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PHOTOSENSITIVE MATERIAL

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6 Claims. (Cl. 95—7)

This invention relates to photosensitive materials of the type commonly designated as diazonium compounds, to the production of sheets sensitized with these materials and to reproductions made from such sensitized sheets.

It has heretofore been proposed to prepare light-sensitive sheets for the production of direct positive images by the application to suitable bases of various light-sensitive materials of many types. Of the diazonium compounds used for sensitizing, there have been used such compounds as diazo anhydrides and particularly a class of compounds in which there were substituents in an amino group para to the diazonium group. These substituted amines attached to the benzene nucleus at the position para to the diazonium group include dialkyl substituted amines, phenylamines, acylamines, and alkyl esters of carbamic acid. Many derivatives of the above classes of compounds have been prepared with a view to securing certain desirable characteristics in the reproductions through the use of the light-sensitive diazotized products of these amines. In addition to the group in the para position, the aryl nucleus that carries the diazonium group can be substituted in a variety of ways that influence the character of the compound.

The diazonium compounds heretofore used have in one or more respects been subject to limitation for use in sensitizing base sheets. Among the important and desirable characteristics of the diazonium compounds for this purpose are:

1. Ease of preparation in a reasonably pure state and free from tarry or other objectionable residues which permanently stain the base sheet.

2. Solubility in aqueous solution for purposes of application to the base sheet in sufficient quantities.

3. Stability of the compound during storage after coating.

4. Rapid decomposition of the sensitized film where exposed to light.

5. Ease of development with a suitable developing agent to produce opaque areas where the coating has been shielded from light and clear uncolored areas where exposed to light and where the sensitized coating has been decomposed. This requires a colorless decomposition product.

6. Preferably jet black or other vivid opaque color of the unexposed areas.

7. Permanence of the colored areas and permanence of the uncolored areas; that is, the decomposition products in the exposed areas should not gradually produce colored products reducing the contrast between the exposed and unexposed areas.

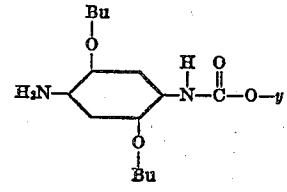
Several types of coatings have been proposed and the new compounds forming the subject matter of this invention may be used in many types of coatings. The diazonium compound may be applied to the surface of the base, usually a hard sized paper, as an aqueous solution, preferably containing a buffering agent with or without a reducing agent to improve keeping qualities. A sheet sensitized in this manner is developed after exposure by treatment with a coupling agent. Alternatively, the sensitizing solution in addition to including the diazonium compound may include the coupling component provided the solution has the proper pH concentration to prevent premature coupling; or, the two materials, diazonium compound and coupling component, may be applied to the sheet separately and under conditions preventing reaction. After exposure to light such papers are usually developed by treatment with an alkali as, for example, by subjecting the sheet to the action of ammonia gas. The first described method of applying the diazonium compound to the paper and treating the exposed paper with a coupling component is generally preferred when using the diazonium compound herein described.

It is an object of the invention to provide a novel diazonium compound which is light-sensitive, is soluble in water to form a coating solution and is stable when applied as a coating to a base.

It is another object of this invention to provide a sensitized sheet which is very light-sensitive yet can be developed to give a print with a high contrast ratio between dense black areas, sharply defined, and exposed areas not discolored by the reagents involved.

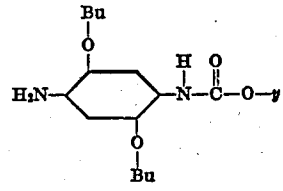
It is another object of this invention to provide a print with a high degree of stability.

A further object resides in providing a reproduction material comprising a base having a photosensitive coating which includes the diazonium compound of



wherein Bu stands for butyl and *y* stands for a lower alkyl radical.

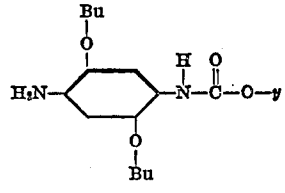
It is also an object to provide a reproduction print wherein the exposed areas are uncolored and the unexposed areas are colored by the reaction product of the diazonium compound obtained by diazotizing a compound of the following general formula:



wherein Bu stands for butyl and *y* stands for a lower alkyl radical, and a hydroxy aryl coupling compound.

It has been found that the foregoing objects can be realized and that improved results over those obtained with the diazonium compounds heretofore known and used can be attained by using as the photosensitive diazonium compound a diazonium salt of N-(4-amino-2,5-dibutoxyphenyl)-alkyl-carbamate also defined as 2,5-didutoxyaniline-4-carbamic-alkyl ester. These diazonium salts, where the alkyl derivative is a lower alkyl radical such as methyl, ethyl, propyl, etc., have sufficient water solubility to provide coating solutions with the desired requisite concentrations of the photosensitive material. The diazonium salts of the aromatic acyl amino derivatives of 2.5 dibutoxyaniline tend to have very limited water solubilities or do not give the desired color on coupling. The diazonium salts of the aliphatic acylamino derivatives of 2,5 dibutoxyaniline do not give images sufficiently dense or as black as those which may be secured with compounds of the type forming the subject matter of this invention.

The new light-sensitive diazonium salts which have been found to produce markedly improved results when applied as coatings to suitable bases are those obtained by diazotizing amines with the following structural formula:



wherein Bu represents the normal butyl radical,

$$CH_3.CH_2.CH_2.CH_2--$$

and *y* represents a lower alkyl radical.

