° C., the yield being 20 grams. 18 grams 5-nitro-2-diethyl-amino-4-methyl-phenyl-beta-phenoxy-ethyl ether were reduced in hydrochloric acid to the amine with zinc dust in the usual manner and then diazotized. 16 grams of diazonium compound were obtained.

EXAMPLE 3

A diazotype base paper with a precoat of colloidal silica and polyvinyl acetate on one side was coated on the precoated surface with a solution containing in 100 cc. water:

4 grams citric acid
3 grams boric acid
2 grams aluminum sulfate
4 grams sulfosalicylic acid sodium salt
1.2 grams resorcinol
2 grams of diazo compound from 1-amino-4-pyrrolidino-3-(beta-ethoxy)-ethoxy benzene (in the form of the zinc chloride double salt) (Formula 1)

The process described in Example 1 was followed and brown images on a white ground were obtained.

EXAMPLE 4

A transparent paper was coated with a solution containing:

3 grams citric acid
1.6 grams boric acid
2 grams aluminum sulfate
2.4 grams thiourea
2 grams cresyl glutaric acid
3 grams of diazo compound from 1-amino-4-piperidino-3-(beta-ethoxy)-ethoxy-benzene (in the form of the zinc chloride double salt) (Formula 3)

in a mixture of 15 cc. isopropanol and 85 cc. water.

The process described in Example 1 was followed and the image was obtained in yellow with good covering power.

The diazonium salt which corresponds to Formula 3 was prepared in a manner analogous to that for the substance of Formula 1, the preparation of which is described in Example 1.

EXAMPLE 5

A diazotype base paper was coated with a solution containing:

0.4 gram tartaric acid
0.4 gram aluminum sulfate
2.2 grams of the diazo compound from 1-amino-4-morpholino-3-(beta-propyloxy)-ethoxy-benzene (in the form of the zinc chloride double salt) (Formula 4)

in 100 cc. water.

After drying, the sensitized paper was exposed to light under a transparent master and developed with a solution containing in 100 cc. water:

	Grams
Borax	2.5
Sodium carbonate	3
Sodium chloride	2
Thiourea	5
Sodium isopropyl naphthalene sulfonate	0.1
Phloroglucinol	0.6
Resorcinol	0.6

Strong brown images on a white ground were obtained.

The diazo compound was obtained in an analogous manner to that in Example 1.

The 2-chloro-5-nitrophenyl-beta-n-propyloxyethyl ether obtained from 2-chloro-5-nitrophenol and beta-bromoethyl-n-propyl ether was reacted with morpholine to give the 2-morpholino-5-nitrophenyl-beta-n-propyloxyethyl ether. This had a melting point of 71° C. After reduction of the nitro group the diazo compound was prepared in the usual way.

EXAMPLE 6

Instead of 2.2 grams of diazo compound from 1-amino-4-morpholino-3-(beta-propyloxy)-ethoxy-benzene as in Example 5, 2.0 grams of diazo compound from 1-amino-4-N-methyl-N-benzyl-amino-3-(beta-ethoxy)-ethoxy-benzene (Formula 5) were used.

This diazo compound was prepared as follows: 139 grams o-nitrophenol were dissolved in 200 cc. glycol monomethyl ether. A solution of 56 grams KOH in 25 cc. water and 153 grams beta-bromoethyl ethyl ether were added and the mixture was heated under reflux to boiling for three hours with stirring. It was then poured into water, the oil layer separated off, the aqueous phase extracted with benzene, the benzene layer mixed with the oil, washed and dried, the benzene distilled off, and the residue distilled in vacuo. Yield: 139 grams with a boiling point of 177 to 178° C. (12 mm. Hg). The nitro compound obtained was hydrogenated in the autoclave in methanol over finely divided nickel at 50° C.

The yield of o-amino-phenyl-beta-ethoxy ethyl ether with a boiling temperature of 150 to 152° C. (11 mm. Hg) was 91% of the theoretical.

