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DIAZOTYPE LAYERS CONTAINING RESORCINOL MONOESTERS

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8 Claims. (Cl. 95—6)

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This invention relates to a diazotype process and more particularly to the use of certain azo components in the light-sensitive layer or as developers for the diazotype image.

In the reproduction of mechanical drawings, printed material, pictures or other originals to be copied, it is of particular advantage in many cases to first make an intermediate print or transition print on a transparent diazotype copying material by exposing the transparent, sensitized diazotype material to actinic rays by either the printing-through or reflex process and then developing the diazotype material. The image thus produced on the intermediate or transition diazotype print can then be used for the reproduction of further diazotype prints of high contrast. This method is particularly useful when it is desired to make a number of reproductions from a frail or valuable original which would be adversely affected, if not destroyed, in the repeated exposures necessary to make the desired number of copies. The efficiency of the process involving the production of a transition or intermediate print depends upon the opacity of the azo dye image produced upon such intermediate or transition print to ultraviolet light and upon the transparency of the background. It depends also upon the visual density of the image produced on the intermediate or transition print, since images of poor visual density, such as yellow on a white or transparent background which may have the desired degree of opacity to ultraviolet light, nevertheless have the disadvantage of rendering difficult the detection of flaws in the intermediate image and it is often necessary to make a contrasty print from the intermediate before such flaws can be detected.

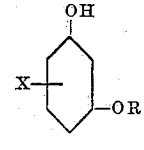
Prints of a deep color having good visual density can be obtained from diazotypes using such azo components as phloroglucin, but despite the density of the color reproducing the image, its actinic opacity or photographic density is not sufficient to reproduce the image satisfactorily in subsequent diazotype copies. The azo dye component used for the production of such images on prints which are to be used as intermediate or transition copies must be such as to produce, upon coupling with the diazo compound employed, a yellow to brown azo dye which will sufficiently absorb ultraviolet light to prevent light decomposition of the diazo compound in the areas to be reproduced from the intermediate or transition copies.

Azo components, such as resorcinol, have heretofore been employed in diazotype transition print light-sensitive layers for the production of color images having the desired light absorption characteristics for transition printing. While resorcinol will produce the image on the transition print in azo dye colors having good opacity to

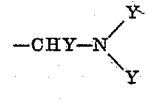
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ultraviolet light and having sufficient visual density to assure detection of printing flaws, the precoupling stability of the diazotype layer is not sufficient to assure prolonged storage before use. It has been found that the carriers, such as transparentized paper or film, having thereon a light-sensitive layer composed of the usual diazo compounds and resorcinol gradually develop a discoloration prior to use, which discoloration is produced by premature coupling of the resorcinol and diazo. This discoloration will, of course, be retained by the transition print and will impair the ability of the background areas to transmit actinic light. Consequently, the light-sensitive diazo compounds in the diazotype media employed for copying from the transition print will not be efficiently decomposed in the background areas. This same discoloration, therefore, will be reproduced in the final copies, diminishing the contrast between the background and the image.

It has now been found that a new class of azo coupling components not heretofore used in diazotype reproduction media may be employed in a light-sensitive layer with a suitable diazo compound on a carrier, such as transparentized paper or film, which will reproduce the image in a sepia color of high actinic opacity and good visual density, while at the same time providing a two-component diazotype light-sensitive layer which has a high degree of stability against precoupling. This class of coupling components may be described as resorcinol monoesters and can be represented by the following general formula:



wherein R is an acyl radical including aliphatic carbacyl radicals such as formyl, acetyl, propionyl, butyryl, carbamyl and aminocarbamyl radicals; aromatic carbacyl radicals such as benzoyl, naphthoyl, toluyl, and salicylyl radicals; aliphatic sulfonyl radicals such as methyl sulfonyl, ethyl sulfonyl, propyl sulfonyl and butyl sulfonyl radicals; and aromatic sulfonyl radicals such as benzsulfonyl and naphthsulfonyl radicals; and wherein X indicates that the nucleus may be substituted further by any of the usual substituents excepting those which would adversely affect the coupling capacity, such as NO_2, NH_2 and SO_3H. Suitable substituents include alkyl, halogen, hydroxyalkyl, aryl, alkaryl, aralkyl, cycloalkyl, alkoxy, carboxy and the radical



wherein the Y's, which may be the same or different, are selected from the group consisting of hydrogen, alkyl, hydroxyalkyl, aryl, alkaryl, aralkyl or cycloalkyl. Examples of resorcinol esters of this class are: resorcinol monoacetate, resorcinol monocarbazate (amino-carbamate), resorcinol mono-N(β-aminoethyl) carbamate, resorcinol mono-N,N-diethyl carbamate, resorcinol monoethylcarbonate, benzene-sulfonic acid monoester of 2-diethylaminomethyl resorcinol, orcinol monoacetate, 4-chlororesorcinol monoacetate, 4-methoxyresorcinol monoacetate, β-resorcylic acid monoacetate, and diethylaminomethyl-resorcinol monoacetate.

