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DIAZOTYPES CONTAINING 6-HYDROXY-1,3-BENZOXATHIOLONE-2 AND ITS DERIVATIVES

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8 Claims. (Cl. 95—6)

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This invention relates to diazotype photo-reproduction media and more particularly to the use of certain hydroxy benzoxathiolones as azo components in the development of the diazotype light sensitive layers.

The diazotype process, as is well known, involves the treating of a carrier or base, usually paper which may be either opaque or transparentized, or film of the cellulose ester or cellulose ether type, with a sensitizing composition containing a diazo compound as the light sensitive element. This treated base is exposed to actinic light through a pattern and a positive reproduction of the original obtained by development of the undecomposed diazo compound under the protected portions of the pattern, by means of alkaline coupling with an azo dye coupling component. The azo dye coupling component used for development of the image may be contained in an alkaline developing solution, as is the case in the so-called wet development or one-component process. In the dry development or two-component diazotype process, the sensitizing composition with which the base material is treated contains both the diazo compound and the azo coupling component. Here, the azo dye image is formed after exposure of the sensitized material by subjecting the exposed material to the action of alkaline vapors such as ammonia vapors. The diazotype photosensitive material for the two-component process must have good stability against precoupling, so that the sensitized layers may be stored for reasonable periods of time under average conditions of temperature and humidity prior to use.

The two-component diazotype process is extensively used for the preparation of intermediate or transition prints in cases where it is desired to make a large number of reproductions. By making such an intermediate diazotype transition print it is only necessary to expose the original once or a few times since the transition print is thereafter used to make the desired number of duplicates. Consequently, a valuable original drawing may be spared the rigorous treatment of repeated exposures which might result in the impairment or even destruction of the original drawing. In producing an intermediate diazotype print, a transparent or semi-transparent paper or film is coated with a light sensitive diazotype sensitizing solution and dried. It is then exposed to actinic light rays, particularly from a source rich in the ultraviolet band of from 3600 Å. to 4200 Å. under the drawing or picture to be reproduced. The image is then developed

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by contacting the exposed light sensitive surface, if it be a two-component diazotype, to ammonia vapors.

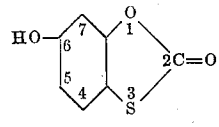
The efficiency of transition prints depends upon the covering power or photographic density of the azo dye image produced and particularly its opacity to ultraviolet light, and also upon the transparency of the background surrounding the developed pattern. The clarity of the background, and hence its transparency, is decreased if color has been produced therein due to the residual or undecomposed diazo compound, or to premature coupling of the dye components prior to use. Such casual color in the background of the intermediate print will be reproduced in subsequent copies due to the ultraviolet absorbing qualities of the transition color.

The efficiency of transition prints also to some extent depends upon the depth or visual density of the image produced. Light colored images of poor visual density which may satisfy the requirements of opacity to ultraviolet light and ability to resist precoupling nevertheless have the disadvantage of rendering difficult the detection of flaws in the intermediate image, and it is often necessary to make a test print from the transition print of a deep contrast before such flaws can be detected, with consequent loss of time, convenience and economy.

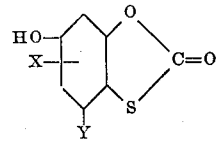
Azo dye coupling components which are used in the diazotype art for the production of deep colors such as blues and purples, and even blacks, do not produce images which have good actinic opacity, so that the diazotypes made from them cannot be used in transition printing to reproduce further copies. Some azo dye coupling components such as resorcinol produce colors when coupled with the diazo compounds ordinarily employed in diazotypes which are of a brown or sepia hue. These colors have good visual density and good actinic opacity, and therefore may be used as intermediate prin's. However, the storage life of two-component diazotypes containing resorcinol as the azo dye coupler is short, since resorcinol has poor stability against precoupling in the diazotype layers. Such precoupling causes the diazotypes containing the diazo compounds and resorcinol to gradually develop discoloration prior to use. This discoloration is retained by the transition print and will be present in the background areas as well as the image areas, thus impairing the ability of the background areas to efficiently transmit actinic light. Consequently, the light sensitive diazo compounds or other light sensitive media

in the reproduction material employed for making further copies from the transition print will not be completely decomposed in the background areas of such subsequent prints. The discoloration appearing in the background area of the transition print will therefore be reproduced in the final copies, reducing the contrast and causing undesired spotty discoloration.

