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DIAZOTYPE LAYERS CONTAINING DIAZOS OF N-(2-HYDROXYPROPYL)-PHENYLENE-DIAMINES

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5 Claims. (Cl. 95—6)

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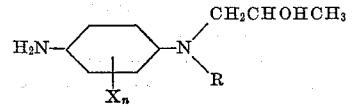
This invention relates to diazotype photoprinting materials and more particularly to diazotype materials wherein the light sensitive agent is a diazonium compound derived from a p-phenylenediamine compound having the following formula



wherein R is a member of the group consisting of hydrogen, alkyl, oxyalkyl, aryl, cyloalkyl, aralkyl and alkaryl; X is a member of the group consisting of hydrogen, halogen, alkyl and alkoxy, and n is an integer not greater than 4.

In the duplication of originals which are transparent or semi-transparent, such as tracings, engineering drawings, typewritten documents or photographic transparencies by the diazotype positive reproduction method, it is highly desirable that the image reproduced on the diazotype be one of high contrast. In order to produce such images of high contrast, it is necessary to select the dye components from a limited class of known light sensitive diazo compounds and azo components which will couple to produce deep shades upon development of the image. Many of the azo dye components which will reproduce the image in deep tones, such as blue, black, maroon, sepia and brown, and are otherwise suitable for diazotype reproduction have a relatively fast coupling rate. Such coupling components as 2,3-dihydroxynaphthalene, acetoacetanilide, resorcinol and phloroglucinol, which are commonly used in the production of these shades, have fast coupling rates when coupled with suitable diazo compounds. When they are applied to a diazotype light sensitive layer in combination with the diazo compound, this fast coupling property of the azo components tends to increase the precoupling tendencies of the composition and, accordingly, reduces the shelf life of the light sensitive diazotype layer. Consequently, unless such diazotypes are used shortly after their manufacture, they will exhibit, as a result of precoupling instability, a background color which not only detracts from the appearance of the reproduction, but reduces the contrast between the developed image and the background.

Background color in diazotype images also may be produced by insufficient sensitivity of the diazo compound to the action of actinic light. A diazo compound which may be stable against precoupling in a diazotype composition containing a fast coupling azo component may nevertheless produce background color if it does not decompose or burn out readily upon exposure to light. An increase in the printing time will, of course, overcome this disability, but increases in printing time add to the cost of operation and also reduce the sharpness of the image due to the decomposition of diazo in the areas of the image adjacent the exposed areas.

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In the duplication of some originals, such as valuable documents or tracings which would not stand the wear of successive exposure necessary to the reproduction of a number of copies, it is often desirable to make an intermediate diazotype transparency which can be used as a substitute original in the production of further diazotype copies. This expediency of producing an intermediate diazotype transparency becomes a necessity where the original to be reproduced is opaque to light and the diazotype copy must be made by the reflex copying process where the diazotype reproduction medium is exposed to both transmitted and reflected light. For efficient reproduction of further copies from such a diazotype intermediate, it is essential that the reproduced image be such that it will have a high opacity to actinic light, such as ultraviolet. The more common coupling components, such as the resorcinol mentioned above, which will produce a sepia image with diazo compounds otherwise suitable for diazotype materials generally have poor precoupling stability. Such precoupling instability is a decided disadvantage in the production of diazotype intermediate transparency since the background color resulting from precoupling of the dye components will absorb light in the background areas where the transparency should transmit all of the light incident upon it. In addition, the contrast of the intermediate transparency itself will be considerably reduced by the presence of such background color, rendering it more difficult to detect flaws in the intermediate reproduction.

We have now found that diazo compounds prepared from the above class of p-phenylenediamines are stable under all ordinary conditions, but decompose readily and completely on exposure to actinic light, such as ultraviolet light. The diazo compounds of this class couple with azo coupling components in the presence of alkali to form fast azo dyes. They are stable against precoupling for long periods of time when used in diazotype compositions containing fast coupling azo components and are therefore eminently suitable for use as light sensitive components in diazotype layers. Upon exposure of a diazotype layer containing a diazo compound of this class under a pattern and upon subsequent alka-

line treatment in the presence of suitable azo coupling components, images are obtained which have good visual appearance, that is, the images are sharp and have an intense bright shade against a white background. The prints obtained by the exposure and development of such diazotypes exhibit good wash and light fastness. When the diazo compounds of this class are used in diazotype layers intended for the production of intermediate prints in combination with azo coupling components which will couple with the diazo compound to give sepia colors, the images obtainable are very opaque to ultraviolet light and do not blur or offset when the print is used as a mask.