In the preparation of diazotype two-component layers intended for use as intermediate or transition print media in accordance with this invention, a suitable transparent base, such as transparentized paper, cellulose acetate film or other transparent material, is coated by means known to the art with a light-sensitive composition containing suitable diazo compounds and the new coupling components in combination with such other materials as are ordinarily used in the preparation of diazotype two-component light-sensitive coating compositions. As diazo compounds, we prefer to use those which are derived from p-diamines of the benzene series, particularly those in which one of the amino groups is substituted by such groups as alkyl, alkoxyalkyl, aryl, aralkyl, alkylol, cycloaliphatic and heterocyclic groups. However, other diazo compounds have been found suitable, such as the diazo anhydrides of amino-hydroxynaphthalene compounds. Examples of amines from which such diazo compounds are derived include N-hydroxy ethyl-N-methylamino p-amino benzene, p-amino diphenylamine, 1-monoethylamino-2-(or 3-)methyl-4-amino benzene, 1-N - hydroxyethyl - N - ethylamino-3-methyl - 4-amino benzene, 1-diethylamino-3-ethoxy-4-amino benzene, 4-amino-1-benzoylamino-2.5-diethoxy benzene, p-amino-N-diethylaniline, 1-N,N-dihydroxy - ethylamino - 3 - chloro-4-amino benzene, p-amino-N-ethyl-N-benzylaniline, p-amino-N-dimethylaniline, 1-ethylamino - 4 - aminobenzene, 1-hydroxyethyl-ethyl-amino - 4 - amino benzene, p-phenylene diamine, 4-amino-N,N-dihydroxyalkylaniline and 4'-ethoxyphenyl-2.5-diethoxyaniline. The diazo compounds are used in the form of their stabilized salts, such as the $ZnCl_2$, $CdCl_2$ or $SnCl_4$ double salts, fluorborates, aryl or alkyl sulfonates and acid sulfates of the diazonium compound.

The following specific examples will serve to further illustrate this invention, it being understood, however, that they are not intended to limit its scope. Unless otherwise stated, the parts are by weight:

Example 1

Transparentized paper is coated with a coating solution containing the following materials per 100 cc. of water:

Resorcinol monoacetate	grams	3.5
N-methyl-N-hydroxyethyl aniline - p - diazo $ZnCl_2$ double salt	grams	4.3
Citric acid	do	8
Phosphoric acid	cc	1
Thiourea	grams	4
Isopropanol	cc	5

The coated transparency is first dried in the usual manner; it is then submitted to accelerating tests and is also stored for a prolonged period under average storage conditions of temperature and moisture. Under both these tests, the coatings proved to be more stable to precoupling than in the case of similar coatings made with resorcinol as the coupling component. Upon exposure to light under an original pattern and development by contact with ammonia fumes in the usual manner, the coated transparency reproduces the image of the original pattern in a deep rich brown color. The azo dye image areas have excellent opacity to ultra-violet light and upon subsequent exposure and development of an ordinary diazotype reproduction medium using the print of this example as an original, excellent reproductions may be obtained in any desired color having clear backgrounds unimpaired by any discoloration due to faulty light decomposition of the diazo in the second diazotype layer. The intermediate images produced from the formula of this example are also fast to light and wetting.

Example 2

Transparentized paper is coated with a coating solution containing the following materials per 100 cc. of water:

Resorcinol monoacetate	grams	3.0
N-ethylamino-o-toluidine-p-diazo $ZnCl_2$ double salt	grams	3.5
Citric acid	do	8
Phosphoric acid	cc	1
Thiourea	grams	4
Isopropanol	cc	5

The coated transparency is first dried in the usual manner; it is then submitted to accelerating tests and is also stored for a prolonged period under average storage conditions of temperature and moisture. Under both these tests, the coatings proved to be more stable to precoupling than in the case of similar coatings made with resorcinol as the coupling component. Upon exposure to light under an original pattern and development by contact with ammonia fumes in the usual manner, the coated transparency reproduces the image of the original pattern in a deep rich brown color. The azo dye image areas have excellent opacity to ultra-violet light and upon subsequent exposure and development of an ordinary diazotype reproduction medium using the print of this example as an original, excellent reproductions may be obtained in any desired color having clear backgrounds unimpaired by any discoloration due to faulty light decomposition of the diazo in the second diazotype layer. The intermediate images produced from the formula of this example are also fast to light and wetting.

