

UNITED STATES PATENT OFFICE

2,528,460

DIAZOTYPE COMPOSITIONS CONTAINING
ETHYLENE OXIDE DERIVATIVES OF
AMINO DIAZOS

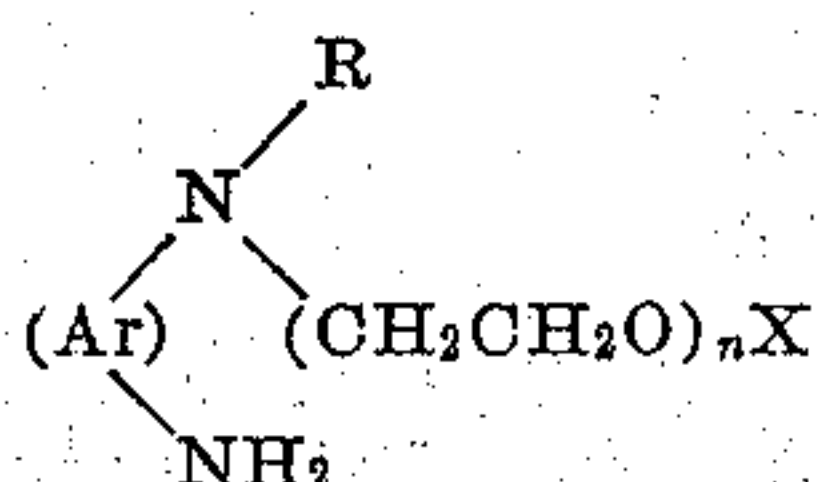
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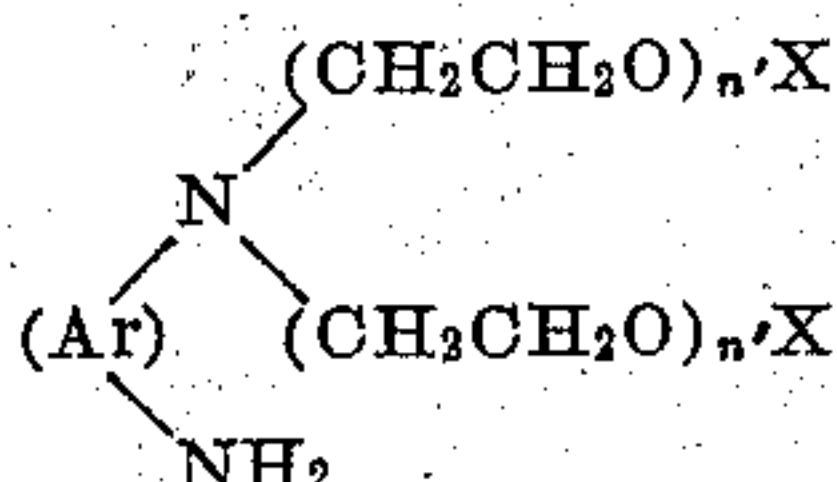
4 Claims. (Cl. 95—6)

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This invention relates to the production of diazotype light-sensitive layers or other diazotype materials and more particularly to diazotype materials wherein the light-sensitive agent is a diazo derivative of an aromatic ortho or para diamine having one of the following formulas:



and



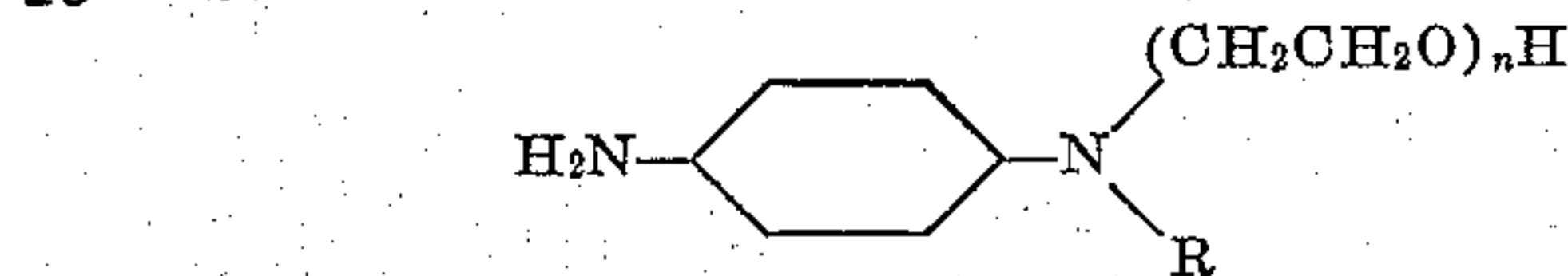
wherein n is any integer greater than 1 and n' is any integer; R is a member of the group consisting of alkyl, hydroxyalkyl, alkoxyalkyl, aryl, aralkyl and acyl; X is a member of the group consisting of hydrogen, aliphatic, aromatic, heterocyclic and acyl such as acetyl, benzoyl and furoyl and Ar is an aromatic radical containing no alkyl substituents of greater than 3 carbon atoms content. The aromatic nuclei may be otherwise substituted by such common substituents as halogen, C_1 to C_3 alkyl, alkoxy, hydroxyalkyl, carboxy, carboalkoxy and sulfo groups.

