

UNITED STATES PATENT OFFICE

2,151,532

LIGHT-SENSITIVE LAYERS

Maximilian Paul Schmidt, Oskar Süs, and
Georg Werner, Wiesbaden-Biebrich, Germany,
assignors to Kalle & Co. Aktiengesellschaft,
Wiesbaden-Biebrich, Germany

No Drawing. Application November 6, 1936, Se-
rial No. 109,550. In Germany November 14,
1935

9 Claims. (Cl. 95—7)

The present invention relates to improved light-sensitive layers.

Only a few groups of diazo-compounds have proved suitable for use in the diazo-type process. At the present time the oxy- and aminodiazo-compounds or their substitution products are the most important. Only a few diazo-compounds of these last named groups have found practical application since the properties required of the light-sensitive layers and pictures produced therefrom have become greater. In addition to the durability and light-sensitivity of the layers containing the diazo-compounds there is still a desire for durability, insensitivity to acid and fastness to light in the finished diazo-type print. The diazo-compounds must be as strongly colored as possible so that the progress of the copying process can be easily followed. Furthermore they must lead to the production of certain tones, particularly dark brown and black shades. The several diazo-compounds at present known exhibit the various desired properties in a varying degree, so that for each purpose one or the other of the diazo-compounds is selected and in practice a large number of these diazo-compounds is used; however, this number still needs to be increased.

According to this invention, diazo compounds are employed for the production of light-sensitive layers which diazo compounds have a hydrogenated ring fused with the benzene nucleus containing the diazo group wherein the said hydrogenated ring consists of at least four carbon atoms and one tertiary amino group having its nitrogen atom in the said hydrogenated ring. For example, by using diazo compounds of hydrogenated quinolines which have a substituent attached to the nitrogen of the hydrogenated ring, highly sensitive strongly colored layers are produced which, in combination with the usual azo components, give pictures in dark lines. This is surprising, since the non-hydrogenated aminoquinolines yield diazo compounds which are unsuitable for the diazo-type process, because they are decomposable, not capable of being completely bleached and of disadvantageous shade. The diazo compounds of hydrogenated indoles and carbazoles which have a substituent attached to the nitrogen of the hydrogenated ring, for instance, alkyl or aralkyl, behave similarly to the hydrogenated diazo-quinolines.

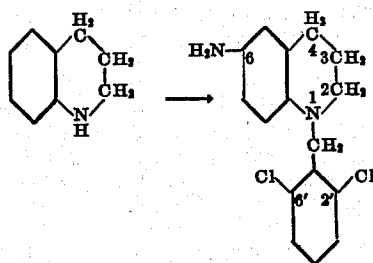
The compounds which are employed according to the invention have a substituent attached to the nitrogen of the hydrogenized ring, for instance, alkyl or aralkyl. Preferably compounds are used in which the diazo-group is in para-position to the nitrogen of the hydrogenized ring.

also contain substituents, for instance halogen, alkoxy-groups or the like. The amines which serve as parent materials for the new diazo-compounds may be made by known methods. Advantageously they are produced by coupling the hydrogenized quinoline, indole or carbazole with a diazo-compound, for example diazotized sulphanilic acid, and then reducing the dye-stuff produced. The hydrogenized amines obtained in this manner are then further diazotized by any known process.

The diazo-compound may be applied alone or together with an azo-component. There may be added to the layers and pictures metal salts, thiourea and other additions which have hitherto been used in the diazo-type process. The picture is developed in known manner by a vapor, for example ammonia or steam or by a developing solution, depending upon whether the diazo-compound exists in the layer alone or together with an azo-component, and if desired in presence of alkali or a substance of alkaline action.

The following examples illustrate the invention:

1. 35 grams of the zinc chloride double salt of the diazo-compound from 2':6'-dichloro-N-benzyl-1:2:3:4-tetrahydro-6-aminoquinoline, obtainable from tetrahydroquinoline (Ber. 16, page 728)



by reaction with dichlorobenzylchloride (boiling point of the reaction product=198° C. at 0.5-0.6 mm.), coupling the base with para-diazobenzene sulphonic acid, reducing the dyestuff to an amino-compound and diazotizing the base in the usual manner, are dissolved with addition of

	Grams
Tartaric acid.....	10
Boric acid.....	10
Thiourea.....	40
1:3:6-naphthalene-trisulphonic acid.....	40
Ammonium sulphate.....	10
Aluminium sulphate.....	15

in 1 liter of water and the solution is brushed on

paper. The prints obtained by exposing the layer are developed with a solution of

	Grams
Sodium carbonate.....	10
Trisodium phosphate.....	40
Borax.....	20
Sodium thiosulphate.....	80
Phloroglucinol, anhydrous.....	3.6
Resorcinol.....	2

in 1 liter of water.