Example 3

Transparentized paper is coated with a coating solution containing the following materials per 100 cc. of water:

Resorcinol monoacetate	grams	3.5
N,N-diethylaniline p-diazo $ZnCl_2$ double salt	grams	4.5
Citric acid	do	8
Phosphoric acid	cc	1
Thiourea	grams	4
Isopropanol	cc	5

The coated transparency is first dried in the usual manner; it is then submitted to accelerating tests and is also stored for a prolonged period under average storage conditions of temperature and moisture. Under both these tests, the coatings proved to be more stable to precoupling than in the case of similar coatings made with resorcinol as the coupling component. Upon exposure to light under an original pattern and development by contact with ammonia fumes in the usual

manner, the coated transparency reproduces the image of the original pattern in a deep rich brown color. The azo dye image areas have excellent opacity to ultraviolet light and upon subsequent exposure and development of an ordinary diazotype reproduction medium using the print of this example as an original, excellent reproductions may be obtained in any desired color having clear backgrounds unimpaired by any discoloration due to faulty light decomposition of the diazo in the second diazotype layer. The intermediate images produced from the formula of this example are also fast to light and wetting.

Upon substitution of 3.8 grams of N-phenylaniline p-diazonium acid sulfate for the diazo salt of this example, light-sensitive coatings which will reproduce the image in the same deep rich brown color having the same properties as the images produced from the formula of this example may be obtained.

Example 4

Transparentized paper is coated with a coating solution containing the following materials per 100 cc. of water:

Resorcinol monocarbazate	grams	4
N-ethylaniline p-diazo $CdCl_2$ double salt	grams	3.6
Citric acid	do	8
Phosphoric acid	cc	1
Thiourea	grams	4
Isopropanol	cc	5

The coated transparency thus produced is first dried in the usual manner. It is then submitted to accelerated aging tests and is stored for prolonged period under average storage conditions of temperature and humidity. Both of these tests proved that the coatings obtained from the formula of this example are more stable to precoupling than similar coatings made with resorcinol as the coupling component. Upon exposing the coatings of this example to light under an original pattern and developing the image by contact with ammonia fumes, the pattern is reproduced in a dark sepia color on a clear white background. The azo dye image areas have excellent opacity to ultraviolet light and also very good fastness to light and wetting. Upon subsequent exposure and development of an ordinary diazotype reproduction medium under these dark sepia reproduced images as originals, further copies or reproductions may be produced in any desired color, which images will be of sharp contrast against clear backgrounds which have no discoloration due to incomplete decomposition of the diazo in the final copy.

Example 5

Transparentized paper is coated with a coating solution containing the following materials per 100 cc. of water:

Resorcinol mono-N(β-aminoethyl) carbamate	grams	4.3
N-methylaniline p-diazo $CdCl_2$ double salt	grams	3.5
Citric acid	do	8
Phosphoric acid	cc	1
Thiourea	grams	4
Isopropanol	cc	5

The coated transparency thus produced is first dried in the usual manner. It is then submitted to accelerated aging tests and is stored for a prolonged period under average storage conditions of temperature and humidity. Both of these tests proved that the coatings obtained from the formula of this example are more stable to precoupling than similar coatings made with resorcinol as the coupling component. Upon exposing the coatings of this example to light under an original pattern and developing the image by contact with ammonia fumes, the pattern is reproduced in a dark sepia color on a clear white background. The azo dye image areas have excellent opacity to ultraviolet light and also very good fastness to light and wetting. Upon subsequent exposure and development of an ordinary diazotype reproduction medium under these dark sepia reproduced images as originals, further copies or reproductions may be produced in any desired color, which images will be of sharp contrast against clear backgrounds which have no discoloration due to incomplete decomposition of the diazo in the final copy.

Example 6

Transparentized paper is coated with a coating solution containing the following materials per 100 cc. of water:

Resorcinol mono-N,N-diethyl carbamate	grams	4.3
N-hydroxyethylaniline p-diazo $ZnCl_2$ double salt	grams	3.6
Citric acid	do	8
Phosphoric acid	cc	1
Thiourea	grams	4
Isopropanol	cc	10

The coated transparency thus produced is first dried in the usual manner. It is then submitted to accelerated aging tests and is stored for a prolonged period under average storage conditions of temperature and humidity. Both of these tests proved that the coatings obtained from the formula of this example are more stable to precoupling than similar coatings made with resorcinol as the coupling component. Upon exposing the coatings of this example to light under an original pattern and developing the image by contact with ammonia fumes, the pattern is reproduced in a sepia color on a clear white background. The azo dye image areas have excellent opacity to ultraviolet light and also very good fastness to light and wetting. Upon subsequent exposure and development of an ordinary diazotype reproduction medium under these sepia reproduced images as originals, further copies or reproductions may be produced in any desired color, which images will be of sharp contrast against clear backgrounds which have no discoloration due to incomplete decomposition of the diazo in the final copy.

