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DIAZOTYPE COMPOSITION CONTAINING
N - HYDROXYETHYL-m-TOLUIDINE-p-DIAZOS

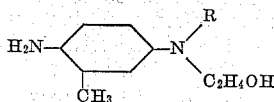
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1 Claim. (Cl. 95—6)

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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 a p-phenylene diamine compound having the following formula:



wherein R is a member of the group consisting of hydrogen, methyl, ethyl and hydroxyethyl groups.

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 rather 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 images in deep tones, such as blue and black, and are otherwise suitable for diazotype reproduction nevertheless have a relatively fast coupling rate for the diazo compounds known to be suitable for the production of such images. Such relatively fast coupling components include 2,3-dihydroxynaphthalene and acetoacetanilide which are highly desirable for use in the production of deep blue and black tones when coupled with suitable diazo compounds. When used in a diazotype light-sensitive layer together with the diazo compound in a typical two-component system, this fast coupling property of such azo components tends to increase the precoupling tendencies of the composition and, therefore, reduce the shelf life of the light-sensitive diazotype layer in which such components are employed. Consequently, unless such diazotypes are used by exposing and developing 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.

In the duplication of some originals, such as valuable documents or tracings, which would

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not stand the wear of successive exposures 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 on either a transparent or opaque background. 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 diazotype intermediate transparencies, it is essential that the reproduced image be of such a composition that it will have a high opacity to actinic light, such as ultraviolet. It has been found that dye components which will produce a sepia tone have this desirable property. The more common coupling components such as resorcinol which will produce a sepia image with diazo compounds otherwise suitable for diazotype light-sensitive layers generally have poor precoupling stability. Such precoupling instability is a decided disadvantage in the production of diazotype intermediate transparencies since the background color resulting from precoupling of the dye components will absorb actinic light in the background areas where the transparency should transmit the light. Since precoupling will not be uniform, the background of the final reproduction taken from the intermediate transparency will obtain various degrees of exposure and will, consequently, be colored in varying depths of the sepia color. Furthermore, the contrast of the intermediate transparency will be considerably reduced by the background color rendering it more difficult to detect flaws in the intermediate reproduction.

We have now found that the precoupling stability of diazotype light-sensitive layers for either final reproduction work in deep tones or intermediate transparency work in sepia or other ultra violet opaque tones is greatly improved by using as the light-sensitive diazo component, diazo derivatives of the above-described substituted phenylene diamines. Diazo compounds of this class are stable compounds under ordinary conditions but decompose readily upon exposure to light to produce colorless non-coupling decomposition products. They thus provide the characteristic of photo-sen-

sitivity necessary to any diazo compound used for the production of diazotype copies. Their precoupling stability or resistance to coupling with the azo components during storage and prior to development eminently suits these diazo derivatives to use in two-component diazotype papers in combination with the desirable fast coupling components, such as 2,3-dihydroxynaphthalene and acetoacetanilide which are used to produce the desirable deep blue and black tones for final copies and the resorcinol type of coupling components which will produce the desirable sepia shades for intermediate transparencies.

An added advantage of the p-phenylene diamine diazo derivatives of the above-described class is the ability of these compounds to remain in a solution with the other components which are used in diazotype coating solutions and particularly in those cases where the coating solution is relatively concentrated, such as coating solutions for the production of intermediate transparencies or diazotype media for the copying of transparent microphotographs. This factor is important since in the case of hitherto known diazos containing a methyl group ortho to the diazo group it is difficult to achieve practical concentrations of the diazo component in such diazotype coating solutions. For example, when N-diethyl-m-toluidine-p-diazonium chloride-ZnCl₂ double salt or N-hydroxyethyl-N-furfuryl-m-toluidine-p-diazo-ZnCl₂ double salt is used as the diazo component in a heavily loaded coating solution for intermediate foils and microphotographs, the diazo tends to precipitate out, thus impairing uniform penetration and producing a high surface concentration of the diazo. Due to the excellent solubility of p-phenylene diamine diazos of the above class, this disadvantage is overcome even in the case of the most concentrated coating solutions employed.

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 light-sensitive compounds, azo dye components and other coating materials is coated, dipped, brushed or sprayed with the sensitizing solution by means known to the art, the particular type of application depending upon the carrier employed. As carriers, such materials as paper or cloth, either of which may be opaque, semi-transparent or of a transparentized type, or a film, such as prepared from cellulose nitrate, cellulose acetate or other cellulose esters or regenerated cellulose and the like, or a glass plate 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, however, be brushed or sprayed. When a film is used as the support, in order to obtain proper penetration swelling agents are added to the coating solution and the solution is applied by dipping. In addition to the diazo compound, azo component and possible impregnating or swelling agents, the coating solution may contain the usual agents, such as 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 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. Furthermore, although this invention is described with particular reference to the so-called dry development process, that is, wherein the diazo and azo components are applied to the support in combination and are then exposed to light under an image, followed by development with ammonia or other alkaline vapor, 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, omitting such as are peculiar to the needs of the two-component system but does not contain any azo dye coupling component. Here 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 with a solution of alkaline agents containing the coupling component.