Blue-black line prints are produced. Instead of the diazo-compound from 2':6'-dichloro-N-benzyl-6-aminotetrahydroquinoline the diazo-compound from N-benzyl-6-aminotetrahydroquinoline may be used.

2. 31 grams of the tin chloride double salt of the diazo-compound from N-benzyl-1:2:3:4-tetrahydro-3-oxy-6-aminoquinoline are dissolved in 1 liter of water and together with the additions named in Example 1 and prints obtained as usual. By developing with the developer prescribed in Example 1 black-blue lines are obtained.

Instead of the aforesaid diazo-compound the diazo-compounds from N-benzyl-1:2:3:4-tetrahydro-3-oxy-5-methyl-6-aminoquinoline, N-benzyl-1:2:3:4-tetrahydro-3-oxy-5-chloro-6-aminoquinoline, N-benzyl-1:2:3:4-tetrahydro-3-oxy-5-ethoxy-6-aminoquinoline or 2':6'-dichloro-N-benzyl-1:2:3:4-tetrahydro-3-oxy-6-aminoquinoline may be used.

According to the speed of coupling exhibited by these diazo-components it is advantageous to vary the proportion of the alkali in the developer prescribed in Example 1. In this manner deep dark tones can be obtained in every case. The diazo-compounds named in this Example may be made by coupling the corresponding 1:2:3:4-tetrahydro-3-oxyquinoline with diazotized sulphanilic acid and reducing the azo-dyestuff to the corresponding tetrahydro-3-oxy-6-aminoquinolines which may then be diazotized in the usual manner.

In cases in which coupling with diazobenzene sulphonic acid does not occur the amino-group may be introduced by way of the nitroso-compound.

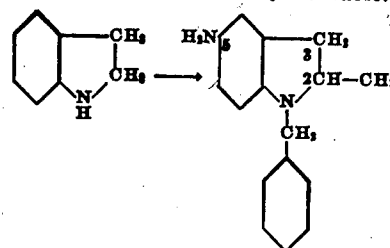
3. A solution of 31 grams of the tin chloride double salt of the diazo-compound from N-benzyl-1:2:3:4-tetrahydro-6-aminoquinoline are dissolved in 1 liter of water together with the additions named in Example 1 and the solution is applied to paper. The prints obtained on development are in deep brown lines.

The diazo-compound is made by starting with tetrahydroquinoline and converting this into the benzoyl compound; by nitrating in glacial acetic acid with nitric acid (specific gravity=1.41) there is obtained a well-crystallized nitro-body from which the amino-compound is produced by reducing with zinc dust and alcoholic hydrochloric acid. The amino-compound may be diazotized in the usual manner. Instead of the diazo-compound from N-benzoyl-tetrahydroaminoquinoline that from N-benzoyl-1:2:3:4-tetrahydro-5:8-diethoxy-6-aminoquinoline may be used. It can be made from the 1-amino-2:5-diethoxybenzene by ring condensation by the Skraup method (Ber. 14, page 1002), hydrogenating and finally nitrating the benzoylated product, reduction and diazotization.

4. 31 grams of the tin chloride double salt of the diazo-compound from N-benzyl-1:2:3:4-tetrahydro-3-oxy-6-aminoquinoline are dissolved together with the equivalent quantity of R-salt and the mixture is brushed on paper. By

development with ammonia gas deep blue-violet line prints are obtained.

5. Instead of the diazo-compound named in Example 1 there may be used in a mixture of the same composition 33.8 grams of the tin chloride double salt of the diazo-compound from 5-amino-2-methyl-N-benzyl-2:3-dihydroindole.



The print may be developed with the developer named in Example 1, whereby black-brown lines are obtained.