In general, it may be said that in order to be of value for use in intermediate prints or transition printing, it is necessary that the azo components used in a two-component diazotype be stable to precoupling and that they yield dyes that have a high degree of opacity to ultraviolet light, a high color density and a high resistance to washing, light and offset. By offset reference is made to the rubbing off of the dye by abrasive means, especially when using hot printer rolls. It has been found that transition prints having all of these properties to a high degree may be obtained when using as an azo component 6-hydroxy-1,3-benzoxathiolone-2 of the formula:

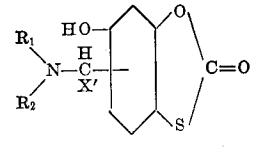


or one of its halogen, alkyl, alkoxy, sulfonic acid, carboxy or aminoalkyl derivatives. When one of the said derivatives is employed, it must have at least one of the coupling positions numbered 5 and 7 unsubstituted. The said 6-hydroxy-1,3-benzoxathiolone-2 and its derivatives comprise the class which may be represented by the formula:



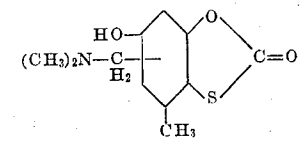
wherein X is a member of the group consisting of hydrogen, halogen, alkyl, alkoxy, sulfonic acid, carboxy and aminoalkyl; and Y is a member of the group consisting of hydrogen and alkyl.

The azo dye coupling components of this class may be prepared by reacting resorcinol or suitable derivatives of resorcinol with potassium thiocyanate in the presence of copper sulfate, precipitating the imino-thiocarbonate of the resorcinol compound and hydrolyzing in a warm weakly acid solution. Examples of resorcinol compounds which may be employed to produce the 6-hydroxy-1,3-benzoxathiolone-2 or its various derivatives are: resorcinol, 4-chloro-resorcinol, 4-methyl-resorcinol, 4-methoxy-resorcinol, 5-methyl-resorcinol, resorcinol-4-sulfonic acid and β-resorcyclic acid. In order to obtain an aminoalkyl derivative, a resorcinol compound is converted into the corresponding 6-hydroxy-1,3-benzoxathiolone-2, which compound is then treated with an aldehyde and a secondary amine in accordance with the so-called Mannich reaction. A typical aminoalkyl derivative is one having the following formula:



wherein X' represents hydrogen or lower alkyl,

and R_1 and R_2 represent lower alkyl. One of the positions 5 or 7 must remain unsubstituted after the formation of the aminoalkyl derivative, but any other position may be substituted. As a specific example, orcinol (5-methyl-resorcinol) is converted into the 4-methyl-6-hydroxy-1,3-benzoxathiolone-2, which latter is treated with formaldehyde and dimethylamine to produce the product having the formula:



In the preparation of two-component diazotype layers intended for use as intermediate or transition prints in accordance with this invention, a suitable transparent base such as transparentized paper, cellulose acetate film or other transparent material is coated by spraying or other means of application known to the art with a light sensitive coating composition containing a suitable diazo compound and the azo coupling component in combination with other materials ordinarily used in the preparation of diazotype compositions. As diazo compounds, we prefer to use those which are obtained by diazotization from p-diamines of the benzene series. As a practical matter diazo compounds of this preferred class have at least one of the hydrogens of one of the amino groups substituted by such groups as alkyl, alkoxy-alkyl, aryl, aralkyl, alkylol, cycloaliphatic and heterocyclic groups but the unsubstituted compounds are included. Other diazo compounds have been found to be suitable such as diazo-anhydrides of amino-hydroxy naphthalene compounds and these are not excluded. The diazo compounds may be used as such or in the form of their stabilized derivatives such as the zinc chloride, cadmium chloride or tin chloride double salts, the fluoro-borates or naphthalene sulfonates of the diazonium chloride. Examples of amines from which the light sensitive diazo compounds may be obtained by the usual process of diazotization and salting out in the form of the stabilized diazonium complexes include:

