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PYRAZOLONE DIAZOTYPE COUPLERS

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4 Claims. (Cl. 95—6)

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This invention relates to a diazotype photoprinting material. More particularly, in one embodiment, it relates to a photoprinting material containing a coupling component which will couple with an undecomposed diazonium compound in the density areas, after exposure to light and upon development in an alkaline medium, to produce an azo dye image. In another embodiment, it relates to a photoprinting material containing a coupling component which will couple with a decomposed diazonium component in the high-light areas upon exposure to light to give an azo dye image.

Many processes have been suggested for the production of photoprinting material, such processes differing principally in the chemical used as the light-sensitive element and in the manner of developing a dye image. The most widely known of these processes are those which are based upon the light sensitivity of aromatic diazo compounds. Other such processes of less importance include processes based upon the light sensitivity of the leuco compounds of the coal tar dyestuffs; processes based upon the oxidizing action of o-nitro groups in aromatic systems having aliphatic side chains, as for instance, o-nitrophenyl lactic acid methyl ketone; and processes based upon the light sensitivity of the o-nitro-diaminotriphenylmethane bases. With the exception of the processes based upon the light sensitivity of aromatic diazo compounds, these suggested photoprinting processes have found no commercial adaptability either because of the instability of the compounds employed or the difficulty of developing the dye image from the undecomposed light-sensitive material. The aromatic diazo compounds have found wide commercial acceptance in two well known processes which are designated respectively as the one-component or wet-development process, and the two-component or dry-development process.

In the one-component process, the aromatic diazo compound is incorporated into a light-sensitive layer on the carrier which may be paper, foil, glass, textile material or a metallic surface. After exposure under the original to be copied, this light-sensitive layer is developed by contact with an alkaline solution of the coupling component necessary to produce the ultimately desired image.

In the two-component process, the aromatic diazo compound and the coupling component necessary to produce the dye image are both incorporated in the light-sensitive layer on the carrier. In this case, the development of the

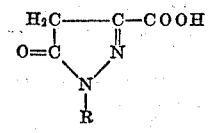
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dye image is effected after exposure by contacting the light-sensitive layer with ammonia gas. When employing a diazonium salt as the light-sensitive material, for optimum results, it is preferable to use the diazo salts derived from aromatic p-diamines and o-amino-naphthols. Other diazos have been used with varying degrees of success.

In photoprinting processes of these types it is highly desirable to produce a copy which will have a distinctive color, preferably a dark shade on a clear white background, so that the image will be sharp. It is also desirable to have a material which will give gradation of shade throughout the high-light and half-tone areas.

For the production of red tones, combinations of the o-diazo naphthols and such azo dye couplers as resorcinol, phloroglucinol, and methyl-phenyl-pyrazolone have been used, as disclosed in U. S. 1,444,469. These combinations reproduce the image in red tones of varying depth of shade from light red to violet. The white backgrounds of these images are readily discolored by oxidation. It has been found necessary, particularly for the improvement of the wash fastness properties, to add metallic salts which form lakes with the azo dyes of the images.

I have found that diazotype images in deep red tones of improved density, good light fastness, and excellent wash fastness properties can be obtained when the azo dye coupling component is a derivative of pyrazolone having the formula



wherein R is an aryl radical such as phenyl, tolyl, and naphthyl radicals.

The pyrazolone derivatives of this invention will couple with diazo compounds derived from p-diamines of the benzene series to form excellent dye images of deep red tone, which images have good light fastness and excellent wash fastness properties.

In a preferred embodiment, the process of this invention is carried out by coating a suitable base, such as paper, a cellulose or cellulose ester film, glass plate, textile material, gelatinized surface or metallic surface with a coating preparation containing the pyrazolone derivative, a light-sensitive diazonium salt, a mild acid such as citric acid, thiourea and water. The coating is effected in the usual manner by applying the coating so-

lution to the surface of the carrier or base material with a doctor-blade or by spraying. The coated material is then dried, exposed under an original positive or negative picture or drawing, and developed by treatment with ammonia or other suitable alkaline materials. In the sensitizing or coating of plastic surfaces, organic solutions of high volatility such as alcohols, ethers and ketones, may be employed partly or wholly in the place of water. Such diluents may also be employed to make up the coating solution in cases where the base material or carrier is such that the diluent exerts no appreciable solvent action on the carrier material. High temperature drying may thus be avoided.

In another manner of carrying out this process, only the light-sensitive diazonium salt is added to the mild acid solution and coated onto the carrier. The exposure under a suitable positive is effected as above, but the image is developed by bathing the exposed element in an alkaline bath containing the pyrazolone derivative coupling component necessary to combine with the undecomposed diazonium salt to form the red azo dye image in the unexposed areas.

In still another manner of carrying out this process, a diazonium sulfonate may be employed as the light-sensitive material. A solution of a diazo sulfonate and a coupling component is coated on a suitable carrier, dried, and exposed to strong actinic light under a suitable positive or negative. The exposed diazonium sulfonate is thereby converted into a diazo component which couples with the coupling component to form an azo dye image.