It has been found that diazo compounds of this class when developed with one of the azo components generally employed for diazotype work, either by the dry development process wherein the azo component and diazo compound are both contained in the light-sensitive layer or by the wet development process where only the diazo compound is contained in the light-sensitive layer and the azo component is applied as part of an alkaline developing solution, reproductions can be obtained having images of bright dark tones on a clear white background wherein the images are washfast and possess great permanency. These diazos also possess good stability when used in a two-component system together with the azo component for the dry developing diazotype process and are particularly characterized by their excellent printing speed in either a two-component or one-component system. When used in conjunction with the proper azo components such as resorcinol and resorcinol derivatives, these diazos will reproduce the image in the sepia shade which has excellent photographic density or opacity to ultraviolet light. Accordingly, when used in such a combination the diazos of this class are eminently suited for transition printing where a transparent or semi-transparent intermediate diazotype print is made

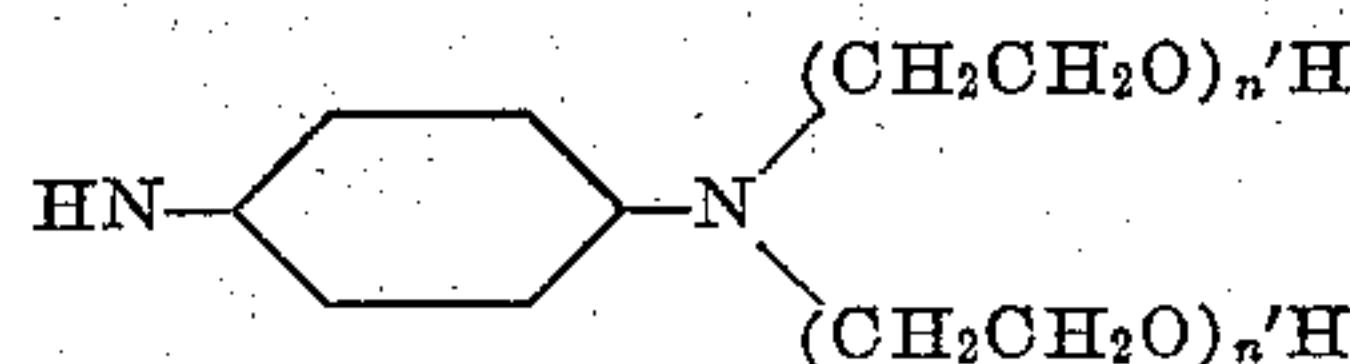
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for the purpose of using such intermediate print as an original in making further copies.

Although this invention embraces all diazo derivatives of the aromatic ortho and para diamines of the foregoing class, a preferred group of such diazos which is particularly suitable for two-component diazotype compositions comprises the diazo compounds derived from substituted p-phenylene diamines having the following formulas:



15 and



wherein the variables n , n' and R have the same values as above and wherein the phenylene nucleus may be further substituted as indicated above but when substituted by alkyl, such alkyl substituent should not contain more than three carbon atoms. The invention will be particularly described with reference to this preferred class of diazo derivatives but it is understood that such description is exemplary of the class of ortho and para aromatic diamines wherein the phenylene nucleus of this preferred class may be substituted by naphthalene, anthracene or other aromatic nuclei, wherein the diazotized amino group and the substituted amino group may bear either an ortho or para relationship to each other on the aromatic nucleus and wherein the terminal hydroxy group and the polyethylene oxide members of the substituted amino group may be substituted as indicated in the general formula.

In producing the diazotype materials from coating solutions containing the diazo compounds of this invention as the light-sensitive agents, the base or support carrying or containing the light-sensitive compounds, the azo components and other coating materials is coated, dipped, brushed or sprayed with the sensitizing solution by means well known to the art, the particular type of application depending upon the carrier employed. As carriers, such materials as paper or cloth which may be opaque, semi-transparent or of a transparent type; film such as prepared from cellulose nitrate, cellulose acetate or other cellulose esters or regenerated cellulose; glass plates or sheet metal may be employed. Where paper is used as the base or support for the light-sensitive coating, the coating solution is generally applied by using a trough and doctor blade but may, if desired, be brushed on or sprayed. When a film is used as a support, swelling agents should be

added to the coating solution in order to obtain proper penetration and the solution is generally applied by a dipping method. In addition to the diazo compound, azo component and such swelling agents as may be added, the coating solution may contain the usual adjuvants such as metal salts designed to intensify the dye images, aluminum sulfate, titanium ammonium fluoride, nickel sulfate and the like for increasing water proofing qualities; stabilizing agents such as thiourea, thio-sinamine, naphthalene trisulfonic acid and the like; acids designed to retard precoupling such as citric acid, tartaric acid, boric acid and the like; and hygroscopic agents such as glycol, glycerine, dextrin and the like. As coupling components we may use any azo coupling component known to be suitable for diazotype light-sensitive layers. As suitable azo components, there may be mentioned 2,3-dihydroxy naphthalene and its sulfonic acid derivatives, phloroglucin, naphthalene guanidines such as 7-hydroxy naphthalene-1-guanidine and 5-hydroxy naphthalene-1-biguanidine; acetoacetic acid amides such as acetoacetic acid cyclohexyl amide, acetoacetic acid benzylamide and acetoacetic acid- α -amino pyridine; substituted naphthols such as 1-methyl- ω -dimethylamino-2-hydroxy naphthalene, 2,6 dimethyl-8-hydroxy naphthalene and its reaction product with formaldehyde dimethylamine; hydroxynaphtho-imidazoles such as 7'-hydroxy naphtho-1',2':4,5 imidazole and 2-carboxyethyl-7'-hydroxynaphtho-1',2':4,5-imidazole; phenol and phenol derivatives, cresols, resorcinol and resorcinol derivatives such as 4-chlororesorcinol and dichlororesorcinol and resorcinol esters and ethers. Some of these azo components, notably those of the resorcinol family which will produce sepia images, have a fast coupling rate. This tends to impair the precoupling stability of a two-component system containing such an azo component. Since it is desirable to use these azo components which will produce sepia shades in the production of diazotype transparencies, precoupling instability is a decided disadvantage as precoupling instability will produce background color in the transparency, which background color will absorb actinic light in areas where the transparencies should transmit the light. This disadvantage is overcome when using the diazos of this invention since the diazos of the aromatic ortho and para diamines having the polyethylene oxide substitutions on the undiazotized amino group have a high degree of resistance to precoupling even in combinations containing azo components having a fast coupling rate.

