Patented Dec. 8, 1936

2,063,832

UNITED STATES PATENT OFFICE

2,063,832

LIGHT SENSITIVE DIAZO LAYERS

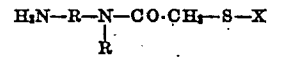
Georg Werner, Wiesbaden-Biebrich, Germany, assignor to Kalle & Co. Aktiengesellschaft, Wiesbaden-Biebrich, Germany

No Drawing. Application February 12, 1936, Serial No. 63,641. In Germany November 29, 1934

7 Claims. (Cl. 95—7)

The present invention relates to the production of light sensitive diazo layers and photographic prints therefrom.

Objects of the invention are light sensitive layers on a suitable base containing as light sentive substances diazo compounds of aromatic aminoacylamines which contain as the acid residue a thioglycol acid residue (R—S—CH_2—CO—). The aminoacylamines forming the basis of these diazo compounds preferably correspond to the following general formula:



wherein R denotes an aromatic residue that is substituted or unsubstituted aromatic nucleus, R′ denotes hydrogen, alkyl or aryl and X denotes an aromatic or aliphatic aromatic residue which may, if desired, be substituted. As aromatic nucleus preferably nucleus of the benzene series are employed.

The diazo compounds employed according to the present invention yield copies having very dark tones and possessing great permanency. Furthermore, the light sensitive layers are only very slightly sensitive to alkali and as a result of this render possible, when developed with azo components such as, for example, phloroglucine, the production of copies having deep black lines even from originals having faint lines, such as pencil drawings—which latter property is particularly valuable in practice. Moreover the said diazo compounds are of particular value for the reason that even when used in very thin layers they still give upon subsequent development dark lines exhibiting marked contrast, whilst on the other hand—and this fact is of technical importance—by the employment of thin layers the light sensitiveness is considerably increased. The diazo compounds may be applied alone or together with coupling components on or in the support. After exposure to light beneath a suitable pattern the described light sensitive layers are developed with an alkaline gas or an alkaline solution. If the light sensitive layers contain no coupling component, an azo component is added to the developing solution.

The following examples illustrate the invention:

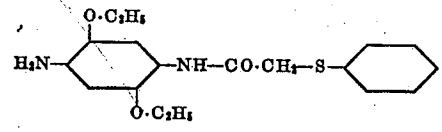
(1) A solution of

10 grammes of citric acid or another suitable acid,

10 grammes of boric acid,

15 grammes of aluminium sulphate, and

20 grammes of the hydrochloride of the diazo compound from 2.5-diethoxy-4-phenylmer-captoacetylamino-1-aminobenzene of the following formula:



in 1000 grammes of water is applied in the usual manner to a support, for example paper. With the solution the additions usual in the diazo type process, such as, for example, means for preventing subsequent yellowing of the ground or for the increase of the solubility, moistening means and also dyestuffs and so forth, may be incorporated. After drying and exposing under a pattern development is effected by the application of a thin coating of an alkaline solution of a developing substance. For example by the employment of a solution of

10 grammes of borax,

20 grammes of sodium bicarbonate,

40 grammes of sodium chloride,

2.5 grammes of phloroglucine,

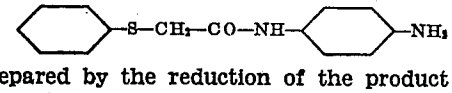
90 grammes of crystalline sodium acetate,

in 1000 grammes of water very beautiful deep black lines are obtained.

The 2.5-diethoxy-4-phenylmercaptoacetylamino-1-aminobenzene employed according to Example 1 is prepared by the nitration of the product obtained from phenylthioglycol acid chloride and aminohydroquinonediethylether (for example in glacial acetic acid with nitric acid d=1.2) and subsequent reduction, for example catalytically in an autoclave in the presence of nickel. The base thus obtained is diazotized in mineral acid solution and yields a diazo compound which can readily be isolated with the aid of sodium chloride.

(2) Instead of the diazo compound named in Example 1 the following diazo compounds may be employed:

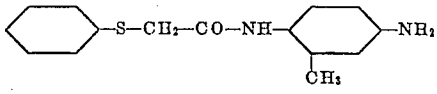
the hydrochloride of the diazo compound from 4-phenylmercaptoacetylamino-1-aminobenzene of the following formula:



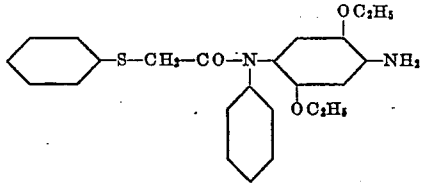
(prepared by the reduction of the product obtained from phenylthioglycol acid chloride and p-nitraniline in toluene),

the zinc chloride double salt of the diazo compound from 4-phenylmercaptoacetylamine-3-

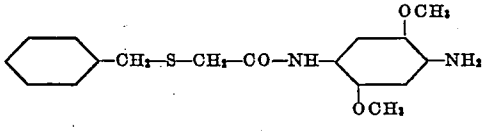
methyl-1-aminobenzene, of the following formula:



the hydrochloride of the diazo compound from 2.5-diethoxy-4-(N-phenyl-phenylmercaptoacetylamino)-1-aminobenzene of the following formula:

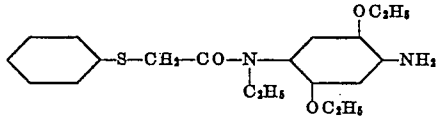


or the hydrochloride of the diazo compound of 2.5-dimethoxy-4-benzylmercaptoacetylamino-1-aminobenzene of the following formula:

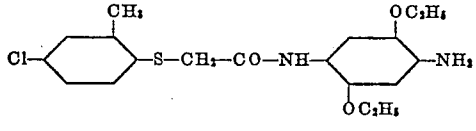


(3) If, instead of the compound named in Example 1, the diazo compounds of 2.5-diethoxy-4-(N-ethyl-phenylmercaptoacetylamino)-1-aminobenzene or 2.5-diethoxy-4-(2-methyl-4-chlorophenylmercaptoacetylamino)-1-aminobenzene are employed prints with properties equally as good as those of the prints produced according to Example 1 are obtained.