These new compounds which are derivatives of carbamic acid can be made in the following manner illustrative of the invention. Hydroquinone is reacted with n-butyl bromide in the presence of butanol and n-sodium butylate to yield the hydroquinone dibutyl ether. This is nitrated in glacial acetic acid forming the mono-nitro compound with may be reduced in the usual manner to produce the amine. The amine is condensed in an inert solvent with ethyl-chlorocarbonate. By nitrating in glacial acetic acid there is produced N-(4-nitro-2,5-dibutoxy-phenyl)-ethyl-carbamate which is reduced in an aqueous solution of alcohol with ammonium chloride and zinc dust to yield N-(4-amino-2,5-dibutoxy-phenyl)-ethyl-carbamate, a grey solid melting at 170–175° C.

Another method of producing the same compound consists in first producing 2,5-dibutoxy-4-nitroaniline, condensing the same in an inert solvent with ethyl-chlorocarbonate, followed by a suitable reduction process to yield the amine. The N-(4-amino-2,5-dibutoxy-phenyl)-ethyl-carbamate can be advantageously diazotized by suspending the amine in dilute mineral acid and adding the requisite quantity of sodium nitrite at room temperature. Some tarry by-products are generally produced during the diazotization process, and these can be removed by filtration to leave a clear solution of the desired diazonium salt.

The following illustrative examples show the application of the invention to the preparation of light-sensitive sheets, and the use of such sheets to make reproductions:

Example I

The diazonium sulfate of N-(4-amino-2,5-dibutoxy-phenyl)-ethyl-carbamate is dissolved in a dilute solution of phosphoric acid according to the following formula:

Dry diazonium salt	g--	65
Phosphoric acid	c. c--	7
Water	liter--	1

This solution is applied uniformly over a paper surface and then allowed to dry.

The dried sheet is exposed to light under a suitable pattern such as a tracing, and is then developed by moistening the surface of the paper with the following solution:

Ammonium carbonate	g--	28
Dibasic ammonium citrate	g--	56
Phloroglucinol	g--	4
Water	liter--	1

The printed image, a positive of the tracing, is reproduced in dense black on a clear white background.

Example II

A solution is made up as follows:

Dry diazonium salt of Example I	g--	65
Citric acid	g--	30
Sucrose	g--	50
Water	liter--	1

This solution is applied to a paper surface as described in Example I and the paper is printed and then developed with the following solution:

Sodium formate	g--	150
Thiourea	g--	20
Phloroglucinol	g--	3
Water	liter--	1

The printed image is reproduced in black on a clear white background.

Example III

To one liter of an aqueous solution containing 60 g. of the diazonium chloride of N-(4-amino-2,5-dibutoxy-phenyl)-ethyl-carbamate are added the following materials:

Citric acid	g--	30
Thiourea	g--	30

This solution is applied to a paper surface as

described in Example I, and the paper is printed and then developed with the following solution:

Sodium formate	g.	150
Thiourea	g.	20
Phloroglucinol	g.	3
Resorcinol	g.	3
Water	liter	1

The printed image is reproduced in black on a clear white background.

Example IV

Paper coated, dried, and printed as described in Example I is developed with the following solution:

Potassium citrate	g.	200
B naphthol	g.	0.4
Resorcinol	g.	5
Water	liter	1

A vivid red-brown image on a white background is produced.

Example V

The diazonium sulfate of N-(4-amino-2,5-dibutoxy-phenyl)-methyl-carbamate is applied to paper, dried, printed, and developed according to the formulas of Example I. A black image on a white background is produced.

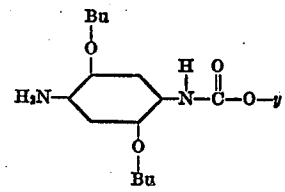
Example VI

The diazonium chloride of N-(4-amino-2,5-dibutoxy-phenyl)-propyl-carbamate is applied to paper, dried, printed, and developed according to the formulas of Example I. A black image on a white background is produced.

It will thus be seen that this invention provides certain new diazonium compounds, derivatives of carbamic acid, forming photosensitive coatings on paper—preferably high in rag content or all rag and hard sized—which may be developed after exposure with mono-, di- or trihydroxy aryl coupling components to form vivid dense positive images with stable backgrounds.

We claim:

1. The light-sensitive photographic element comprising a diazonium compound obtained by diazotizing a compound of the following general formula:

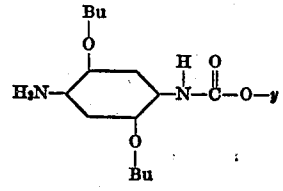


wherein Bu stands for butyl and *y* stands for a lower alkyl radical.

2. The light-sensitive photographic element comprising a diazonium compound obtained by diazotizing N-(4-amino-2,5-dibutoxy-phenyl)-ethyl-carbamate.

3. The light-sensitive photographic element comprising a diazonium compound obtained by diazotizing N-(4-amino-2,5-dibutoxy-phenyl)-methyl-carbamate.

4. A reproduction material comprising a base having a photosensitive coating which includes the diazonium compound of



wherein Bu stands for butyl and *y* stands for a lower alkyl radical.

5. A reproduction material comprising a base having a photosensitive coating which includes the diazonium compound of N-(4-amino-2,5-dibutoxy-phenyl)-ethyl-carbamate.

6. A reproduction material comprising a base having a photosensitive coating which includes the diazonium compound of N-(4-amino-2,5-dibutoxy-phenyl)-methyl-carbamate.

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