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DIAZOTYPES ON PLASTIC SURFACED CARRIER CONTAINING 5,5' DIRESORCINOL

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This invention relates to diazotype light sensitive media and particularly to the use of certain azo components in the light sensitive layer or coating of a plastic surfaced diazotype material.

The term "plastic surfaced" as used in this application is intended to include supports made entirely of plastic materials such as cellulose esters and ethers and regenerated cellulose and supports of non-plastic materials such as paper which have been surfaced with a coating integral therewith of such a plastic material.

In the photo-reproduction of line or continuous tone originals by means of the diazotype process, such as tracings or semi-transparent engineering drawings or typewritten documents by the diazotype positive reproduction method, it is highly desirable that the image be reproduced in a shade which will give high contrast to the reproduced lines or other figures of the original. The photo-reproduction must also be fast to light and to water and possess good photographic density. Accordingly, the selection of dye components for the production of the light-sensitive layer and the developer cannot be made merely on the basis of obtaining diazo compounds and azo coupling components which will couple to produce a desired shade. It is necessary that the choice of the light-sensitive diazo compound and the coupling component be such as to produce a dye image possessing the most desirable characteristics of shade, density, fastness to light and to water. Many investigations in this art have been concerned with the discovery of proper light-sensitive diazo compounds which will have the necessary properties of decomposing on exposure to light, particularly light which emits rays in the 3600 Å. to 4200 Å. line and, in the undecomposed form, will combine with the azo coupling component to produce the desired image. When the diazo compound and the azo component are both contained in the light sensitive layer in a two-component dry development system, it is further necessary that the diazo compound and the azo component be of such coupling capacity with respect to each other that they will not prematurely couple prior to exposure and development. The results of these investigations have generally proven that diazos derived from p-diamines of the benzene series are most suitable for the requirements of two-component diazotypes.

In the reproduction of drawings, printed material, pictures, or other originals to be copied, it is often of particular advantage to make an intermediate print or transition print on a transparent diazotype copying material by exposing a transparent sensitized diazotype material to actinic rays, such as ultraviolet light, by either the printing through or reflex process and then developing the diazotype exposure. The development of the diazotype material can be carried out by any of

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the methods known to the art for the development of exposed diazotypes. Thus, where a two-component system has been employed, which contains the azo component in the light-sensitive layer in combination with the diazo compound, development may be effected by passing the exposed diazotype through an atmosphere of ammonia vapors. Where a one-component system has been employed, which contains the diazo compound as the only dye component in the light-sensitive layer, the image is developed by treating the exposed diazotype with an alkaline solution containing the azo component by a dipping or fog spraying method. In either case, the image produced on the transparent intermediate or transition diazotype print can be used for the reproduction of further diazotype prints or, if desired, for the reproduction of the image on any photoprinting material capable of further reproducing the image.

This method of producing intermediate or transition diazotype prints is particularly useful when it is desired to make a large number of reproductions from a frail or valuable original which could not stand the wear of repeated exposures which would be necessary to make the desired number of copies. The efficiency of this process for the production of further photo copies from a transition or intermediate diazotype print depends upon the opacity of the azo dye image to ultraviolet light, and upon the transparency of the background to such light. It also depends upon the visual density of the image produced on the transition print. Images of poor visual density, such as light yellows on a white background, although they 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.

Diazotype prints of a deep or dark color having good visual density have been obtained from diazotypes using azo components known to the art for general diazotype work, such as phloroglucinol, 2,3-dihydroxynaphthalene and β-naphthol-3,6-disulfonic acid. However, despite the good visual density of the colors obtained and, in some cases, the satisfactory fastness to light and to water of the image, they do not have the light opacity or photographic density necessary to reproduce the image satisfactorily in subsequent copies. The azo dye component used for the production of transition print images must be such as to produce, on coupling with the diazo compound employed, a color which will sufficiently absorb the ultraviolet light incident upon it during exposure to prevent light decomposition of the diazo compound in the areas to be reproduced from the transition copies. It is, therefore, a further object of this invention to produce a light-sensitive material which will reproduce the

image of the original in a shade having improved photographic density or opacity to ultraviolet light.

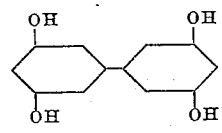
Azo components, such as resorcinol, have heretofore been employed in the production of diazotype prints and others have been suggested in order to obtain color images having the necessary light absorption characteristics for transition printing. Resorcinol will reproduce the image on the transition print in a sepia or orange-brown color which has good visual density and good opacity to ultraviolet light. However, the prints obtained from these components are often lacking in the properties of fastness to light and to water, and their coupling capacities are such that they do not have the proper resistance to premature coupling for use in two-component systems. The dye images produced on transparent intermediate prints, particularly when the support used for the print is a plastic unsupported film or a plastic coated base, have a tendency to diffuse, thereby reducing the contrast of the image and producing blurred effects on the final reproduced copy.