6. In 1 liter of water are dissolved

	Grams
Citric acid.....	10
Boric acid.....	10
Thiourea.....	40
Naphthalene-1:3:6-trisulphonic acid.....	40
Ammonium sulphate.....	20
Double salt of zinc chloride and the diazo-compound from 5-amino-2-methyl-N-2':6'-dichlorobenzyl-2:3-dihydroindole and applied to paper.....	34.2

As a developer for this paper there may be used a solution containing in 1 liter of water

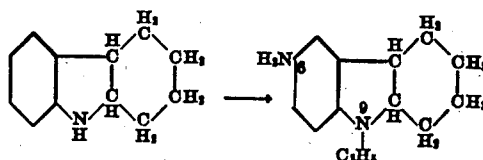
	Grams
Sodium carbonate.....	10
Trisodium phosphate.....	40
Borax.....	20
Sodium thiosulphate.....	80
Dihydro-resorcinol.....	2
Phloroglucinol, anhydrous.....	3.6

In this manner brown line prints are obtained.

7. Instead of the diazo-compound used in Example 6 34.8 grams of the tin chloride double salt of the diazo-compound from 5-amino-2:3-dimethyl-N-benzyl-2:3-dihydroindole are used; with the same developer as is prescribed in Example 1 more black-brown tones are obtained.

8. In 1 liter of water are dissolved

	Grams
Tartaric acid.....	15
Boric acid.....	5
Thiourea.....	40
1:3:6-naphthalenetrisulphonic acid.....	40
Ammonium sulphate.....	5
Sodium sulphate.....	5
Aluminium sulphate.....	15
Phloroglucinol, anhydrous.....	3.6
Orsinal.....	2.5
Chloro-tin double salt of the diazo-compound from 6-amino-9-ethylhexahydrocarbazole.....	32



The solution is brushed on a suitable support and after exposure under a pattern the print is developed with ammonia, whereby brown-black lines are obtained.

The diazo compounds of the dihydroindole se-

ries and hydrocarbazole series are obtainable from the hydroindoles or hydrocarbazoles, respectively, which can be made in the known manner by suitable reduction, (for example, with tin and hydrochloric acid) of the indoles or carbazoles, respectively. The obtained compounds are alkylated or aralkylated and then further converted, as described in Example 2.

We claim:

1. A light sensitive layer comprising as the light sensitive substance a diazo compound of a substance selected from the group consisting of tertiary hydrogenized quinolines, tertiary hydrogenized indoles and tertiary hydrogenized carbazoles.

2. A light sensitive layer comprising as light sensitive substance the diazo-compound from 2':6'-dichloro-N-benzyl-1:2:3:4-tetrahydro-6-aminoquinoline.

3. A light sensitive layer comprising as light sensitive substance the diazo-compound from N-benzyl-1:2:3:4-tetrahydro-3-oxy-6-aminoquinoline.

4. A light sensitive layer comprising as the light sensitive substance a diazo-compound which has a hydrogenated ring fused with the benzene nucleus containing the diazo-group wherein the said hydrogenated ring consists of at least four carbon atoms and one tertiary amino group having its nitrogen atom in the ring.

5. A light sensitive layer comprising as the light sensitive substance a diazo-compound which has a hydrogenated ring fused with the benzene nucleus containing the diazo-group wherein the said hydrogenated ring consists of

at least four carbon atoms and one tertiary amino group having its nitrogen atom in the ring and attached to the said benzene nucleus in para-position to the said diazo-group.

6. A light sensitive layer comprising as the light sensitive substance a diazo-compound which has a hydrogenated ring fused with the benzene nucleus containing the diazo-group wherein the said hydrogenated ring consists of at least four carbon atoms and one nitrogen atom which latter carries a benzyl residue as substituent and is attached to the said benzene nucleus in para-position to the said diazo-group.

7. A light sensitive layer comprising as the light sensitive substance a diazo-compound which has a hydrogenated ring fused with the benzene nucleus containing the diazo-group, the said hydrogenated ring consisting of at least four carbon atoms and one tertiary amino group having its nitrogen atom in the ring and attached to the said benzene nucleus in para-position to the said diazo-group wherein the said benzene nucleus carries two alkoxy groups in 5- and 8-positions as substituents.

8. A light sensitive layer, according to claim 1, wherein the diazo-group of the said diazo-compound stands in para-position to the nitrogen atom of the hydrogenated ring.

9. A light sensitive layer comprising as light sensitive substance the diazo-compound from N-benzoyl-1:2:3:4-tetrahydro-5:8-diethoxy-6-aminoquinoline.

MAXIMILIAN PAUL SCHMIDT.
OSKAR SÜS.
GEORG WERNER.