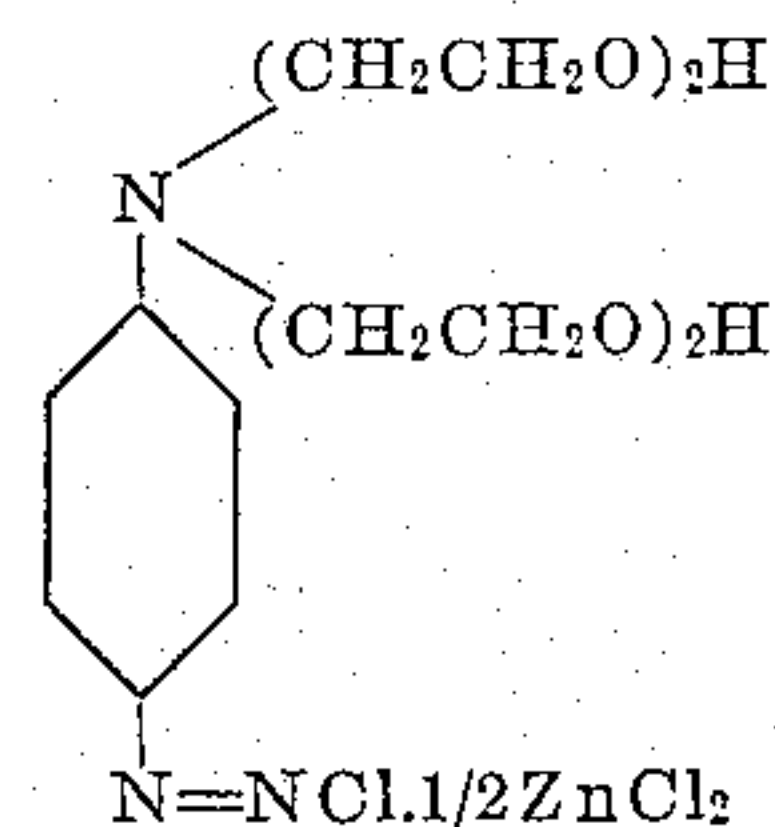
The diazo compounds may be applied to the support either from a solution containing the diazo compound as the only dye component or from a solution containing both the diazo compound and the azo component. Where the coating solution contains no azo component, precoupling stability is, of course, no problem. However, such factors as printing speed and ability to produce images having good wash fastness, good photographic resolution and shades of good photographic density as well as visual density are just as important in evaluating the efficiency of such a single component process as they are in the case of the two-component process where the azo component is also contained in the coating solution. In the single component process, the azo component is added to the developing solution which is applied by a contact or fog spray method to the exposed diazotype layer in order to produce the dye image.

The following examples will serve to illustrate further the preparation of diazotype photoprinting materials from the diazo compounds of our 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

Paper is coated in the usual manner with a solution containing per 100 cc. of water:

2.5 g. N,N-di(hydroxyethoxyethyl) aniline
p-diazo ZnCl₂ double salt



1.7 g. 2,3 dihydroxynaphthalene-6-sulfonic acid

8.0 g. citric acid

4.0 g. thiourea

The thus coated paper is dried and exposed to light under a pattern and the print developed by drawing the exposed diazotype coated paper through ammonia fumes. The developed image of the pattern is a bright blue on a clear white background. When submitted to accelerated aging tests or stored for a period of time under average conditions of temperature and humidity, the coated paper exhibits good storage stability. Its printing speed during exposure is excellent.

Example 2

A paper support is coated in the usual manner with a solution containing per 100 cc. of water:

2.5 g. N,N-di(hydroxyethoxyethyl) aniline
p-diazo ZnCl₂ double salt

1.1 g. 2,3 dihydroxynaphthalene

8.0 g. citric acid

4.0 g. thiourea

After exposing this coating which has been dried under a pattern the image is developed by drawing through ammonia fumes to a bright blue on a clear white background. The printing speed during exposure is excellent and the coated paper has very good storage stability when tested either under average storage conditions over a period of time or by accelerated aging tests.