The Schiff's base obtained from this ether and benzaldehyde was hydrogenated in a duck-shaped shaking vessel under the usual conditions and then alkylated with dimethyl sulfate in a manner analogous to that described in Example 2 and then nitrated as described in Example 2. The non-purified nitro compound was converted over Raney nickel in a duck-shaped shaking vessel into the amino compound and was then diazotized in the usual manner. Golden yellow crystals were obtained.

EXAMPLE 7

Instead of the 2.2 grams diazo compound from 1-amino-4-morpholino-3-(beta-propyloxy)-ethoxy-benzene as in Example 5, 2.0 grams diazo compound from 1-amino-2-chloro-4-diethylamino-5-(beta-ethoxy)-ethoxy benzene (Formula 6) were used.

This diazo compound was prepared as follows: 4-chloro-2-nitrophenol was reacted with beta-bromo-ethyl-ethyl ether and then reduced to the amine. This was dialkylated with diethyl sulfate. The resultant 4-chloro-2-diethylene-amino-phenyl-beta-ethoxy ethyl ether (35 grams) was dissolved in a mixture of 39 grams concentrated sulfuric acid and 190 cc. water. A solution of 62 grams $NaNO_2$ in 1100 cc. water was added dropwise while cooling with ice and the nitro compound obtained by gradual heating to room temperature. Yellow crystals with a melting point of 75° C. were obtained after recrystallization from methanol. The diazo compound was obtained therefrom in the usual manner.

EXAMPLE 8

A diazotype base paper was coated with a solution containing:

4 grams citric acid
2 grams boric acid
2 grams aluminum sulfate
4 grams thiourea
2.5 grams 2,7-dihydroxy-naphthalene-3,6-disulfonic acid sodium salt
2.4 grams of diazo compound from 3-amino-6-pyrrolidino-phenoxy acetic acid-pyrrolidide (in the form of the zinc chloride double salt) (Formula 7)

in 100 cc. water.

The process described in Example 1 was followed and blue images on a white ground were obtained.

The diazo compound was obtained as follows: 92.5 grams 2-chloro-5-nitrophenol potassium salt were kept at boiling, with stirring, for five hours in 250 cc. glycol monomethyl ether with 53.3 grams chloroacetic acid ethyl ester. After cooling, water was added and the solution shaken with benzene. The benzene solution was dried and the benzene distilled off. 82 grams 2-chloro-5-nitrophenoxy acetic acid ethyl ester with a melting point of 97 to 105° C. were obtained. 60 grams were heated with 96 cc. pyrrolidine for three hours under reflux. After cooling, water was added and the precipitate filtered off with suction, washed well with water and recrystallized from methanol. 52 grams 5-nitro-2-pyrrolidino-phenoxyacetic acid pyrrolidide with a melting point of 163° C. were obtained.

The diazo compound was obtained in the usual manner after reduction with zinc dust and diazotization. Yield: 84.3% of the theoretical.

EXAMPLE 9

A diazotype base paper was coated with a solution containing:

0.6 gram tartaric acid
0.05 gram saponine
4.0 grams naphthalene-1,3,6-trisulfonic acid sodium salt
2.5 grams of diazo compound from 1-amino-4-morpholino-3-(beta-benzyloxy)-ethoxy-benzene (in the form of the cadmium chloride double salt) (Formula 8)

in 100 cc. water.

After drying, the sensitized base paper was exposed to light under a transparent master and developed with the solution described in Example 5. Brown images on a white ground were obtained.

The diazo compound was prepared as follows: 44 grams 2-chloro-5-nitrophenol were heated for five hours under reflux in 160 cc. glycol monomethyl ether with 10.2 grams NaOH dissolved in a small amount of water and 57.4 grams beta-bromoethyl benzyl ether. After the addition of water, 54 grams 2-chloro-5-nitrophenyl-beta-benzyloxy-ethyl ether with a melting point of 60° C. were isolated from the mixture. 26 grams were kept at boiling for twelve hours with 37 cc. morpholine. The golden yellow flakes which precipitated out after the addition of water were recrystallized from methanol. Yield: 24 grams 5-nitro-2-morpholinophenyl-beta-benzyloxy-ethyl ether of a melting point of 50° C. 20 grams of the ether thus obtained were hydrogenated in 300 cc. methanol in the presence of finely divided nickel. After the product had been filtered and the solvent distilled off, diazotization was carried out in hydrochloric acid in the usual way without further purification. The diazo compound was isolated in the form of the cadmium chloride double salt.

