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3,563,752

DIAZOTYPE MATERIAL AND DIAZONIUM COMPOUNDS THEREFOR

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7 Claims

ABSTRACT OF THE DISCLOSURE

The use of diazonium compounds derived from uni-laterally diazotized p-phenylene diamine and substituted in the o-position to the diazo group with a trifluoromethyl group provides a diazotype material of high coupling rate and improved light sensitivity from which may be obtained azo dye images of particularly good light- and water-fastness.

BACKGROUND OF THE INVENTION

For the preparation of diazotype materials, it is known to use light-sensitive benzene diazonium compounds containing a tertiary amino group as substituent in p-position to the diazo group. Such of these compounds are suitable for being used in one-component material as are distinguished by a high coupling speed. Such compounds primarily are compounds with aralkyl or cycloalkyl radicals in the tertiary amino group but also such in which this amino group is a constituent of a certain heterocyclic ring, e.g. of a morpholino ring. The coupling speed of the latter group of diazonium compounds, however, generally has to be increased by certain further substituents in the benzene nucleus, advantageously in 3-position to the diazo group, in order to meet the requirements of use in one-component material.

Another requirement to be met by all diazotype materials is a light sensitivity as high as possible. It could be achieved to improve the coupling speed and light-sensitivity of diazonium compounds of the above type by certain combinations of substituents but the number of such compounds is still very small so that in the case of one-component material where also the number of suitable coupling components is comparatively small only a limited number of azo dyes can be produced in the copy. Particularly such dyestuffs are desirable here as are suitable for the production of intermediate originals, i.e. dyestuffs absorbing in the same wave-length range as light-sensitive diazonium compounds.

It is known from Belgium Pat. No. 676,820 that benzene diazonium compounds of the above-described type which, in m-position to the diazonium group, contain a trifluoromethyl group have a substantially higher coupling speed. The light-sensitivity of these compounds, however, is not improved by the introduction of the trifluoromethyl group in that position.

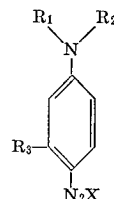
SUMMARY OF THE INVENTION

It has now been discovered that by substituting a trifluoromethyl group in the o-position rather than the m-position to the diazonium group there results new compounds having an increased light-sensitivity as well as an increased coupling speed.

The present invention provides an improved diazonium compound useful in one-component diazotype materials comprising a support and a light-sensitive layer, char-

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acterized in that the light-sensitive diazonium compound has the general formula:



wherein:

R₁ stands for a cycloalkyl or an aralkyl group with at most 10 carbon atoms,

R₂ stands for an alkyl or a hydroxyalkyl group with 1 to 3 carbon atoms or,

R₁ and R₂ together with the nitrogen atom to which they are attached stand for a 6- or 7-membered heterocyclic radical,

R₃ stands for the trifluoromethyl group, and

X stands for the anion of the diazonium compound.

The heterocyclic radicals may contain in known manner further substituents, e.g. alkyl groups. The anion of the diazonium compound may be derived from any acid suitable and usual for this purpose and, furthermore, the compound may be present in known manner as a double salt or as a complex salt, e.g. with ZnCl₂, CdCl₂, SnCl₄, HBF₄ or HPF₆.

The diazo compounds in accordance with the invention have a substantially higher light-sensitivity than the corresponding compounds non-substituted in the benzene ring and a considerably higher light-sensitivity than such diazo compounds as, instead of the CF₃ group, carry other substituents, such as alkyl, halogen or alkoxy groups. The light-sensitivity is also considerably better compared with such compounds as contain a trifluoromethyl group in m-position to the diazo group.

Furthermore, the coupling energy is markedly increased compared with such diazo compounds as carry no or another substituent in o-position to the diazo group.

Due to their high coupling speed, the new diazo compounds may be used for the semi-wet process whereas this is not the case with the corresponding compounds which are not substituted or substituted by other groups.

The dyestuffs achieved by means of the claimed diazo compounds and suitable coupling components usually employed in the wet development are very fast to light and, owing to their light absorption in the ultraviolet range, suitable for the preparation of intermediate originals. Also the white in the background of the finished copies is markedly good.