Example 3

Transparentized paper is coated in the usual manner with a solution containing per 100 cc. of water:

5.0 g. N,N-di(hydroxyethoxyethyl) aniline
p-diazo ZnCl₂ double salt

2.5 g. resorcinol

8.0 g. citric acid

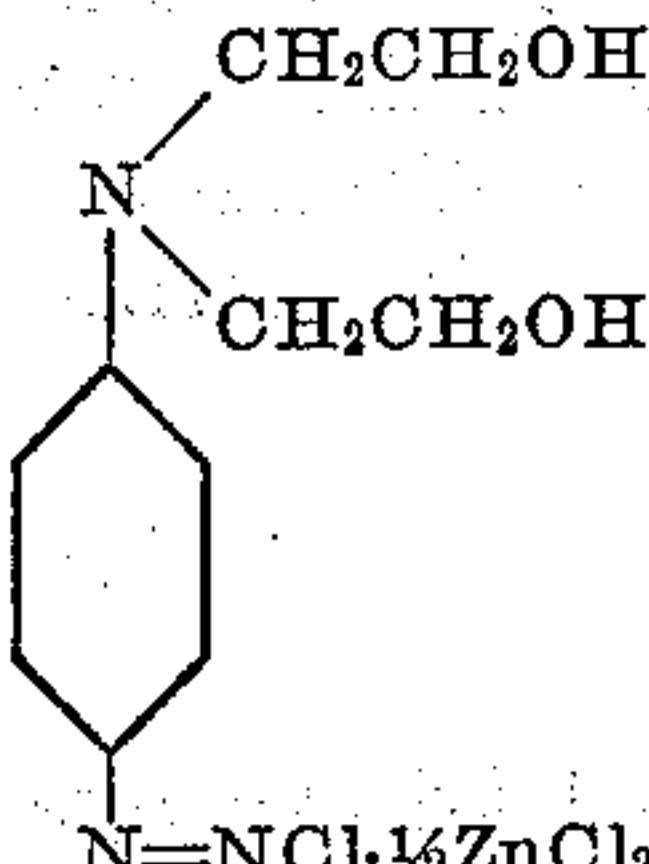