EXAMPLE 10

A diazotype base paper was coated with a solution containing:

0.3 gram aluminum sulfate
0.4 gram citric acid
0.03 gram saponine
2.7 grams of diazo compound from 1-amino-4-morpholino-3-(beta-morpholino)-ethoxy-benzene (in the form of the hydrochloric acid zinc chloride double salt) (Formula 9)

in 100 cc. water.

After drying, the sensitized paper was exposed under a transparent master and developed with the solution described in Example 5.

Red brown images were obtained on a white ground.

The diazo compound was obtained as follows: A solution of 260 grams 2-chloro-5-nitrophenol in 150 cc. NaOH (40%), 350 cc. water and 550 cc. glycol monomethyl ether was introduced dropwise over a period of one hour, with stirring, into a mixture of 560 grams ethylene bromide and 200 cc. glycol monomethyl ether at the boiling point. The mixture was heated to boiling for one hour with stirring, evaporated in vacuo to dryness, treated with water, filtered off with suction and recrystallized from methanol. The yield of 2-chloro-5-nitrophenyl-beta-bromo-ethyl ether was 232 grams with a melting point of 77 to 78° C. 56 grams were heated with 100 cc. morpholine and 10 cc. water for 15 hours under reflux, cooled, mixed with ice water, filtered off with suction, washed with water, and recrystallized from methanol. The yield was 53 grams 5-nitro-2-morpholinophenyl-beta-N-morpholino-ethyl ether with a melting point of 114° C.

From 49 grams of the nitro compound, 52 grams of the corresponding diazo compound were obtained in the usual way as the chloride/zinc chloride double salt.

EXAMPLE 11

A diazotype base paper with a precoat of colloidal silicic acid and polyvinyl acetate on one side, was coated on the precoated surface with a solution containing:

3.5 grams citric acid
3.5 grams boric acid
5.0 grams thiourea
1.2 grams 3,5-dihydroxy-4-bromo-benzoic acid amide
2.4 grams of diazo compound from 1-amino-4-pyrrolidino-3-(beta-diethylamino)-ethoxy-benzene (in the form of the hydrochloric acid zinc chloride double salt) (Formula 10)

in 100 cc. water. The process described in Example 1 was followed and red images on a white ground were obtained.

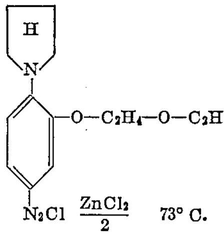
The diazo compound was obtained as follows: 2-chloro-5-nitrophenol was reacted in glycol monomethyl ether in the presence of alkali with 1-chloro-2-diethylamino-ethane and the reaction product was isolated in the form of hydrochloric acid salt with a melting point of 224° C. The corresponding free base (2-chloro-5-nitro-phenol-beta-diethyl-amino-ethyl ether) had a melting point of 33° C. It can also be prepared from 2-chloro-5-nitro-phenyl-beta-bromo-ethyl ether (from Example 10) and diethylamine. After the aromatic chlorine atom of the base had been exchanged for pyrrolidine, the nitro compound was reduced in the usual way and then diazotized.

EXAMPLE 12

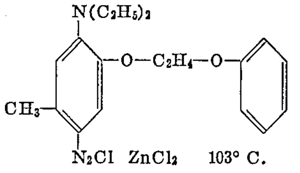
Each of the diazonium salts corresponding to Formulas 11 to 38 was used in a manner analogous to one of the processes described in Examples 1 to 11 for the preparation of diazotype papers. The diazotype papers thereby obtained also proved to be very light-sensitive with good keeping qualities.