The amines from which the diazo compounds of this class are prepared may be produced by treating one mol of aryl amine with one mol of propylene oxide together with a catalytic amount of hydrochloric acid in an autoclave at a temperature of 75 to 80° C. for nine hours followed by vacuum distillation. In the preparation of di-N-(2-hydroxypropyl) aryl amines, two mols of the propylene oxide are used per mol of aryl amine. The diazo compounds are prepared from the N-(2-hydroxypropyl)-aryl amines in the usual manner by nitrosation, reduction with zinc-hydrochloric acid, diazotization and conversion to the corresponding stabilized compound, such as the zinc chloride, cadmium chloride, tin chloride or boron fluoride double salts.

The diazo compounds may be applied to any suitable support, such as paper, cloth or film, such as film prepared from cellulose ethers and esters (cellulose ethyl ether and cellulose acetate), regenerated cellulose, superpolymers and polymerization products. As coupling components any compound which will function as a coupling component and which will produce the desired shade when coupled with a diazo compound of this class may be employed either in the coating composition together with the diazo compound as a two-component system or in the developing solution as a color-forming developer for a one-component or wet development diazotype. Examples of preferred coupling components are the sodium salt of 2-amino-8-naphthol-3,6-disulfonic acid, 2,3-dihydroxynaphthalene or its 6-sulfonic acid derivative, β-naphthol-3,6-disulfonic acid, 2,7-dihydroxynaphthalene, 1,7-aminonaphthol, 2-hydroxynaphthalene-8-biguanide, 1-amino-8-naphthol-3,6-disulfonic acid, 1-naphthol-4-sulfonic acid, 1-naphthol-3,8-disulfonic acid, phloroglucinol, m-hydroxyphenyl urea, acetoacetanilide, 7-hydroxy-1,2-naphthimidazole, cyclohexyl acetoacetamide, resorcinol, 4,6-dichlororesorcinol, 3-hydroxyphenyl biguanide, 4-chlororesorcinol and 2,8-dihydroxynaphthalene-6-sulfonic acid.

In producing a diazotype light sensitive layer from coating solutions containing the diazo compounds of this invention as the light sensitive agents, the base or support material is dipped, brushed or sprayed with the sensitizing or coating solution by means known to the art, the particular type of application depending upon the carrier employed. Where paper is used as the base for the light sensitive coating, the coating solution is generally applied by using a trough and doctor blade, the paper being drawn past the trough and excess solution being scraped off with the doctor blade. The paper also may be brushed or sprayed with the coating solution. When a film material is used as the support, in order to obtain proper penetration of the active agents, solvents or swelling agents are added to the coating solution and the solution is generally applied by dipping. In addition to the diazo compound, azo component and impregnating or swelling solvents, the coating solution also may contain dissolved metal salts designed to intensify the dyestuff images, such as aluminum sulfate, titanium ammonium fluoride, nickel sulfate and the like, stabilizing agents such as thiourea, thiosinamine, naphthalene trisulfonic acid and the like, acids to effect complete solubility of the solid components and assist in retarding precoupling tendencies such as citric acid, tartaric acid and boric acid and hygroscopic agents such as glycol, dextrin and the like.

Although this invention is described with particular reference to the so-called dry development process, that is, development of a diazotype layer containing both the diazo and azo component in a two-component diazotype coating, by contacting the exposed diazotype with ammonia vapor or vapors of other volatile alkaline materials, nevertheless the invention is also applicable to the so-called moist development process. In accordance with this latter process, the solution applied to the support contains as the only dye component the diazo compound of the class set forth above. It may contain other adjuncts, such as those mentioned above, for particular purposes. In this process the coated support is exposed and the diazo decomposed in the exposed areas in the same manner as in the case of the two-component system, but the unexposed areas are developed by contacting the exposed diazotype with a solution of alkaline agents containing the coupling component.

The following examples will serve to further illustrate the preparation of diazotype photographic printing materials from the diazo compounds of this invention, it being understood that the invention is not limited to the particular materials or proportions therein described. Unless otherwise specified, the parts are by weight.