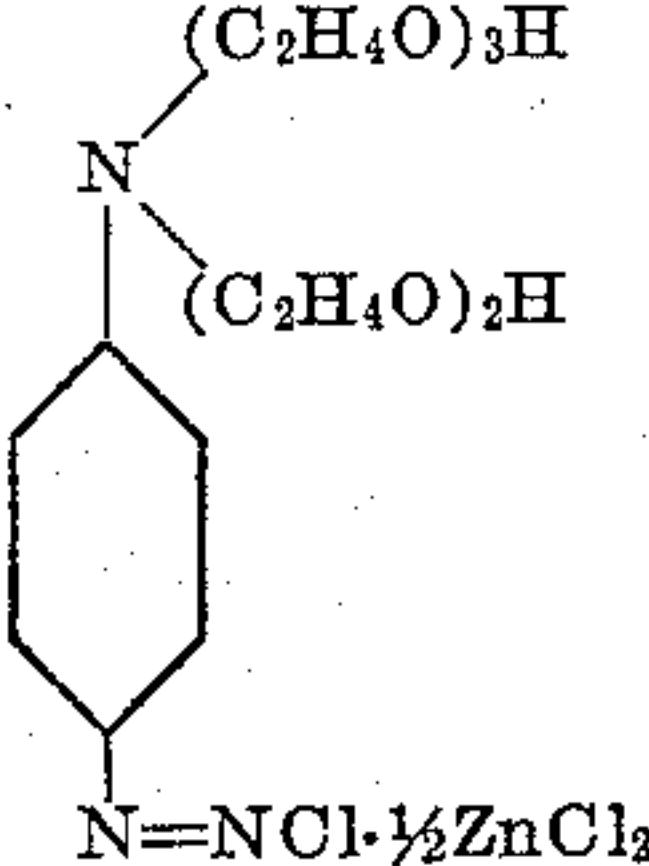
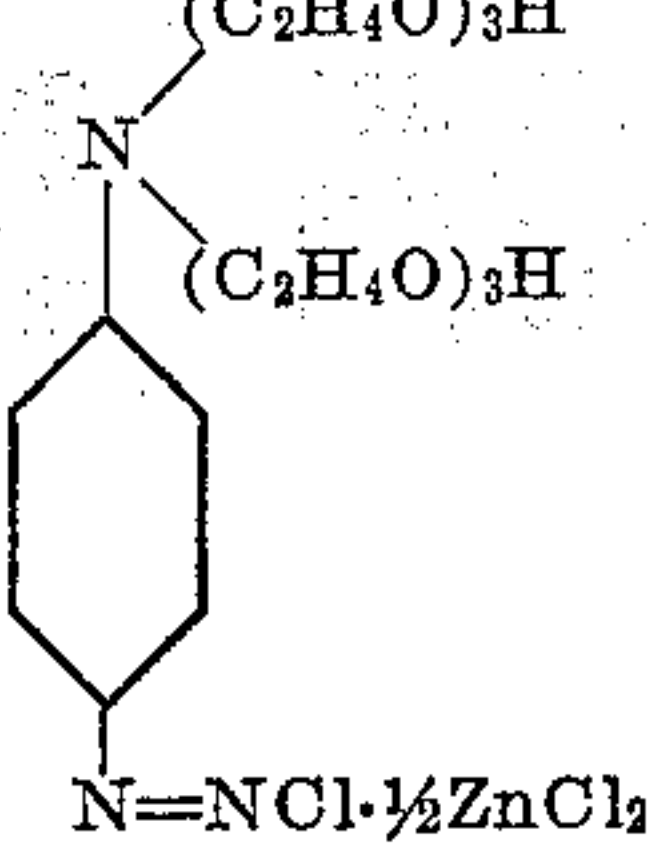
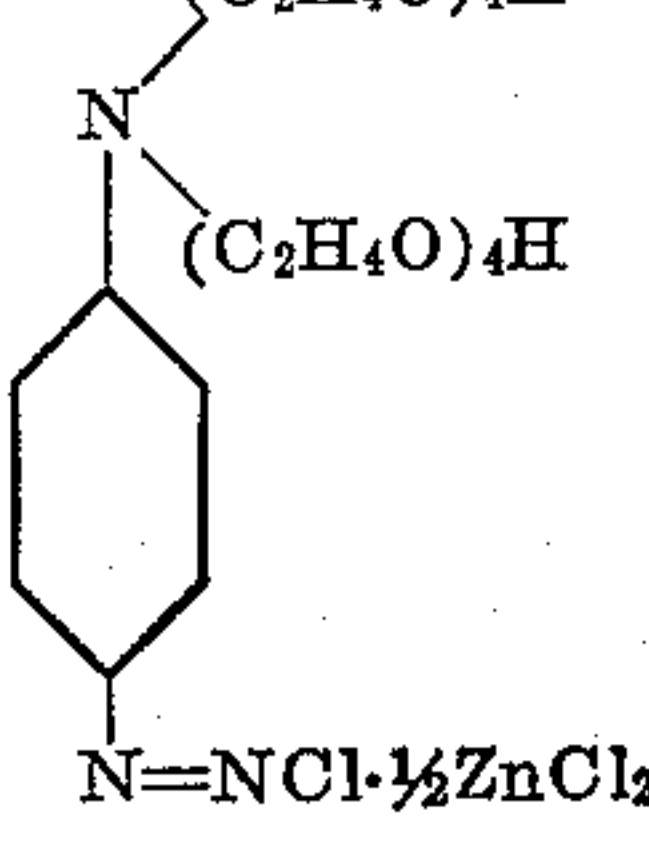
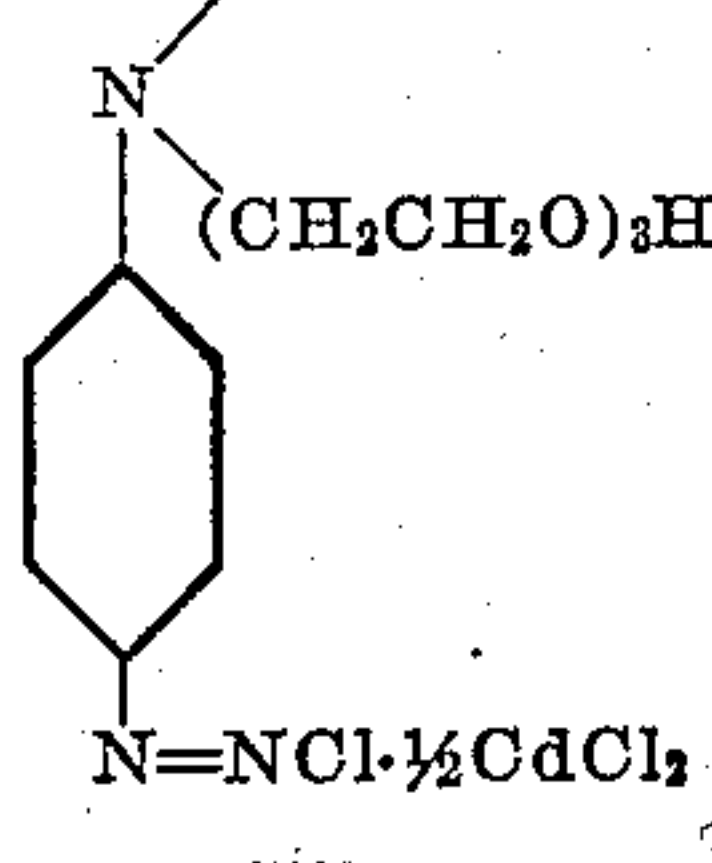
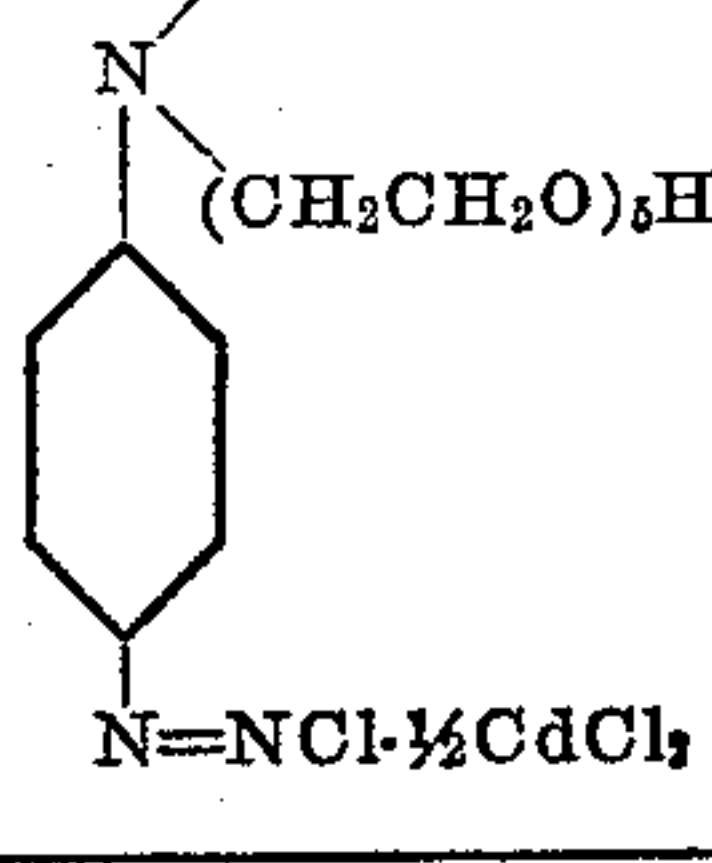
4.0 g. thiourea