5-amino-2-monoethylamino toluene
1-diethylamino-3-ethoxy-4-aminobenzene
1-dimethylamino-3-methoxy-4-aminobenzene
1-(N-ethyl-N-propylamino)-3-ethoxy-4-aminobenzene
1-(N-ethyl-N-butylamino)-3-methoxy-4-aminobenzene
p-Aminodiphenylamine
1-(N-ethyl-N-hydroxyethyl)-4-aminobenzene
1-benzoylamino-2,5-diethoxy-4-aminobenzene
1-diethylamino-4-aminobenzene
1-(N-ethyl-N-benzylamino)-4-aminobenzene
1-(2',6'-dichlorobenzylamino)-4-aminobenzene
1-(2',6'-dichlorobenzylamino)-2-phenoxy-4-aminobenzene
1-dimethylamino-4-aminobenzene
1-dimethylamino-3-methyl-4-aminobenzene
p-aminophenylmorpholine
1-(N-hydroxyethyl-N-methylamino)-4-aminobenzene
2-amino-1-naphthol-5-sulfonic acid

Although this invention has been particularly described as applied to the two-component method of diazotype reproduction wherein the stabilized diazo compound and coupling component are applied simultaneously to the paper

or film, nevertheless, it should be obvious that the new coupling components may also be used in the one-component or moist development diazotype process, wherein the paper or film is sensitized with a solution containing the stabilized diazo, and the image after exposure is developed in an alkaline solution containing the coupling component.

The following examples will serve to further illustrate the invention, it being understood that no limitations are intended on the scope of the invention either as to proportions or as to specific materials employed. Unless otherwise stated, the parts are by weight:

Example 1

A transparentized diazotype paper stock is coated with a solution of the following materials:

3.2 gs. 6-hydroxy-1, 3-benzoxathiolone-2
4.0 gs. diethylaminobenzene p-diazonium chloride $ZnCl_2$ double salt
8.0 gs. citric acid
4.0 gs. thiourea
10.0 cc. isopropanol
5.0 cc. glycol
0.5 gs. saponin
Add water to make 100 cc.

The coated transparentized paper thus obtained has excellent stability to precoupling even under the temperature and moisture conditions which ordinarily cause rapid aging. It is particularly stable to the conditions of an accelerated aging test. Upon exposure under a pattern and subsequent development with ammonia vapors, prints are obtained in a dark reddish-brown shade of good opacity to ultraviolet light, having excellent visual appearance and good fastness to washing, light and offset.

Example 2

Transparentized paper is coated with a solution containing the following materials:

4.0 gs. N-hydroxyethyl-N-methylaminobenzene p-diazonium chloride $ZnCl_2$ double salt
3.2 gs. 6-hydroxy-1, 3-benzoxathiolone-2
8.0 gs. citric acid
4.0 gs. thiourea
10.0 cc. isopropanol
5.0 cc. glycol
0.5 gs. saponin
Water is added to make 100 cc.

The thus coated paper is dried in the usual manner and submitted to accelerated aging tests in which it is found to be extremely stable to precoupling under the conditions of these tests. Upon exposing the coatings to light under an original pattern and developing the image with ammonia fumes, the pattern is reproduced in dark reddish-brown shades having good opacity to ultraviolet light, excellent photographic density and good fastness to washing, light and offset.

Example 3

Transparentized paper is coated with a solution containing the following materials:

3.0 gs. 5-chloro-6-hydroxy-1,3-benzoxathiolone-2
3.3 gs. N-ethyl-o-toluidine p-diazo $ZnCl_2$ double salt
8.0 gs. citric acid
4.0 gs. thiourea
10.0 cc. isopropanol
5.0 cc. glycol
0.5 gs. saponin
Water is added to make 100 cc.