In addition to the high degree of stability in precoupling and resistance to precipitating out of the coating solutions, which qualities characterize hydroxyethyl-m-toluidine-p-diazo of this invention, these diazos have the further advantage of producing sepia images of outstanding opacity to ultra violet light when they are used with couplers which will produce sepia shades, such as resorcinol, resorcinol sulfonic acid, dichlororesorcinol, 4-bromoresorcinol, 3-hydroxyphenoxy acetic acid, 3-acetaminophenol, 3-hydroxyphenyl guanide and 3-hydroxyphenyl bi-guanide.

The following examples will serve to further illustrate the preparation of diazotype photographic printing 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

A transparent paper stock is coated with a solution containing per 100 cc. of water:

3.5 g. N-ethyl-N-hydroxyethyl-m-toluidine-p-diazo-ZnCl₂ double salt
2.2 g. Resorcinol
8.0 g. Citric acid
4.0 g. Thiourea

This coated paper is submitted to accelerated aging tests under conditions of high temperature and humidity in comparison with a standard prepared by coating a similar paper stock with a similar solution containing a diazo of similar constitution but being unsubstituted in the position ortho to the diazo group, i. e., N-ethyl-N-hydroxyethylaniline-p-diazo-ZnCl₂ double salt. Under such a test the precoupling stability of the coating made in accordance with the formula of this example is far superior to that of the standard of comparison. Upon being submitted to natural storage for more than a year, it is observed that the background of a print made from a diazotype coated paper of this example is still a clear white. As compared with other similar diazos, for instance, those lacking an N-hydroxyethyl group, such as N-diethyl-m-toluidine-p-di-

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azo or N-ethyl-m-toluidine-p-diazo, the solubility, ease of coating and penetration into the paper is considerably improved and prints made in accordance with this example have much sharper contrast and have no background color due to non-uniform penetration of the diazo into the support as in the case of the standards.

Upon exposure of the transparent paper, coated by the formula of this example, under an image and subsequent development by contact with ammonia fumes, a dark sepia print having excellent visual density and a high degree of opacity to ultra violet light is obtained. There is very little, if any, off-set when such a print is used as an intermediate positive. Its wash and light fastness are also good. The intermediate positive may be used as an original with other diazotype papers to produce positives of any desired shade.

Example 2

A transparent paper stock is coated with a solution containing per 100 cc. of water:

- 3.5 g. N-ethyl-N-hydroxyethyl - m - toluidine-p-diazo-ZnCl₂ double salt
- 3.5 g. 1,3-dihydroxybenzene-4-sulfonic acid
- 8.0 g. Citric acid
- 4.0 g. Thiourea

When submitted to accelerated aging tests in the same manner as in Example 1, the diazotype coating of this example is found to have the same high degree of precoupling stability as the composition of Example 1 when compared with the same standards. It also has the same solubility, ease of coating and penetration qualities as Example 1 and produces upon exposure and development a dark sepia print having excellent visual density and the same high degree of photographic density or opacity to ultra violet light as the prints obtained in accordance with Example 1.

Example 3

A transparent paper stock is coated with a solution containing per 100 cc. of water:

- 3.5 g. N-ethyl-N-hydroxyethyl - m - toluidine-p-diazo-ZnCl₂ double salt
- 3.2 g. 4,6-dichlororesorcinol
- 8.0 g. Citric acid
- 4.0 g. Thiourea

When submitted to an accelerated aging test, the paper coated in accordance with the formula of this example also has the same high degree of precoupling stability as that of Example 1 in comparison with the same standards as were compared in Example 1. Its solubility, coating and penetration properties are also excellent in comparison with the named standards of Example 1. Upon exposure under an image and subsequent development by contact with ammonia, a dark-reddish sepia print is obtained which has excellent visual and photographic density. These prints make excellent intermediate or transition positives. It is also noted that the combination of this example has particularly good properties for use in reflex printing wherein the translucent sheet coated as above is placed over an opaque original and light is transmitted through the translucent coated sheet to be reflected in part from the original thereby forming a latent positive image in the translucent sheet to be developed in the usual manner and used as an intermediate, if desired, for the production of further diazotype copies.

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Example 4

A transparent paper stock is coated with a solution containing per 100 cc. of water:

- 3.4 g. N-hydroxyethyl-N-methyl - m - toluidine-p-diazo ZnCl₂ double salt
- 2.2 g. Resorcinol
- 8.0 g. Citric acid
- 4.0 g. Thiourea

This coated paper is submitted to accelerated aging tests under conditions of high temperature and humidity in comparison with a standard prepared by coating a similar paper stock with a similar solution containing a diazo of similar constitution but being unsubstituted in the position ortho to the diazo group, f. i., N-ethyl-N-hydroxyethylaniline - p - diazo - ZnCl₂ double salt. Under such a test the precoupling stability of the coating made in accordance with the formula of this example is far superior to that of the standard of comparison. Upon being submitted to natural storage for more than a year, it is observed that the background of a print made from a diazotype coated paper of this example is still a clear white. As compared with other similar diazos, for instance, those lacking an N-hydroxyethyl group, such as N-diethyl-m-toluidine-p-diazo or N-ethyl-m-toluidine-p-diazo, the solubility, ease of coating and penetration into the paper is considerably improved and prints made in accordance with this example have much sharper contrast and have no background color due to non-uniform penetration of the diazo into the support as in the case of the standards.