After drying the thus coated transparentized paper, it is exposed to light under a pattern and the image developed by drawing it through ammonia fumes. The resulting image of the original pattern is in a sepia shade on a clear transparent background. This sepia image has good photographic density as well as visual density and thus is eminently suited for use as an intermediate transparency in the production of further copies. The coated transparentized

paper prior to exposure and development has good storage stability thus eliminating any background color in the transparency or the final copy due to premature coupling of the dye components during storage.

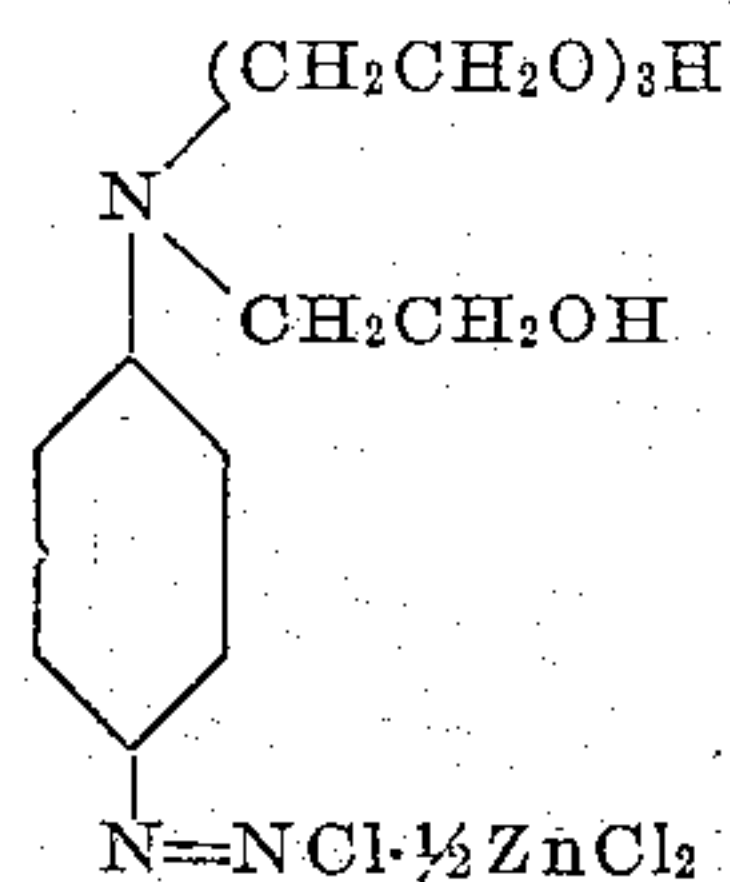
The diazo compound employed in these examples may be prepared by the autoclave reaction of 2 mols of ethylene oxide at 90° C. on 1 mol of N,N-dihydroxyethyl aniline or the reaction of 4 mols of ethylene oxide upon 1 mol of aniline. The resulting base is nitrosated or nitrated in the usual manner. The nitroso or nitro group is then reduced by zinc dust and HCl and the thus obtained amine is diazotized in the usual manner to give the zinc chloride double salt.

The diazo compound employed in Examples 1, 2 and 3 may be replaced by the following diazo compounds of the class contemplated by this invention with similar results. Thus by substituting any one of the following diazos for the N,N - di(hydroxyethoxyethyl) aniline - p - diazo ZnCl₂ double salt of Examples 1 and 2, bright blue images on a white background may be obtained from a coating which has good printing speed and good storage stability and by making the same substitutions in Example 3, sepia colored images having good opacity to ultraviolet light or good photographic density in the dye areas may be obtained from coatings which have good printing speed and good storage stability.