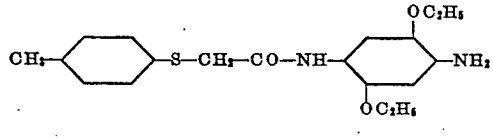
The formulas of the amino compounds, from which the named diazo compounds are obtained, are:



and

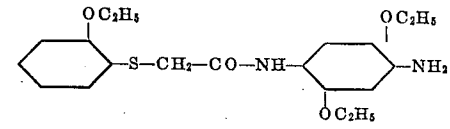


(4) A paper having the same excellent properties and precisely similar tones to those of the papers according to the previous examples is obtained by the employment of the diazo compound of 2.5-diethoxy-4-(4-methyl-phenylmercaptoacetylamino)-1-aminobenzene of the following formula:



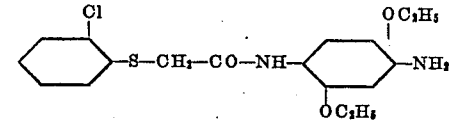
20 grammes of this diazo compound precipitated, for example, in the form of the hydrochloride together with 30 grammes of thiourea and the additions mentioned in Example 1 are dissolved in 1000 grammes of water and after application to a support and exposure development is effected as above indicated. Beautiful black lines are obtained.

(5) 30 grammes of the hydrochloride of the diazo compound of 2.5-diethoxy-4-(2-ethoxy-phenylmercaptoacetylamino)-1-aminobenzene of the following formula:



together with the additions set forth in Example 1 are dissolved in 1000 grammes of water and the solution is applied to paper. After exposure and development deep black or somewhat brownish black tones respectively are obtained, just according to whether the prints have been made from ink originals or pencil originals.

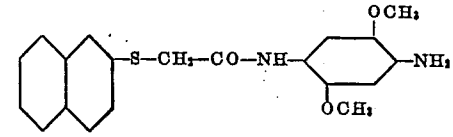
(6) If, in similar manner to that according to example 4, the diazo compound of 2.5-diethoxy-4-(2-chloro-phenylmercaptoacetylamino)-1-amino-benzene of the following formula:



is employed tones are obtained which merge more into red. To the solution prepared with 25 grammes of the diazo compound it is advantageous to add about 10% of alcohol.

(7) A solution of

10 grammes of tartaric acid,
5 grammes of boric acid,
20 grammes of aluminium sulphate and
22 grammes of the hydrochloride of the diazo compound from 2.5-dimethoxy-4-β-naphthylmercaptoacetylamino-1-aminobenzene of the formula:



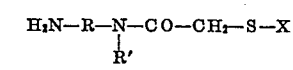
in 1000 grammes of water is applied to paper. After drying and exposing under a pattern development is effected with the following solution:

10 grammes of borax,
20 grammes of sodium bicarbonate,
40 grammes of potassium chloride,
2 grammes of phloroglucine,
0,6 grammes of arcine,
90 grammes of sodium acetate.

I claim:

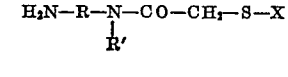
1. Light sensitive layers comprising the diazo compound of an acylamino-arylamine, said aryl being of the benzene series containing as the acid residue a thioglycol acid residue.

2. Light sensitive layers comprising the diazo compound of the compound of the following general formula:



wherein R denotes an aryl residue of the benzene series, R′ denotes a member of the group consisting of hydrogen, alkyl and aryl of the benzene series and X denotes a member of the group consisting of aryl or aralkyl of the benzene series and aryl of the naphthalene series.

3. Light sensitive layers comprising the diazo compound of a compound of the following general formula:



wherein R denotes an aryl residue of the benzene series, R' denotes a member of the group consisting of hydrogen, alkyl and aryl of the benzene series and X denotes an aryl or aralkyl residue of the benzene series.

4. Light sensitive layers comprising the diazo compound of a 4-arylmercaptoacetylamino-1-arylamine, the aryls being aryls of the benzene series.

5. Light sensitive layers comprising the diazo compound of 2.5-diethoxy-4-phenylmercaptoacetylamino-1-aminobenzene.

6. Light sensitive layers comprising the diazo compound of 2.5-diethoxy-4-(N-ethyl-phenylmercaptoacetylamino)-1-aminobenzene.

7. Light sensitive layers comprising the diazo compound of 2.5-diethoxy-4-(2-ethoxy-phenylmercaptoacetylamino)-1-aminobenzene.

GEORG WERNER.

Certificate of Correction

Patent No. 2,063,832. December 8, 1936.

GEORG WERNER

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, lines 12–14, strike out the formula and insert instead the following:

$$H_2N—R—N(R')—CO \cdot CH_2—S—X;$$

and second column, lines 16–17, for "incorported" read *incorporated*; page 2, first column, line 34, for "2-methyl" read *2'-methyl*; line 57, for "4-methyl" read *4'-methyl*; line 75, and page 3, second column, line 7, claim 7, for "2-ethoxy" read *2'-ethoxy*; page 2, second column, line 18, for "2-chloro" read *2'-chloro*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 13th day of April, A. D. 1937.

[SEAL]

HENRY VAN ARSDALE,
Acting Commissioner of Patents.