PREFERRED EMBODIMENTS

Example 1

White photoprinting base paper was coated with a solution of:

Gum arabic	G.
Tartaric acid	0.3
Sodium salt of naphthalene-1,3,6-trisulphonic acid	0.5
1-diazo-2-trifluoromethyl - 4 - piperidinobenzene (as stannic chloride double salt)	4.0
	1.7

in 100 ccm. of water and dried. After image-wise exposure to light, development was carried out by applying a solution of

Phloroglucinol	G.
Resorcin	0.6
Thiourea	0.6
Potassium tetraborate	1.5
	7.2

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Potassium hydroxide ----- 0.8
Sodium salt of isopropyl-naphthalenesulphonic acid - 0.1
in 100 ccm. of water.

Copies with dark brown lines on a white background were obtained.

The diazo compound used can easily be obtained from the reaction product of piperidine with 3-chloro-6-nitro-benzotrifluoride (melting point 63 to 64° C.) by reduction (catalytically with Ni+H₂) and diazotization in the form of a perfectly crystalline tin chloride double salt.

If, instead of the above diazo compound, an equimolar quantity of 1-diazo-4-piperidino-benzene is used, a diazo-type material is obtained which is markedly less light-sensitive, couples more slowly and, upon development, shows considerable bleeding of the dyestuffs. Diazotype material using the above diazo compound is additionally substantially more light sensitive than material using the corresponding 5-trifluoromethyl diazo compound.

Example 2

White photoprinting base paper provided with a pre-coat of polyvinyl acetate and colloidal silica was coated with a solution of

	G.
Gum arabic -----	0.3
Citric acid -----	0.5
Sodium salt of naphthalene-1,3,6-trisulphonic acid --	3.5
1-diazo-2-trifluoromethyl - 4 - (4'-acetylpiperazino)-benzene (as hexafluorophosphate) -----	1.8

in 100 ccm. of water and dried. By image-wise exposure to light and development with the developer of Example 1, copies with brown lines on a white background were obtained.

For the preparation of the diazo compound used, 21.5 g. (0.25 mol) of piperazine were dissolved in 100 ccm. of dimethyl sulphoxide, the solution was heated to 120 to 130° C., 11.3 g. (0.05 mol) of 3-chloro-6-nitro-benzotrifluoride were slowly dropwise added and the reaction mixture was then refluxed for 7 to 8 hours at 120 to 130° C. The reaction mixture was stirred into water and, upon working up, 12 g. of 1-nitro-2-trifluoromethyl-4-piperazino-benzene having a melting point of 77 to 78° C. were then obtained. For the purpose of acetylation, 12 g. of the nitro-body thus obtained were dissolved with 1 g. of anhydrous zinc chloride in 500 ccm. of acetic anhydride and heated on the water bath until the initially red colour of the solution had changed to yellow. The reaction mixture was then stirred into water and the initially oily acetyl compound was triturated with ethanol. Upon working up, 9 g. of 1-nitro-2-trifluoromethyl-4-(4'-acetyl-piperazino)-benzene having a melting point of 118 to 119° C. were then obtained.

After reduction with Raney nickel and hydrogen in the autoclave, the 1-amino - 2 - trifluoromethyl-4-(4'-acetyl-piperazino)-benzene was obtained which, after normal diazotization, led to the diazo compound as crystalline hexafluorophosphate.

It is likewise successful to employ, instead of this diazo compound, an equimolar quantity of 1-diazo-2-trifluoromethyl-4-morpholino-benzene.

Example 3

Transparentized paper was coated with a solution of

	G.
Citric acid -----	0.5
Sodium salt of naphthalene-1,3,6-trisulphonic acid --	3.5
Saponin -----	0.1
Diazo compound from 2-trifluoromethyl - 4 - (N-methyl - N - benzyl)amino-aniline (as tetrafluoroborate) -----	3.0

in 90 ccm. of water, and 10 ccm. of isopropanol and dried. After image-wise exposure to light, development was carried out with the developer solution indicated in Exam-

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ple 1. Copies with deep dark brown lines on a transparent background were obtained which were very suitable as intermediate originals for making further copies.