TABLE 1

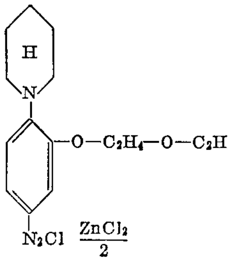
Formula 1



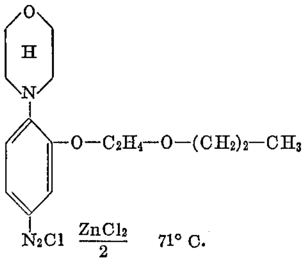
Formula 2



Formula 3

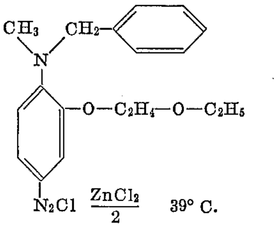


Formula 4



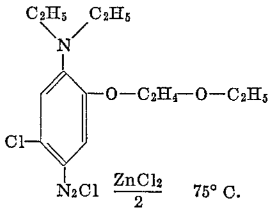
71° C.

Formula 5



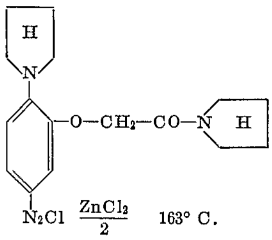
39° C.

Formula 6



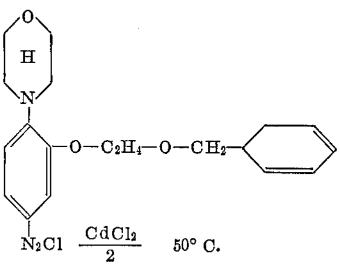
75° C.

Formula 7



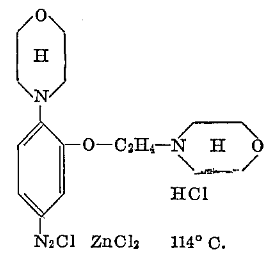
163° C.

Formula 8



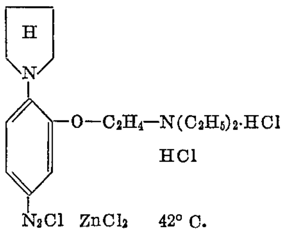
50° C.

Formula 9



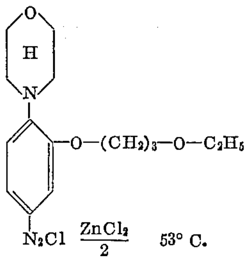
114° C.

Formula 10



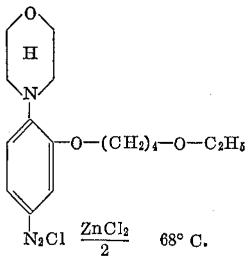
42° C.

Formula 11



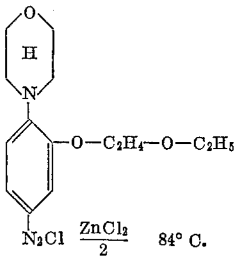
53° C.

Formula 12



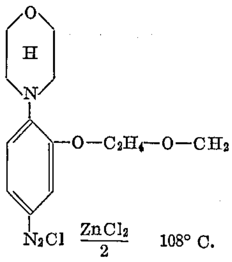
68° C.

Formula 13



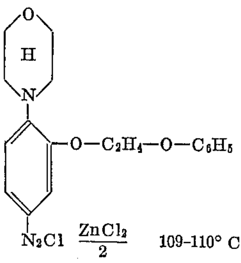
84° C.

Formula 14



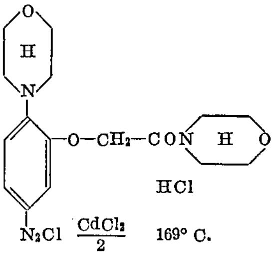
108° C.

Formula 15



109-110° C.