Some components have been studied which will not migrate in the plastic layer and produce dye images which will have no tendency to migrate or "off-set." Such components have, however, produced colors of low visual density. It is, therefore, the object of this invention to produce a diazotype composition on a plastic surfaced layer which will combine good visual density with non-migratory properties, good opacity to actinic light and good resistance to precoupling.

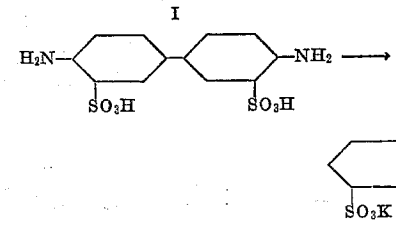
With this object in view it has now been found that 3,3', 5,5'-tetra hydroxy biphenyl can be successfully employed as the coupling component in a two component diazotype light sensitive layer on a plastic surface. When so used it does not prematurely couple with the diazo compound nor does it migrate or diffuse in the plastic layer and upon exposure and development by coupling in the usual way with p-phenylene diamine diazo compounds produces images of high visual density and high opacity to ultra-violet or other actinic light. The images produced from the 3,3', 5,5'-tetra hydroxy biphenyl will not diffuse into the plastic layer of the carrier and will remain sharp and have no tendency to "bleed" or "off-set" under pressure onto other plastic surfaces which may be in contact with the surface carrying the reproduced image. These images will also have good fastness to light and to water.

Having this unique combination of properties, the 3,3', 5,5'-tetra hydroxy biphenyl coupling component is particularly suited for use in two component diazotype coatings for plastic surfaced carriers which may be employed in transition diazotype printing.

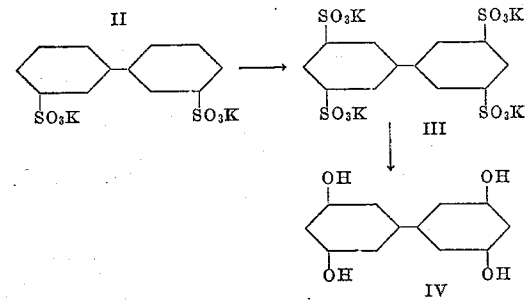
The azo coupling component 3,3', 5,5'-tetrahydroxy biphenyl or 5,5'-biresorcinol has the structural formula—



It may be prepared by first deaminating 3,3'-benzidinedisulfonic acid by tetrazotizing and decomposing as described by Schultz and Kohlhans, Berichte 39, III, 3342, to produce 3,3'-diphenyldipotassiumsulfonate according to the schematic reaction—



3,3', 5,5'-diphenyltetrapotassiumsulfonate is then prepared from product II by heating 5 pts. of the latter with 3.45 pts. sulfuric acid monohydrate and 7.85 pts. 65% oleum for 15 hours at 220° C.; the reaction product is diluted with water, SO_4 ion removed as $BaSO_4$, filtered, the filtrate neutralized with KOH and the potassium salt isolated. 50 pts. of the latter are then fused with 425 pts. KOH for 3 hours at 310° C.; the fusion mixture diluted with water, acidified with HCl and the final product isolated by extraction, the schematic reaction being as follows:



In the preparation of the diazotype photoprinting materials of this invention, a base material or carrier such as plastic coated paper is coated by means known to the art, as for instance by the "bead-dip" method, with a coating solution containing the 3,3', 5,5'-tetra hydroxy biphenyl and a suitable diazo compound. The plastic material comprising the coating on the carrier may be cellulose acetate, cellulose butyrate and other cellulose esters, cellulose ethers, and polyvinyl plastics. The carrier may be composed entirely of one of these plastic materials.

In addition to the dye components the coating solution may contain such other materials as are ordinarily used in the preparation of diazotype two-component light sensitive coating. These include stabilizing materials for the coating composition, such as citric acid, phosphoric acid and thiourea; swelling agents for cellulose acetate or other plastic material, such as isopropanol, gamma valerolactone, ethyl alcohol, methyl alcohol, butanol, ethyl lactate acetone, diacetone alcohol, ethyl methyl ketone and methyl glycol; and other adjuvants and addition agents designed to improve the resistance of the diazotype solution and coating to premature coupling and to prevent aging of the decomposition products and consequent discoloration in the background.