Although it is not essential, it is understood that, if desired, auxiliary materials may be added to the coating solution in any of the modifications of this process, which materials may function as stabilizers, preservatives, extenders, and the like.

The following examples illustrate preferred methods of carrying out this invention but it is understood that these examples are given by way of illustration and not of limitation. Unless otherwise specified the parts are by weight.

Example I

A coating solution is made up by mixing the following ingredients into 50 cc. of water:

25 cc. alcohol
10 cc. formic acid
1 gram thiourea
10 grams citric acid
1 gram 1-phenyl-pyrazolone (5)-3-carboxylic acid
6 grams 1-monoethylamino-4-diazobenzene-$ZnCl_2$ double salt

This coating solution is coated onto a sheet of cellulose acetate film by the usual method of drawing the film in a taut condition past a trough and doctor-blade into which the solution has been introduced. (Spraying methods of coating may be substituted if desired.) The coated film is then dried in the usual manner by drawing it through a heated drying chamber. Upon submitting the thus processed sensitized film to accelerated aging tests or prolonged storage tests, it is found to have a high degree of resistance to precoupling or spontaneous coupling under the conditions of storage. Upon exposing the coated and dried film to proper actinic light, such as light rich in ultraviolet emissions, under an original pattern and developing by drawing the exposed sensitized film through an

atmosphere of ammonia vapors, the image is reproduced in a deep red color which has good light fastness and excellent wash fastness properties. The background is clear and colorless and no bleeding of the image into the background can be observed.

Upon substituting 1 gram of 1-naphthyl-pyrazolone (5)-3-carboxylic acid for the 1 gram of 1-phenyl-pyrazolone (5)-3-carboxylic acid in the above coating solution formula, light-sensitive coatings having similar properties and producing images of a similar red tone having good light fastness and excellent wash fastness properties may be obtained.

Example II

A coating solution is prepared by mixing the following ingredients into 100 cc. of water:

5 grams thiourea
10 grams citric acid
1 gram 1-tolyl-pyrazolone (5)-3-carboxylic acid
3 grams 1-diethylamino-3-ethoxy-4-diazobenzene-$ZnCl_2$ double salt

This coating solution is coated onto diazotype paper stock by the usual method of drawing the paper in a taut condition past a trough and doctor-blade into which the coating solution has been introduced (spraying methods of application may be substituted). The coated 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 or prolonged storage tests, it is found to have a high degree of resistance to precoupling or spontaneous coupling under storage conditions. Upon exposing the coated and dried paper to proper actinic light in the same manner as in the case of Example I and developing the image by drawing the exposed sensitized paper through an atmosphere of ammonia vapors, the image is reproduced in a very rich maroon shade of red. The image thus produced has excellent light fastness and wash fastness properties and does not bleed into the background. The background is clear and colorless and the image sharp.

Example III

A coating solution is prepared by mixing the following ingredients into 100 cc. of water:

3 grams citric acid
3 grams 2,5,4′-triethoxy biphenyl-1-diazonium chloride $ZnCl_2$ double salt

This solution is coated onto a well sized paper by applying it to one surface of the paper and doctoring off the excess solution in the usual manner. The coated paper is then dried in the usual manner by drawing it through a heated drying chamber. It is then exposed to ultraviolet light under a suitable original and the image is developed by moistening the sensitized and exposed side of the coated paper with a solution containing the following ingredients in 200 cc. of water:

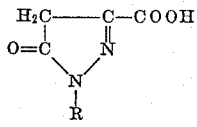
2.5 grams 1-phenyl-pyrazolone (5)-3-carboxylic acid
90 grams sodium citrate
$\frac{1}{10}$ gram saponin

A deep red positive image is produced which has excellent light fastness and wash fastness properties.

I claim:

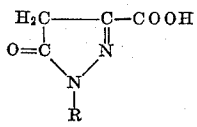
1. A diazotype photo-reproduction material comprising a light-sensitive layer on a suitable

base containing as the azo dye coupling component a compound of the formula



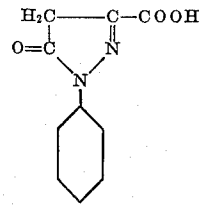
wherein R is an aryl radical and a light-sensitive monodiazonium salt of a p-diamino benzene compound.

2. A diazotype photo-reproduction material comprising a light-sensitive layer on a suitable base containing as the azo dye coupling component a compound of the formula



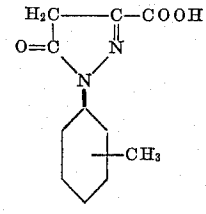
wherein R is an aryl radical and a light-sensitive monodiazonium salt of a benzene compound having a substituted amino group in para position to the diazonium group.

3. A diazotype photo-reproduction material comprising a light-sensitive layer on a suitable base containing as the azo dye coupling component a compound of the formula



and 1-monoethylamino-4-diazo benzene $ZnCl_2$ double salt.

4. A diazotype photo-reproduction material comprising a light-sensitive layer on a suitable base containing as the azo dye coupling component a compound of the formula



and 1-diethylamino-3-ethoxy-4-diazo benzene $ZnCl_2$ double salt.

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