Formula 16



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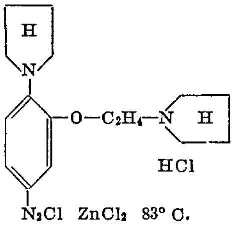

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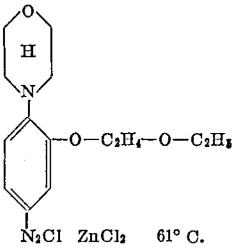

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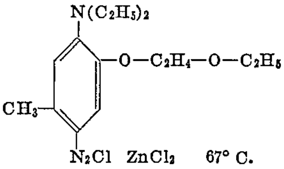

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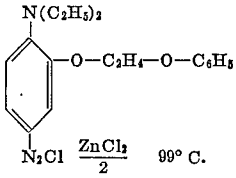

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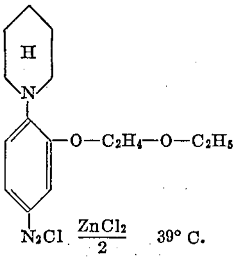

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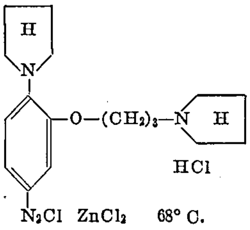

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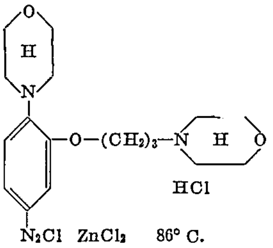

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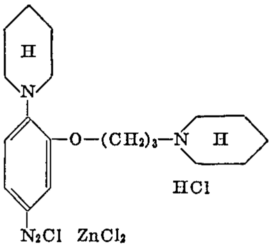

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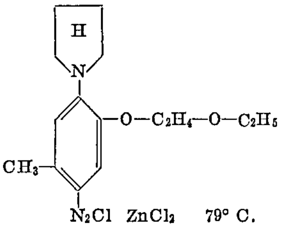

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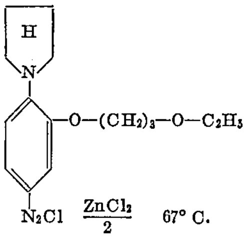

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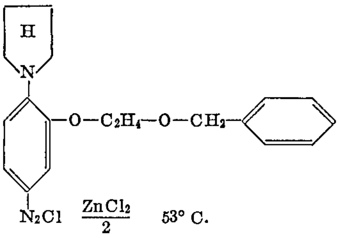

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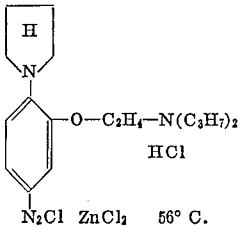

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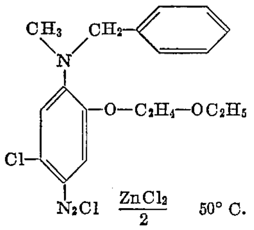

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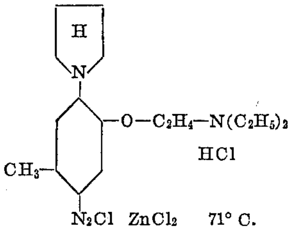

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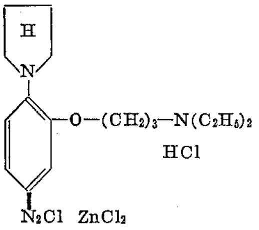

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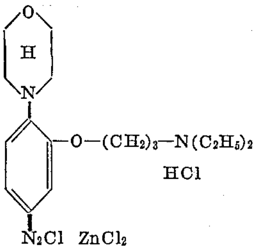

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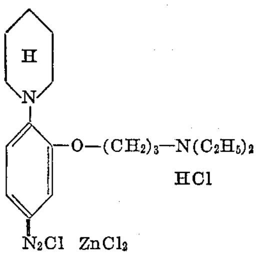

