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CHEMICAL COMPOSITION

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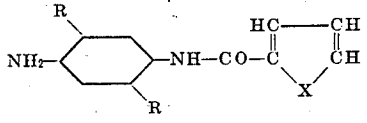
9 Claims. (Cl. 95—7)

This invention relates to the production of light-sensitive diazo-type layers and to the use of such layers in the production of photographic copies.

This invention has for an object the preparation of light-sensitive diazo-type layers containing novel and improved diazo compounds which yield coloured dyes of dark shade by coupling with a coupling component. A further object is the production of photographic elements containing diazo compounds which are stable under conditions of manufacture and storage of the element. A still further object is the preparation of diazo-type prints which do not show signs of "bleeding" of the lines of the print into the white background when the print is developed in neutral or acid solution. Still further objects will appear hereinafter.

The above and other objects are accomplished by the following invention which involves the use of diazo compounds derived from amines of the general formula:



wherein X represents an atom selected from the group consisting of oxygen, sulphur and nitrogen and R represents a radical selected from the group consisting of hydrogen and alkoxy, which diazo compounds couple with coupling components known for diazo compounds, such as phloroglucinol, to form dyes of dark colour shades.

Amines of the above general formula may contain substituents not only in the benzene nucleus but also, or alternatively, in the heterocyclic nucleus containing the radical X. Substituents in the heterocyclic nucleus are, for example, bromine atoms and phenyl groups. Examples of suitable alkoxy groups for substitution in the benzene nucleus in the 2- and 5-positions are ethoxy groups. In general, the colour of the dyestuff produced on reaction between the diazo compound and a coupling component is substantially unaffected by the nature of the substituent(s), if any, in the heterocyclic nucleus. It will, however, be understood that substituents tending substantially to lighten the shade of, or adversely to affect the properties of, the dyestuff produced should be avoided.

Particularly good results are obtained by the use in accordance with the present invention of the diazo compounds obtained from 1-amino-2,5-diethoxy-4-furoylamino benzene. Other specific examples of diazo compounds obtained from amines of the foregoing general formula are diazo compounds derived from 1-amino-2,5-diethoxy-4-thiophenoylamino benzene and from 1-amino-2,5-diethoxy-4-pyrroloylamino benzene.

The present invention includes a process for the production of diazo-type prints which comprises exposing to light behind an original (e. g., a drawing) a light-sensitive layer which contains a diazo compound derived from an amine of the general formula above set forth, and developing the exposed layer with a developing solution which contains a coupling component and which is neutral or acid in reaction. A suitable coupling component is phloroglucinol.

The new diazo compounds of the present invention may be made by methods known per se. In general, the diazo compounds of the present invention may be produced by first acylating a substituted or unsubstituted aniline with the acid chloride of the appropriate heterocyclic acid (e. g., pyromucic acid) by the normal Schotten-Baumann procedure, nitrating the resulting anilide to produce the corresponding para-nitro compound, reducing this latter compound to produce the corresponding para-amino compound, which is then diazotized in the usual way. As a specific example of this procedure, the following description is given of the production of a diazo compound of 1-amino-2,5-diethoxy-4-furoyl-amino benzene.

Furoyl chloride in slight excess of the calculated quantity is added in small portions with vigorous shaking to a flask containing a suspension of 2:5-diethoxy aniline in 5% aqueous caustic potash solution. After completion of the addition, the flask is warmed on the water bath until the smell of the furoyl chloride has disappeared (the solution to remain alkaline). When cold, the then solid product is collected, washed and crystallised from dilute alcohol, with treatment with activated charcoal. The anilide obtained melts below 60° C.

A solution of 10 g. of the anilide (furoyl-2:5-diethoxy anilide) in 75 ccs. glacial acetic acid is then cooled in ice water, without freezing the acid. 3.5 ccs. of nitric acid (specific gravity 1.42) diluted with 10 ccs. glacial acetic acid, are slowly run in with stirring and more vigorous cooling as the reaction proceeds. Yellow crystals soon appear, the liquid quickly becoming a thick sludge. After 15 minutes stirring, water is added, the material collected and crystallised from alcohol. 12 g. fibrous light yellow crystals (melting point 139–141° C.) are obtained.

11 g. of this nitro compound are then reduced by adding it to a stirred and boiling suspension of 10 g. of fine iron filings in 143 ccs. of 98–99% alcohol, 10 ccs. of water and 0.7 cc. of concentrated hydrochloric acid. Reduction is complete in 3 to 4 hours. The solution is then made just alkaline, filtered, and the insoluble materials extracted with boiling alcohol. The combined al-

coholic solutions are evaporated nearly to dryness, cooled, and the crystalline product purified by crystallisation from dilute alcohol with activated charcoal treatment. 5 g. of 1-amino-2,5-diethoxy-4-furoylamino benzene are obtained. Diazotisation of this amine is then carried out in the ordinary way, the reaction proceeding quite smoothly. The diazonium chloride readily forms an insoluble double salt with zinc chloride, this double salt being one of the preferred diazo compounds of the present invention. For preparing similar derivatives of α-carboxylic acids of thiophenes and pyrroles, analogous procedure can be used, commencing from the acid chloride.