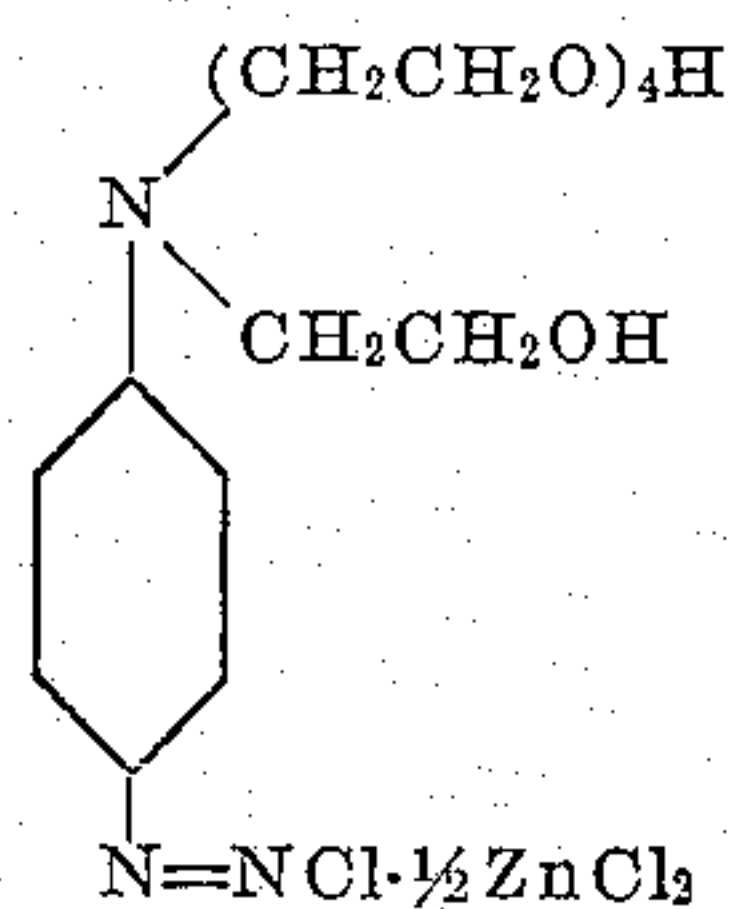
Diazo Compound	Probable Formula	Preparation
N,N-di-hydroxyethyl aniline-p-diazo ZnCl ₂ double salt.		Prepared by autoclave reaction of 2 mols of ethylene oxide at 90° C with 1 mol of aniline followed by nitrosation or nitration, reduction of the nitroso or nitro group and diazotization of the amino group.
N-(hydroxydiethoxyethyl) - N - (hydroxyethoxyethyl) aniline - p - diazo ZnCl ₂ double salt.		Prepared by similar reaction of 3 mols of ethylene oxide on 1 mol of N-dihydroxyethyl aniline followed by nitrosation or nitration, reduction of the nitroso or nitro group and diazotization of the amino group.
N,N-di(hydroxydiethoxyethyl) aniline - p - diazo ZnCl ₂ double salt.		Prepared by similar reaction of 4 mols of ethylene oxide on 1 mol of N-dihydroxyethyl aniline followed by nitrosation or nitration, reduction of the nitroso or nitro group and diazotization of the amino group.
N,N-di(hydroxytriethoxyethyl) aniline - p - diazo ZnCl ₂ double salt.		Prepared by similar reaction of 6 mols of ethylene oxide on 1 mol of N,N-dihydroxyethyl aniline followed by nitrosation or nitration, reduction of the nitroso or nitro group and diazotization of the amino group.
N-methyl, N-(hydroxy diethoxyethyl) aniline - p - diazo CdCl ₂ double salt.		Prepared by similar reaction of 3 mols of ethylene oxide on 1 mol of N-methyl aniline followed by nitrosation or nitration, reduction of the nitroso or nitro group and diazotization of the amino group.
N-methyl-N-(hydroxy tetraethoxyethyl) aniline - p - diazo CdCl ₂ double salt.		Prepared by similar reaction of 5 mols of ethylene oxide on 1 mol of N-methylaniline followed by nitrosation or nitration, reduction of the nitroso or nitro group and diazotization of the amino group.

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The formulas given for these diazos are the most probable ones. However, it is possible that the ethylene oxide enters the molecule in different ratios than indicated in the formulas thus forming isomers. For example, the formula for the diazo compound of Example 1 could be:



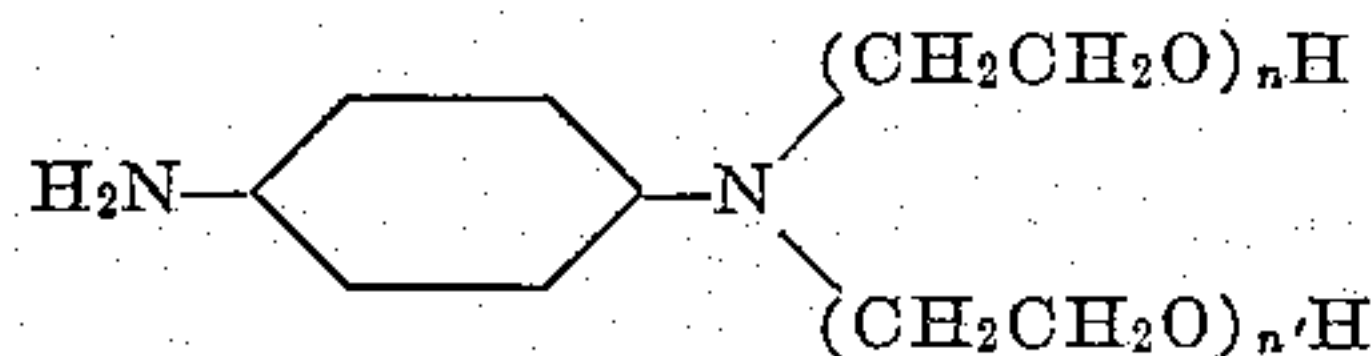
and that of the second diazo compound in the table could be:



while two additional isomers for the third compound in the table and three for the fourth compound readily suggest themselves.