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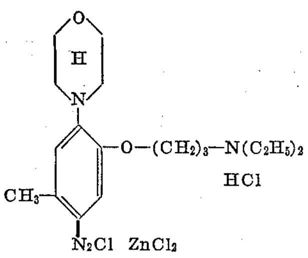

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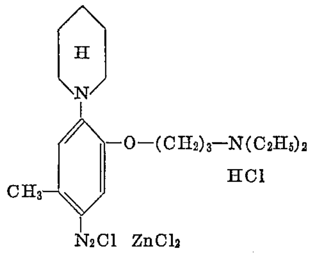

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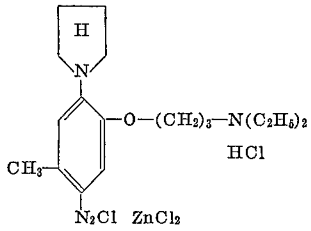

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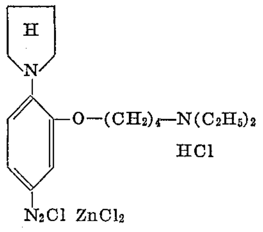

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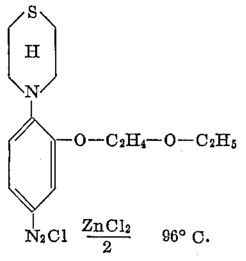
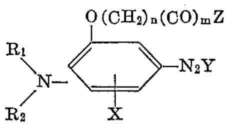


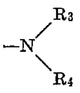
The examples described herein are capable of many variations and modifications within the scope of the present invention. All such variations and modifications are to be included in the present invention.

What is claimed is:

1. A light sensitive-diazotype reproduction material comprising a sheet-like support and a like-sensitive diazotype layer coated on said support, said layer comprising a light-sensitive diazonium compound of the following 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 alkoxy, arylated alkoxy, aryloxy and



wherein R_3 and R_4 are members selected from the groups consisting of: group C wherein R_3 and R_4 are alkyl radicals containing up to 4 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; Y is the anion of an acid; *n* is an integer from 1 to 4; *m* is one of the integers 0 and 1; and where the sum of *n* and *m* is at least 2.

2. A material in accordance with claim **1** in which said diazonium compound is a member selected from the group consisting of:

4-pyrrolidino-3-(beta-ethoxy)-ethoxy-benzene diazonium salt,
4-diethylamino-3-(beta-phenoxy)-ethoxy-5-methyl-benzene diazonium salt,
4-piperidino-3-(beta-ethoxy)-ethoxy-benzene diazonium salt,
4-morpholino-3-(beta-propyloxy)-ethoxy-benzene diazonium salt,
4-N-methyl-N-benzyl-amino-3-(beta-ethoxy)-ethoxy-benzene diazonium salt,
2-chloro-4-diethylamino-5-(beta-ethoxy)-ethoxy-benzene diazonium salt,
3-pyrrolidinyl carbonyl-methoxy-4-pyrrolidino-benzene diazonium salt,
3-(beta-benzyloxy)-ethoxy-4-morpholino-benzene diazonium salt,
3-(beta-morpholino)-ethoxy-4-morpholino-benzene diazonium salt,
3-(beta-diethylamino)-ethoxy-4-pyrrolidino-benzene diazonium salt,
3-(gamma-ethoxy)-propyloxy-4-morpholino-benzene diazonium salt,
3-(delta-ethoxy)-butoxy-4-morpholino-benzene diazonium salt,
3-(beta-ethoxy)-ethoxy-4-morpholino-benzene diazonium salt,
3-(beta-methoxy)-ethoxy-4-morpholino-benzene diazonium salt,
3-(beta-phenoxy)-ethoxy-4-morpholino-benzene diazonium salt,
3-(morpholino-carbonyl)-methoxy-4-morpholino-benzene diazonium salt,
3-(beta-pyrrolidino)-ethoxy-4-pyrrolidino-benzene diazonium salt,
2-methyl-4-morpholino-5-(beta-ethoxy)-ethoxy-benzene diazonium salt,
2-methyl-4-diethylamino-5-(beta-ethoxy)-ethoxy-benzene diazonium salt,
3-(beta-phenoxy)-ethoxy-4-diethylamino-benzene diazonium salt,
3-(beta-ethoxy)-ethoxy-4-piperidino benzene diazonium salt,
3-(gamma-pyrrolidino)-propyloxy-4-pyrrolidino-benzene diazonium salt,
3-gamma-morpholino-propyloxy-4-morpholino-benzene diazonium salt,
3-(gamma-piperidino)-propyloxy-4-piperidino-benzene diazonium salt,
2-methyl-4-pyrrolidino-5-(beta-ethoxy)-ethoxy-benzene diazonium salt,
3-(gamma-ethoxy)-propoxy-4-pyrrolidino-benzene diazonium salt,
3-(beta-benzyloxy)-ethoxy-4-pyrrolidino-benzene diazonium salt,
3-(beta-dipropylamino)-ethoxy-4-pyrrolidino-benzene diazonium salt,
2-chloro-4-N-methyl-N-benzyl-amino-5-(beta-ethoxy)-ethoxy-benzene diazonium salt,
2-methyl-4-pyrrolidino-5-(beta-diethylamino)-ethoxy-benzene diazonium salt,
4-pyrrolindino-3-(gamma-diethylamino)-propoxy-benzene diazonium salt,
4-morpholino-3-(gamma-diethylamino)-propoxy-benzene diazonium salt,