The light sensitive layer produced by this coating on the transparentized paper possesses excellent stability to precoupling under the temperature and moisture conditions which generally cause rapid aging. Upon exposure under an original pattern and subsequent development with ammonia fumes, prints are obtained in a dark reddish-brown hue on a clear background. The image has good opacity to ultraviolet light, excellent visual density and good fastness to washing, light and offset. It is eminently suited for use as an intermediate copy in the transition printing of further copies on dark-lined diazotype media. When so used, the further dark-lined copies will have good contrast and clear backgrounds due to the good stability against precoupling of the coating of this example and the opacity to ultraviolet light of the image produced thereby.

Example 4

Transparentized paper is coated with a solution containing the following materials:

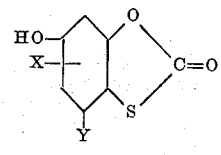
3.4 gs. dimethylamino - methyl - 4 - methyl-6-hydroxy-1,3-benzoxathiolone-2
4.0 gs. dimethylamino-3-methoxybenzene-p-diazo $ZnCl_2$ double salt
8.0 gs. citric acid
4.0 gs. thiourea
10.0 cc. isopropanol
5.0 cc. glycol
0.5 gs. saponin
Water is added to make 100 cc.

The coating comprising the light sensitive layer of this diazotype material has excellent stability to precoupling even under the conditions of temperature and humidity prevailing in the accelerated aging tests. Upon exposure under an original pattern and subsequent development with ammonia fumes, prints are obtained in dark reddish-brown shades which have good opacity to ultraviolet light, excellent visual density and good fastness to washing, light and offset. These prints are eminently suitable for use as intermediate copies in the transition printing of further dark-lined diazotype copies.

In the accelerated aging tests used to determine the stability of the diazotype coatings of these examples against precoupling and decomposition of the dye components, the sensitized carrier is subjected after the usual drying to a temperature of 120° F. for 48 hours at a relative humidity of 50%.

We claim:

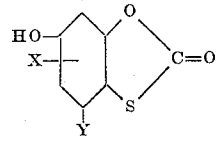
1. Diazotype light sensitive layers on a suitable base containing a suitable diazo light sensitive compound and an azo coupling component of the class represented by the formula:



wherein X is a member of the group consisting of hydrogen, halogen, alkyl, alkoxy, sulfonic acid, carboxy and aminoalkyl; and Y is a member of the group consisting of hydrogen and alkyl.

2. Diazotype light sensitive layers on a suitable base containing a mono-diazo compound of a p-diamino compound of the benzene series and

an azo coupling component of the class represented by the formula:



wherein X is a member of the group consisting of hydrogen, halogen, alkyl, alkoxy, sulfonic acid, carboxy and aminoalkyl; and Y is a member of the group consisting of hydrogen and alkyl.

3. A diazotype light sensitive layer on a suitable base comprising a mono-diazo compound of a p-diamino compound of the benzene series and as an azo component 6-hydroxy-1,3-benzoxathiolone-2.

4. A diazotype light sensitive layer on a suitable base comprising a mono-diazo compound of a p-diamino compound of the benzene series and as an azo component 5-chloro-6-hydroxy-1,3-benzoxathiolone-2.

5. A diazotype light sensitive layer on a suitable base comprising a mono-diazo compound of a p-diamino compound of the benzene series and as an azo component dimethylamino-methyl-4-methyl-6-hydroxy-1,3-benzoxathiolone-2.

6. A diazotype light sensitive layer on a suitable base comprising as the light sensitive element a diethylamino-benzene p-diazo and as the azo component 6-hydroxy-1,3-benzoxathiolone-2.

7. A diazotype light sensitive layer on a suitable base comprising as the light sensitive element an N-ethyl-o-toluidine-p-diazo and as the azo component 5 - chloro - 6 - hydroxy-1,3-benzoxathiolone-2.

8. A diazotype light sensitive layer on a suitable base comprising as the light sensitive element a dimethylamino-3-methoxybenzene p-diazo and as the azo component dimethylamino-methyl-4-methyl-6-hydroxy-1,3-benzoxathiolone-2.

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LESTER N. STANLEY.

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