Upon exposure of the transparent paper, coated by the formula of this example, under an image and subsequent development by contact with ammonia fumes, a dark sepia print having excellent visual density and a high degree of opacity to ultra violet light is obtained. There is very little, if any, off-set when such a print is used as an intermediate positive. Its wash and light fastness are also good. The intermediate positive may be used as an original with other diazotype papers to produce positives of any desired shade.

Example 5

A transparent paper stock is coated with a solution containing per 100 cc. of water:

- 3.1 g. N - hydroxyethyl - m - toluidine - p-diazo-ZnCl₂ double salt
- 3.2 g. 4,6-dichlororesorcinol
- 8.0 g. Citric acid
- 4.0 g. Thiourea

Upon being submitted to accelerated aging tests in comparison with the same standard as used in the previous example, it is found that the precoupling stability of the light-sensitive coating of this example is far superior to that of the standard. Its solubility, ease of coating and penetration properties also show a great improvement over the same properties of the standard mentioned in the previous example, such as N-ethyl-m-toluidine-p-diazo. Upon exposure under an image and subsequent development by contact with ammonia fumes, a dark sepia print having excellent visual and photographic density is obtained. Such intermediate prints when compared with similar prints made from a similarly coated transparent paper containing N-ethyl-m-toluidine-p-diazo-ZnCl₂ double salt as the diazo compound exhibits a much greater opacity to ultra violet light when the compared

prints are used as intermediate positives for the purpose of producing further diazotype copies.

Example 6

A regular paper stock is coated with a solution containing per 100 cc. of water:

- 2.8 g. N-ethyl-N-hydroxyethyl-m-toluidine-p-diazo-ZnCl₂ double salt
2.0 g. 2,3-dihydroxynaphthalene-6-sulfonic acid
0.5 g. 2,3-dihydroxynaphthalene

The thus coated paper has excellent stability to precoupling and can be stored for a much longer period of time than a paper similarly prepared from a coating solution containing similarly constituted diazos which are unsubstituted in the position ortho to the diazo group, such as N-ethyl-N-hydroxyethylaniline-p-diazo ZnCl₂ double salt wherein coupling of the 2,3-dihydroxynaphthalene occurs in a relatively short time.

Upon exposing paper coated in accordance with this example under an image and subsequently developing by contact with ammonia fumes, a very bright blue print of sharp contrast on a clear white background is obtained.

In addition to the favorable precoupling stability, the composition of this example also has a faster printing speed than similar compositions containing as the diazo compound N-ethyl-m-toluidine-p-diazo ZnCl₂ double salt.

Example 7

A regular paper stock is coated with a solution containing per 100 cc. of water:

- 2.9 g. N,N-dihydroxyethyl-m-toluidine-p-diazo-ZnCl₂ double salt
2.0 g. 2,3-dihydroxynaphthalene-6-sulfonic acid
0.5 g. 2,3-dihydroxynaphthalene

The thus coated diazotype paper has the same superior stability to precoupling and the same fast printing properties as the composition of Example 6 in comparison with the standards of that example. Upon exposure and development, the diazotype coated paper of this example yields an intense bright blue image of sharp contrast on a clear white background.

Example 8

A regular paper stock is coated with a solution containing per 100 cc. of water:

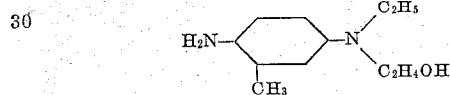
- 2.5 g. 7-hydroxy-1,2-naphthimidazole
2.9 g. N,N-dihydroxyethyl-m-toluidine-p-diazo-ZnCl₂ double salt

The thus coated diazotype paper has the same exceptional precoupling stability and fast printing properties as the diazotype paper of Examples 6 and 7 and yields upon exposure and development a maroon image of sharp contrast on a clear white background.

- Upon substituting in Example 1, 3.5 g. of 4-bromoresorcinol; 3.0 g. 3-hydroxyphenoxyacetic acid; 2.8 g. 3-acetylaminophenol or 3.4 g. 1,3-dihydroxybenzene-5-sulfonic acid as the azo dye component in place of the 2.2 g. of resorcinol used in Example 1, diazotype coatings having the same superior properties as the coating of Example 1 are obtained. In the case of 3-acetylaminophenol, the sepia dye image is a lighter tone than in the case of resorcinol or the resorcinol derivatives.

We claim:

A diazotype photographic material comprising a light-sensitive diazonium salt of the compound having the formula:



and an azo dye coupling component.

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