The following non-limitative examples illustrate the use of diazo compounds according to the present invention.

Example I

14 gms. of the zinc chloride double salt of the product obtained by diazotizing 1-amino-2,5-diethoxy-4-furoylamino benzene were dissolved in 240 ccs. of water at 90°–100° C. The thoroughly cooled solution was filtered from precipitated zinc hydroxide, the following solution added:

	Grams
Potassium sulphate	8
Thiourea	11
Potassium citrate	7
Citric acid	12

in 200 ccs. of hot water and the mixture was vigorously stirred. The solution obtained (if necessary again filtered) was coated on paper, at a temperature of 18 to 20° C. and dried.

After exposure to light behind a tracing, the paper was developed with a substantially natural developing solution (pH value 7.0 to 7.5) consisting of:

Phloroglucinol	grams	2.0
Sodium thiosulphate (anhydrous)	do	30.0
Potassium citrate	do	30.0
Saponin	do	1.5
Water	ccs	400

The resultant print had dark purple lines upon a white background.

Example II

Paper sensitized as in Example I was exposed and then developed with a solution (pH value 7.0 to 7.5) consisting of:

Phloroglucinol	grams	2.0
Sodium sulphate	do	15.0
Sodium acetate	do	30.0
Saponin	do	1.5
Water	ccs	400

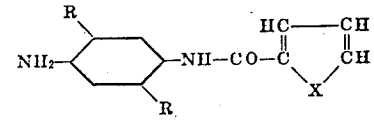
As in the case of Example I, the resultant print showed dark purple lines on a white background.

In the case of both of the foregoing examples, the dyes produced on the paper were of low solubility and did not, therefore, lead to "bleeding" of the lines of the print into the white background.

The diazo compounds of the present invention provide substantial advantages in commercial use. Not only are they quick printing and, with a neutral or acid solution of coupling component, for example, phloroglucinol, produce very dark shades (in many cases approaching black) on a white background without discoloration, but also they are stable under conditions of manufacture and storage of the paper support and, owing to their low solubility, do not give rise to "bleeding" (as indicated in the last preceding paragraph).

I claim:

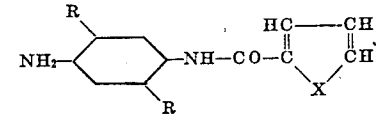
1. A light-sensitive layer for diazo-type printing which contains a diazo compound of an amine of the general formula.



in which X represents an atom selected from the group consisting of oxygen, sulphur and nitrogen and R represents a radical selected from the group consisting of hydrogen and alkoxy.

2. A light-sensitive layer of the type set forth in claim 1 wherein the radical R represents an ethoxy group.

3. A light-sensitive layer for diazo-type printing which contains a diazo compound of an amine of the general formula:



wherein X represents an atom selected from the group consisting of oxygen, sulphur and nitrogen, R represents a radical selected from the group consisting of hydrogen and alkoxy, and the heterocyclic nucleus containing the hetero atom X contains substituents in the ring.

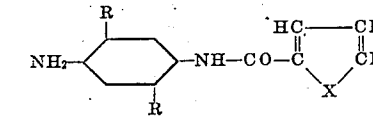
4. A light-sensitive layer of the type set forth in claim 3, wherein the nucleus containing the hetero atom X contains as substituent a radical selected from the group consisting of bromine atoms and phenyl radicals.

5. A light-sensitive layer for diazo type-printing which contains a diazo compound of 1-amino-2,5-diethoxy-4-furoylamino benzene.

6. A light-sensitive layer for diazo type printing which contains a diazo compound of 1-amino-2,5-diethoxy-4-thiophenoylamino benzene.

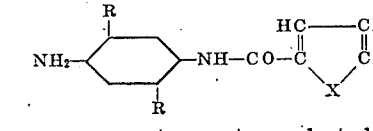
7. A light-sensitive layer for diazo type printing which contains a diazo compound of 1-amino-2,5-diethoxy-4-pyrroloylamino benzene.

8. A photographic element consisting of a support sensitised with a diazo compound of an amine of the general formula:



in which X represents an atom selected from the group consisting of oxygen, sulphur and nitrogen and R represents a radical selected from the group consisting of hydrogen and alkoxy.

9. A photographic element consisting of a support sensitised with a diazo compound of an amine of the general formula:



wherein X represents an atom selected from the group consisting of oxygen, sulphur and nitrogen, R represents a radical selected from the group consisting of hydrogen and alkoxy, and the heterocyclic nucleus containing the hetero atom X contains substituents in the ring.

HUMPHREY DESMOND MURRAY.