Example 7

Transparentized paper is coated with a coating solution containing the following materials per 100 cc. of water:

Resorcinol monoethyl carbonate	grams	4
N-propylaniline p-diazo $ZnCl_2$ double salt	grams	3.8
Citric acid	do	8
Phosphoric acid	cc	1
Thiourea	grams	4
Isopropanol	cc	10

The coated transparency thus produced is first dried in the usual manner. It is then submitted to accelerated aging tests and is stored for a prolonged period under average storage conditions of temperature and humidity. Both of these tests

proved that the coatings obtained from the formula of this example are more stable to precoupling than similar coatings made with resorcinol as the coupling component. Upon exposing the coatings of this example to light under an original pattern and developing the image by contact with ammonia fumes, the pattern is reproduced in a dark sepia color on a clear white background. The azo dye image areas have excellent opacity to ultraviolet light and also very good fastness to light and wetting. Upon subsequent exposure and development of an ordinary diazotype reproduction medium under these dark sepia reproduced images as originals, further copies or reproductions may be produced in any desired color, which images will be of sharp contrast against clear backgrounds which have no discoloration due to incomplete decomposition of the diazo in the final copy.

Example 8

Transparentized paper is coated with a coating solution containing the following materials per 100 cc. of water:

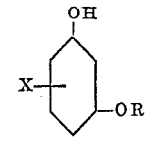
2 - diethylaminomethylresorcinol monobenzene sulfonate	grams	4.0
2.5.4'-triethoxy diphenyl-1-diazonium acid sulfate	grams	3.6
Citric acid	do	8.0
Phosphoric acid	cc	1.0
Thiourea	grams	4.0
Isopropanol	cc	5.0

The coated transparency is first dried in the usual manner. It is then submitted to accelerated aging tests and is also stored for a prolonged period under average storage conditions of temperature and moisture. Under both of these tests the coatings proved to be more stable to precoupling than in the case of similar coatings made with resorcinol as the coupling component. Upon exposure to light under an original pattern and development by contact with ammonia fumes in the usual manner, the coated transparency reproduces the image of the pattern in a dark sepia azo dye color on a clear background. The azo dye image areas have excellent opacity to ultraviolet light and upon subsequent exposure and development of an ordinary diazotype reproduction medium, using the print of the example as an original, excellent reproductions may be obtained in any desired color having clear backgrounds unimpaired by any discoloration due to faulty light-decomposition of the diazo in the second diazotype layer. The intermediate or transition print images produced from the formula of this example are also fast to light and wetting.

The resorcinol mono(β-aminoethyl) carbamate of Example 5 may be prepared by treating resorcinol with phosgene according to Einhorn's method (Ann. 300, 138 and 152) to form polymeric resorcinol carbonate, followed by heat treatment with excess ethylenediamine to give resorcinol mono(β-aminoethyl) carbamate which is purified by treating with activated carbon in the presence of an acid.

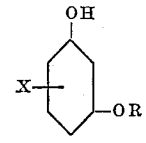
We claim:

1. As new products, light-sensitive layers on a suitable base containing a suitable light-sensitive diazo compound and an azo coupling component selected from the class represented by the formula



wherein R is an acyl radical and X is a member of the class consisting of hydrogen and substituents which do not adversely affect coupling capacity.

2. As new products, light-sensitive layers on a suitable base comprising a diazo compound derived from a p-diamino compound of the benzene series and an azo coupling component selected from the class represented by the following formula



wherein R is an acyl radical and X is a member of the class consisting of hydrogen and substituents which do not adversely affect coupling capacity.

3. As a new product, a light-sensitive layer on a suitable base comprising a diazo derivative of a p-diamino compound of the benzene series and resorcinol monoacetate.

4. As a new product, a light-sensitive layer on a suitable base comprising a diazo derivative of a p-diamino compound of the benzene series and resorcinol monocarbazate.

5. As a new product, a light-sensitive layer on a suitable base comprising a diazo derivative of a p-diamino compound of the benzene series and resorcinol mono-N-(β-aminoethyl) - carbamate.

6. As a new product, a light-sensitive layer on a suitable base comprising as the diazo compound N - methyl - N - hydroxyethyl aniline p - diazo $ZnCl_2$ double salt and as the coupling component resorcinol monoacetate.

7. As a new product, a light-sensitive layer on a suitable base comprising as the diazo compound N-ethylaniline-p-diazo $CdCl_2$ double salt and as the coupling component resorcinol monocarbazate.

8. As a new product, a light-sensitive layer on a suitable base comprising as the diazo compound N-methylaniline-p-diazo $CdCl_2$ double salt and as the coupling component resorcinol mono-N-(β-aminoethyl)-carbamate.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,246,425	Poser	June 17, 1941
2,359,862	Linch	Oct. 10, 1944