Example 1

Transparentized paper stock is coated with a solution containing per 100 parts of water:

2.8 parts N-(2-hydroxypropyl) amino-p-benzene diazonium chloride-$ZnCl_2$ double salt
1.6 parts resorcinol
8.0 parts citric acid
4.0 parts thiourea

The coated transparency has excellent precoupling stability and when exposed to ultraviolet light under a positive original and developed with gaseous ammonia gives a bright orange sepia colored positive reproduction on a clear white background. Its visual appearance and wash fastness are excellent and when said reproduction is used as an intermediate or transition print to produce further copies on ordinary diazotype reproduction materials, it will yield excellent reproductions in any desired color.

Example 2

Transparentized paper stock is coated with a solution containing the following materials per 100 parts of water:

2.8 parts N-(2-hydroxypropyl) amino-p-benzene diazonium chloride-$ZnCl_2$ double salt
2.7 parts of 4,6-dichlororesorcinol
8.0 parts citric acid
4.0 parts thiourea

The coated transparency thus obtained is very stable against precoupling and can be stored for more than nine months under average conditions of natural storage without impairing its efficiency. Upon exposure of the coated and dried material to ultraviolet light under a positive original and development with gaseous ammonia, an image is obtained in a reddish sepia color on a clear white background. Its visual appearance and wash fastness properties are excellent and the print may be used as a transition print for the reproduction of further diazotype copies in view of the high degree of opacity to ultraviolet light which the reproduced image possesses.

Example 3

Transparentized paper stock is coated with a solution containing the following materials per 100 parts of water:

3.3 parts di-N-(2-hydroxypropyl) amino-p-benzene diazonium chloride-$ZnCl_2$ double salt
1.6 parts resorcinol
8.0 parts citric acid
4.0 parts thiourea

The thus coated transparency has the same properties as the coatings obtained in accordance with Examples 1 and 2, except that the color of the image obtained from the coating of this example is a dark brownish sepia.

Example 4

Diazotype paper stock is coated with a solution containing the following materials per 100 parts of water:

1.9 parts N - (2 - hydroxypropyl) - N - methyl amino-p-benzene diazonium chloride-$ZnCl_2$ double salt
1.8 parts 2,3-dihydroxynaphthalene-6-sulfonic acid
8.0 parts citric acid
4.0 parts thiourea
2.0 parts $ZnCl_2$

The thus coated paper upon being dried and stored for long periods of time is found to have excellent precoupling stability. When exposed to ultraviolet light under a positive original and developed with gaseous ammonia, the image is reproduced in a dark blue dye positive reproduction on a clear white background.

Example 5

Diazotype paper stock is coated with a solution containing the following materials per 100 parts of water:

2.1 parts N-(2-hydroxypropyl)-N-ethyl amino-p-benzene diazonium chloride-$CdCl_2$ double salt
1.8 parts 2,3-dihydroxynaphthalene-6-sulfonic acid
8.0 parts citric acid
4.0 parts thiourea
2.0 parts $ZnCl_2$

The diazotype material obtained from this coating solution has the same properties as that obtained in accordance with Example 4 with the exception that the color of the reproduced image is an intense bright blue.

Example 6

Transparentized paper stock is coated with a solution containing the following materials per 100 parts of water:

2.4 parts N-(hydroxyethyl) - N - (2 - hydroxypropyl) amino-p-benzene diazonium chloride-$ZnCl_2$ double salt
2.5 parts 3-hydroxyphenyl biguanide
8.0 parts citric acid
4.0 parts thiourea

The thus coated transparency has good precoupling stability and when exposed to ultraviolet light under a positive original and developed with gaseous ammonia gives a light sepia positive reproduction of the original on a clear white background. This image is sharp and has good wash fastness properties. It also has good opacity to ultraviolet light and may be used as a transition original for the further reproduction of diazotype copies in any desired color.

Example 7

Transparentized paper stock is coated with a solution containing the following materials per 100 parts of water:

3.3 parts 1 - (N - ethyl - N - (2 - hydroxypropyl) amino) -3-methyl-4-benzene diazonium chloride-$ZnCl_2$ double salt
1.6 parts resorcinol
8.0 parts citric acid
4.0 parts thiourea

The thus coated diazotype has similar properties to the diazotype obtained in accordance with Example 6.

Example 8

Transparentized paper stock is coated with a solution containing the following materials per 100 parts of water:

3.7 parts N-(2-hydroxypropyl)-N-phenylamino-p-benzene diazonium chloride-$ZnCl_2$ double salt
2.2 parts 4-chlororesorcinol
8.0 parts citric acid
4.0 parts thiourea
5.0 parts isopropanol

The diazotype coating of this example has similar properties to the diazotype obtained in accordance with Example 6.