The diazo compound from 2-trifluoromethyl-4-(N-methyl-N-benzyl) amino-aniline was prepared as follows: 5-chloro-2-nitro-trifluoromethyl-benzene was reacted with N-methyl-N-benzyl-amine in known manner to give 5-(N-methyl-N-benzyl)-amino - 2 - nitro-trifluoromethyl-benzene (melting point 69 to 70° C.), the nitro group was then catalytically reduced (Raney nickel and hydrogen) to give the amino group which was diazotized as usual in a hydrochloric acid medium. The diazo compound was separated with 40 percent fluoboric acid in the form of tetrafluoroborate. The analytically pure compound was obtained by recrystallization from methanol/ether (intensely yellow flakes).

If, instead of the above diazo compound, 4-diazo-N-methyl-N-benzylaniline is used, a diazotype material is obtained which is about 50 percent less light-sensitive and has a poorer covering power than the material of the present invention.

Example 4

Acetyl cellulose film with 2,5-acetyl groups per glucose unit, which has been superficially saponified to a depth of about 5μ was coated with a solution of

	G.
Tartaric acid -----	0.5
Sodium salt of naphthalene-1,3,6-trisulphonic acid --	3.5
Saponin -----	0.1
Diazo compound from 2 - trifluoromethyl - 4 - (N-methyl-N-cyclohexyl)amino-aniline (as zinc chloride double salt) -----	3.2

in 90 ccm. of water, and 10 ccm. of isopropanol and dried. By exposure to light under an original and development with the developer of Example 1, a copy with deep dark brown lines was obtained on a clear transparent film, which was very suitable as intermediate original for making further copies.

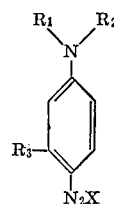
The diazo compound used is prepared as follows:

5-chloro-2-nitro-trifluoromethyl-benzene was reacted in known manner with N-methyl-N-cyclohexylamine to give 5 - (N-methyl-N-cyclohexyl)amino - 2 - nitro-trifluoromethyl-benzene (melting point 107 to 109° C.). The nitro compound thus obtained was catalytically reduced (Raney nickel and hydrogen) to give the corresponding amino compound which was diazotized in concentrated hydrochloric acid. The diazo compound was separated as tin chloride double salt, dried and digested several times with ether to obtain the yellow crystalline product.

The above examples have been presented for the purpose of illustration and should not be taken to limit the scope of the present invention. It will be apparent that the described examples are capable of many variations and modifications which are likewise to be included within the scope of the present invention as set forth in the appended claims.

What is claimed is:

1. A light-sensitive diazonium compound of the general formula:



wherein:

R₁ stands for a cyclohexyl or benzyl group, and

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R₂ stands for an alkyl or a hydroxyalkyl group with 1 to 3 carbon atoms or,

R₁ and R₂ together with the nitrogen atom to which they are attached stand for a saturated 6-membered heterocyclic radical,

R₃ stands for the trifluoromethyl group, and

X stands for the anion of the diazonium compound.

2. Diazotype material comprising a support and a coating thereon of a composition comprising a light-sensitive diazonium compound according to claim 1.

3. Diazotype material according to claim 2 wherein said diazonium compound is 1-diazo-2-trifluoromethyl-4-piperidinobenzene.

4. Diazotype material according to claim 2 wherein said diazonium compound is 1-diazo-2-trifluoromethyl-4-(4'-acetylpiperizino)-benzene.

5. Diazotype material according to claim 2 wherein said diazonium compound is 1-diazo-2-trifluoromethyl-4-morpholinobenzene.

6. Diazotype material according to claim 2 wherein said diazonium compound is 1-diazo-2-trifluoromethyl-4-(N-methyl-N-benzyl)amino-benzene.

7. Diazotype material according to claim 2 wherein said diazonium compound is 1-diazo-2-trifluoromethyl-4-(N-methyl-N-cyclohexyl)amino-benzene.

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