We claim:

1. Diazotype photoprinting materials comprising a light sensitive diazo derivative of a p-phenylenediamine of the class having the formula:

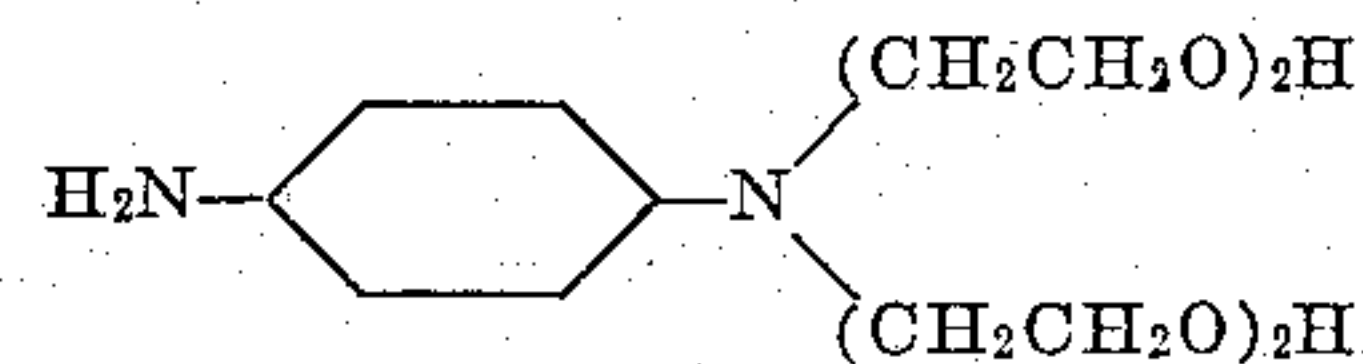


wherein n and n' are the same or different integers from 1-4 and an azo dye coupling component.

2. A diazotype photoprinting material comprising a light-sensitive diazo derivative prepared

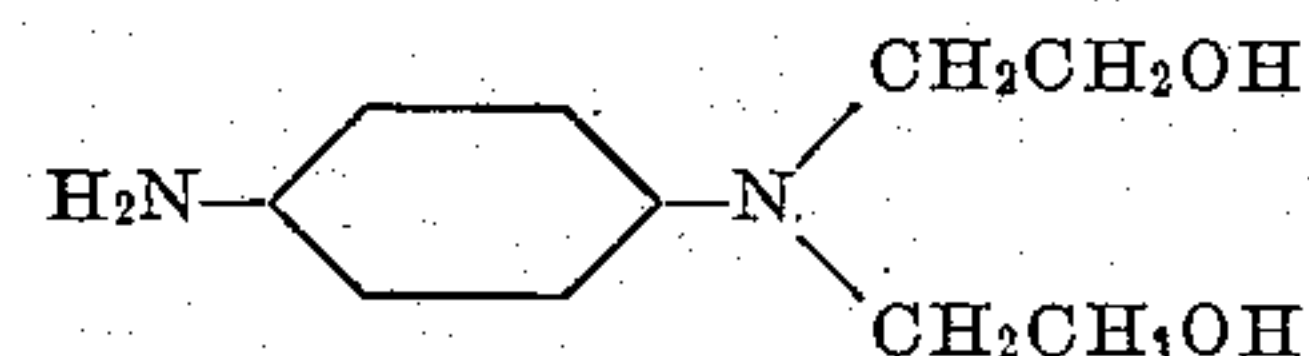
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from an aromatic p-diamine, containing four ethylene oxide groups per molecule, of the probable formula:



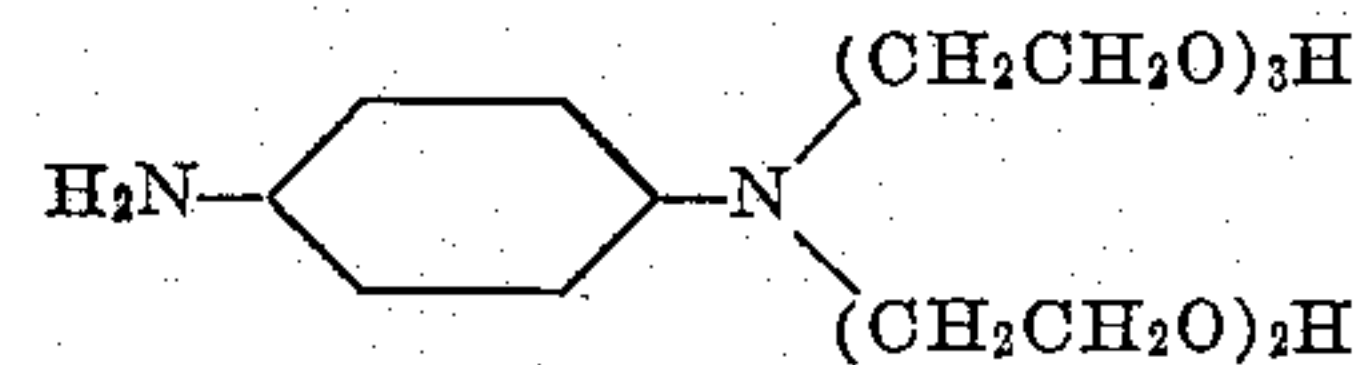
and an azo dye coupling component.

3. A diazotype photoprinting material comprising a light-sensitive diazo derivative prepared from an aromatic p-diamine having the formula:



and an azo dye coupling component.

4. A diazotype photoprinting material comprising a light-sensitive diazo derivative prepared from an aromatic p-diamine, containing five ethylene oxide groups per molecule, of the probable formula:



and an azo dye coupling component.

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GEORGE T. PARKER.

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