As diazo compounds, any suitable light sensitive diazo compound which will couple with the 3,3', 5,5'-tetrahydroxy biphenyl and which has the other properties necessary for use in two-component diazotype compositions may be employed. It is preferred, however, to use diazo compounds derived from p-diamines of the benzene series. Diazo compounds of other classifications, such as diazoanhydrides of o-amino hydroxy naphthalene compounds have been found

suitable for diazotype two-component compositions. However, the diazo compounds of the p-diamines of the benzene series are preferred and of these those which are most suitable carry N-substituents on the undiazotized amino group; the substituent groups being alkyl, alkoxy, aryl, aralkyl, alkylol, alicyclic, aromatic and heterocyclic groups. Examples of these preferred diazo compounds are as follows:

p-Diazo-N-diethylaniline
4-diazo-2-methyl-N-ethylaniline
p-Diazo-diphenylamine
4-diazo-3-methyl - N - hydroxyethyl - N - ethyl-aniline
4-diazo-3-ethoxy-N-diethylaniline
4-diazo-1-benzoyl-amino-2,5-diethoxybenzene
1-N,N-dihydroxyethylamino - 3 - chloro - 4 - diazobenzene
p-Diazo-N-ethyl-N-benzylaniline
1-N-hydroxyethyl-N-ethylamino - 4 - diazobenzene
4-diazo-N,N-dihydroxyethylaniline
1-diazo - 4 - (4'ethoxyphenyl) - amino - 2,5 - diethoxybenzene
4-diazo-1-dimethylamino-3-methoxybenzene
N,N-dimethylamino-p-diazobenzene
p-Diazo-phenylamino-morpholine
2-diazo-1-naphthol-5-sulfonic acid

These diazo compounds may be used in the form of their stabilized salts, such as the $ZnCl_2$, $CdCl_2$, or $SnCl_4$ double salts; the fluoroborates, the aryl or alkyl sulfonates; or the acid sulfates of the diazonium chloride.

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

Example

A coating solution is prepared by mixing the following materials:

50 cc. water
40 cc. isopropanol
2 gs. citric acid
1 gr. zinc chloride
2 gs. thiourea
10 cc. γ valeralactone
5 gs. sulfosalicylic acid
5 gs. formic acid
4.5 gs. zinc chloride double salt of p-diethylamino benzenediazonium chloride
3 gs. 3,3', 5,5' tetra hydroxy biphenyl

After mixing, this coating solution is filtered through a bed of activated charcoal and is then coated on to a cellulose acetate coated paper base by means of the bead-dip coating method. The coated plastic surfaced paper is then dried in the usual manner by drawing it through a heated drying chamber. Upon submitting the thus processed paper to accelerated aging tests and prolonged storage tests under average conditions of

temperature and humidity it is found that the diazotype coating on the plastic surfaced base has a high degree of resistance to precoupling or spontaneous coupling while in storage.

Upon exposing the coated and dried plastic surfaced paper to actinic light such as light rich in ultraviolet emissions under an original pattern to be reproduced and developing by drawing the exposed sensitized paper through an atmosphere of ammonia vapors, the original is reproduced in a deep reddish brown color of excellent contrast against a clear background. This image has excellent light fastness and water fastness properties and is highly absorptive of ultraviolet radiation. The prints containing the reproduced image are, therefore, especially valuable as intermediate or transition prints in the production of further diazotype or other light sensitive copies.

In the above example such diazo compounds as p-diazo-N-methyl-N-hydroxyethylaniline, $ZnCl_2$ double salt and N-benzyl-N-ethylaniline, p-diazoniumchloride $SnCl_4$ double salt may be substituted for the p-diethylamino benzenediazonium chloride $ZnCl_2$ double salt therein used with equivalent results and as indicated above, any other suitable light sensitive diazo compound for the production of a particular color effect may be likewise substituted.

Having now particularly described my invention and illustrated the best manner in which to perform it, what I claim as new and desire to protect by Letters Patent is:

1. A diazotype photoprinting material comprising a plastic surfaced carrier and superimposed on the plastic surface thereof a coating containing 3,3', 5,5'-tetra hydroxy biphenyl and a light sensitive diazo compound.

2. A diazotype photoprinting material comprising a plastic surfaced carrier and superimposed on the plastic surface thereof a coating containing 3,3', 5,5'-tetra hydroxy biphenyl and a light sensitive p-aminobenzene diazo compound.

3. A diazotype photoprinting material comprising a plastic surfaced carrier and superimposed on the plastic surface thereof a coating containing 3,3', 5,5'-tetra hydroxy biphenyl and a light sensitive p-diazo-N-alkyl aniline compound.

4. A diazotype photoprinting material comprising a plastic surfaced carrier and superimposed on the plastic surface thereof a coating containing 3,3', 5,5'-tetra hydroxy biphenyl and p-diazo-N-diethyl aniline.

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