Example 9

Diazotype paper stock is coated with a solution containing the following materials per 100 parts of water:

1.8 parts 2,8-dihydroxynaphthalene-6-sulfonic acid
2.8 parts 3-chloro-N-(2-hydroxypropyl) aniline-p-diazonium chloride-$ZnCl_2$ double salt
8.0 parts citric acid
4.0 parts thiourea

The thus coated diazotype paper has excellent precoupling stability and its efficiency as a reproduction medium is not impaired by long periods of storage under average temperature and humidity conditions of natural storage. Upon exposing the diazotype of this coating to ultraviolet light under a positive original and developing with gaseous ammonia, a sharp image of the original is obtained in a dark blue color on a white background.

Upon substituting 2.5 parts of N-(2-hydroxypropyl)-m-toluidine-p-diazonium chloride-$ZnCl_2$

double salt for the diazo salt of this example, a coated paper is obtained having similar properties. Likewise, upon substituting 3.0 parts of N - (2-hydroxypropyl) -m-phenetidine-p-diazonium chloride-$ZnCl_2$ double salt for the diazo salt of this example, coatings having similar properties are obtained.

Example 10

Diazotype paper stock is coated with a solution containing the following materials per 100 parts of water:

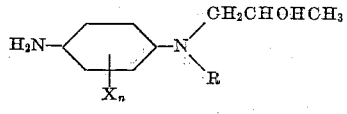
1.8 parts 2,8-dihydroxynaphthalene-6-sulfonic acid
2.8 parts N-(2-hydroxypropyl) -N-cyclohexyl-aniline-p-diazonium chloride-$ZnCl_2$ double salt
5.0 parts isopropanol
8.0 parts citric acid
4.0 parts thiourea

The thus coated diazotype paper when dried exhibits excellent precoupling stability and its efficiency as a reproduction medium is not impaired by long periods of storage under average temperature and humidity conditions maintained in storage. Upon exposing the diazotype of this coating to actinic light, such as ultraviolet rays or rays in the near ultraviolet region, under a positive original and developing with gaseous ammonia, a sharp image of the original is obtained in a dark blue color on a clear white background.

Upon substituting 2.7 parts N-(2-hydroxypropyl) - N - benzyl aniline-p-diazonium chloride-$ZnCl_2$ double salt for the diazo salt of this example, a diazotype reproduction paper is obtained having properties similar to those of the coating of this example.

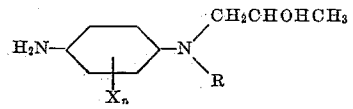
We claim:

1. An alkaline developable diazotype photographic material comprising a light sensitive diazonium compound of a p-phenylenediamine having the formula



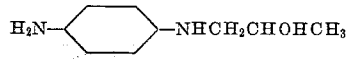
wherein R is a member of the group consisting of hydrogen, alkyl, oxyalkyl, aryl, cycloalkyl, aralkyl and alkaryl; X is a member of the group consisting of hydrogen, halogen, alkyl and alkoxy, and n is an integer not greater than 4.

2. An alkaline developable diazotype photographic material comprising a light sensitive diazonium compound of a p-phenylenediamine having the formula



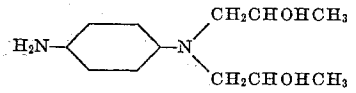
wherein R is a member of the group consisting of hydrogen, alkyl, oxyalkyl, aryl, cycloalkyl, aralkyl and alkaryl; X is a member of the group consisting of hydrogen, halogen, alkyl and alkoxy, and n is an integer not greater than 4, and an azo dye coupling component.

3. An alkaline developable diazotype photographic material comprising a light sensitive diazonium compound of the compound having the formula



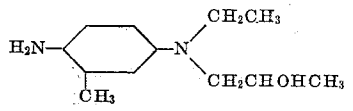
and an azo dye coupling component.

4. An alkaline developable diazotype photographic material comprising a light sensitive diazonium compound of the compound having the formula



and an azo dye coupling component.

5. An alkaline developable diazotype photographic material comprising a light sensitive diazonium compound of the compound having the formula



and an azo dye coupling component.

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REFERENCES CITED

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

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Number	Name	Date
2,217,189	Sus	Oct. 8, 1940