4-piperidino-3-(gamma-diethylamino)-propoxy-benzene diazonium salt,
4-morpholino-3-(gamma-diethylamino)-propoxy-benzene diazonium salt,
2-methyl-4-piperidino-3-(gamma-diethylamino)-propoxy-benzene diazonium salt,
2-methyl-4-pyrrolidino-3-(gamma-diethylamino)-propoxy-benzene diazonium salt,
4-pyrrolidino-3-(delta-diethylamino)-butoxy-benzene diazonium salt, and
4-thio-morpholino-3-(beta-ethoxy)-ethoxy-benzene diazonium salt.

3. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 4-pyrrolidino-3-(beta-ethoxy) - ethoxy - benzene diazonium chloride, zinc chloride double salt, as light-sensitive diazonium compound and 2,3-dihydroxy-naphthalene-6-sulfonic acid, sodium salt, as azo coupling component, said material being suitable for the dry development diazotype process.

4. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 4-diethylamino-3-(beta-phenoxy)-ethoxy-6-methyl benzene diazonium chloride, zinc chloride double salt, as light-sensitive diazonium compound and 3,5-dihydroxy-4-bromo-benzoic acid-2-diethylamino anilide as azo coupling component, said material being suitable for the dry development diazotype process.

5. A ligst-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 4-pyrrolidino-3-(beta-ethoxy) - ethoxy - benzene diazonium chloride, zinc chloride double salt, as light-sensitive diazonium compound and resorcinol as azo coupling component, said material being suitable for the dry development diazotype process.

6. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 4-piperidino-3-(beta-ethoxy) - ethoxy - benzene diazonium chloride, zinc chloride double salt, as light-sensitive diazonium compound and cresyl glutaric acid as azo coupling component, said material being suitable for the dry development diazotype process.

7. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 3-pyrrolindinylcarbonyl-methoxy-4 - pyrrolindino - benzene diazonium chloride, zinc chloride double salt, as light-sensitive diazonium compound and 2,7-dihydroxy-naphthalene-3,6-disulfonic acid, sodium salt, as azo coupling component, said material being suitable for the dry development diazotype process.

8. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 4-pyrrolidino - 3 - (beta-diethylamino)-ethoxy-benzene diazonium chloride, hydrochloric acid zinc chloride double salt, as light-sensitive diazonium compound and 3,5-dihydroxy-4-bromo-benzoic acid amide as azo coupling component, said material being suitable for the dry development diazotype process.

9. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 4-morpholino - 3 - (beta-propyloxy)-ethoxy-benzene diazonium chloride, zinc chloride double salt, as light-sensitive diazonium compound, said material being suitable for the semi-wet development diazotype process.

10. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 4-N-methyl - N-benzylamino-3-(beta-ethoxy)-ethoxy-benzene diazonium chloride, zinc chloride double salt as light-sensitive diazonium compound, said material being suitable for the semi-wet development diazotype process.

11. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 2-chloro - 4 - diethylamino-5-(beta-ethoxy)-ethoxy-benzene diazonium chloride, zinc chloride double salt as light-sensitive diazonium compound, said material being suitable for the semi-wet development diazotype process.

12. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 4 - morpholino-3-(beta-benzyloxy)-ethoxy-benzene diazonium chloride, cadmium chloride double salt as light-sensitive diazonium compound, said material being suitable for the semi-wet development diazotype process.

13. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 4-morpholino - 3-(beta-morpholino)-ethoxy-benzene diazonium chloride, hydrochloric acid zinc chloride double salt as light-sensitive diazonium compound, said material being suitable for the semi-wet development diazotype process.

14. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 3-(beta - ethoxy) - propyloxy-4-morpholino-benzene diazonium chloride, zinc chloride double salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes.

15. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support said layer comprising 3-(delta - ethoxy) - butoxy-4-morpholino-benzene diazonium chloride, zinc chloride double salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes.

16. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 3 - (beta - ethoxy)-ethoxy-4-morpholino-benzene diazonium chloride, zinc chloride double salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes.

17. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 3 - (beta-methoxy)-ethoxy-4-morpholino-benzene diazonium chloride, zinc chloride double salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes.

18. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 3-(beta-phenoxy)-ethoxy-4-morpholino-benzene diazonium chloride, zinc chloride double salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes.

19. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 3 - (morpholinocarbonyl) - methoxy-4-morpholino-benzene diazonium chloride, cadmium chloride double salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes.

20. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 3-(beta-pyrrolidino)-ethoxy-4-pyrrolidino-benzene diazonium chloride, hydrochloric acid zinc chloride salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes.

21. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 2-methyl - 4-morpholino - 5-(beta-ethoxy)-ethoxy-benzene diazonium chloride, zinc chloride salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes.

22. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 2-methyl - 4-diethylamino 5-(beta-ethoxy)-ethoxy-benzene diazonium chloride, zinc chloride salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes.

23. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 3-(beta - phenoxy) - ethoxy-4-diethylamino-benzene diazonium chloride, zinc chloride double salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes.

24. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 3-(beta - ethoxy) - ethoxy-4-piperidino-benzene diazonium chloride, zinc chloride double salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes.

25. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 3-(gamma - pyrrolidino) - propyloxy-4-pyrrolidino-benzene diazonium chloride, hydrochloric acid zinc chloride salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes.

26. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 3-(gamma - morpholino)-propyloxy-4-morpholino-benzene diazonium chloride, hydrochloric acid zinc chloride salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes.

27. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 3-(gamma - piperidino) - propyloxy-4-piperidino - benzene diazonium chloride, hydrochloric acid zinc chloride salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes.

28. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 2-methyl - 4 - pyrrolidino-5-(beta-ethoxy)-ethoxy-benzene diazonium chloride, zinc chloride salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes.

29. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 3-(beta - ethoxy) - ethoxy-4-pyrrolidino-benzene diazonium chloride, zinc chloride double salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes

30. A light-sensitive diazotype reproduction material comprising a paper support and a light-sensitive diazotype layer coated on said support, said layer comprising 3-(beta - benzyloxy)-ethoxy-4-pyrrolidino-benzene diazonium chloride, zinc chloride double salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes.

31. A light-sensitive diazotype reproduction material comprising a paper support and light-sensitive diazotype layer coated on said support, said layer comprising 3-(beta - dipropylamino)-ethoxy-4-pyrrolidino-benzene diazonium chloride, zinc chloride salt, as light-sensitive diazonium compound, said material being suitable for one of the dry developing and semi-wet developing diazotype processes.

No references cited.

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