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DIAZOTYPE CONTAINING AS THE AZO COMPONENT A QUATERNARY SALT OF 2-METHYL - 6 - METHOXY - BENZOSELENAZOLE

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1 Claim. (Cl. 95—6)

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This invention relates to photoprinting material for the direct reproduction of positive prints from positive originals and negative prints from negative originals. More particularly, it relates to a photoprinting material containing a coupling component which will couple with the undecomposed diazonium compound in the density areas after exposure to light and upon development in an alkaline medium, to give an azo dye image, and to the process of producing such photoprinting material.

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 methylketone; and processes based upon the light sensitivity of the o-nitro-diaminotriphenyl-methane bases. With the exception of the processes based upon the light sensitivity of aromatic diazo compounds, these suggested photoprinting processes for the reproduction of positive copies from positive originals 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, and after exposure under the original to be copied is developed by contact with a 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 dye image is effected after exposure by contacting the

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light sensitive layer with ammonia gas. For optimum results, it is usually necessary to limit the selection of the diazo compound to the diazo compounds derived from aromatic p-diamines and o-aminonaphthols, since premature coupling of the dye components may take place if other types of diazos are used in the light sensitive layer together with the coupling component, thus reducing the keeping quality of the coated carrier.

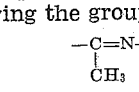
In photoprinting processes of this type, it is highly desirable to produce a copy which will have a distinctive color preferably of a dark shade on a clear white background so that the image will be sharp. It is also desirable to have a material which will give gradation of shade throughout the high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

The coupling components must be stable, fast to light, and insensitive to alkali. They should be soluble in water, yet the dyestuff produced therefrom should be water insoluble. Only few serviceable compounds are available as coupling components, such as phenols, amines, animophenols, pyrazoles, carbazoles, and sultones.

An object of the present invention is to provide new photoprinting material containing a coupling component which will couple with an undecomposed diazonium salt in the density areas after exposure to light and upon development in an alkaline medium to give an azo dye image.

Another object of the invention is to provide a process of producing such photoprinting material.

I have discovered that a valuable photoprinting material may be obtained by incorporating on a carrier a quaternary salt of a heterocyclic compound having the grouping



in the ring. Such heterocyclic compounds may be, for example, quaternary salts of a 2-methyl quinoline, a 2-methyl thiazole, a 2-methyl benzoselenazole, a 2-methyl benzoxazole, a 2-methyl benzothiazole, a 2-methyl oxazole, a 2-methyl pyridine, a 2-methyl pyrimidine, a 2-methyl selenazole, etc. Any suitable light-sensitive diazonium compound may be used in a one-component system. In a two-component system, a diazotized phenylene diamine, in which one amino group is substituted, an o-aminophenol or 3-aminocarbazole may be used.

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 quaternary salt of the heterocyclic compound, a light sensitive diazonium compound, a mild acid such as citric acid, thiourea, and water. The coating is effected in the usual manner by applying the coating solution 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 vapor or other suitable alkaline materials.

As a diluent for the coating solution organic solvents of high volatility, such as alcohols, ethers, ketones, etc., may be mixed with water. Such diluents may be employed in the coating solution in cases where the base material or carrier is such that it will resist the penetrating and solvent action of the diluent.

In another manner of carrying out this process, light-sensitive diazonium compound only is added to the mild acid solution and coated on to 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 coupling component necessary to combine with the undecomposed diazonium compound to form a dye in the unexposed areas.

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, color-intensifiers and light sensitive intensifiers.

A wide range of colors may be produced by this process. By proper selection of the coupling component and the diazonium salt an image can be reproduced in almost any desired color.

The diazonium compounds are sensitive to light waves in the violet and ultra-violet range. Consequently, any source of light such as a quartz mercury vapor arc lamp which emits rays in that region may be employed for exposing the light-sensitive layer for the purpose of decomposing the diazonium compound in the high-light areas. Other sources of light which may be employed include incandescent lamps, arc lamps, and fluorescent lamps. However, the process is not restricted to the frequencies of the violet and near ultra-violet range, since the sensitivity of the diazonium compounds can be adjusted to permit the absorption of other frequencies such as those in the red and blue ranges.

The practice of this invention may be best understood by reference to the following specific examples, which are presented as illustrative of the process involved without any intention of introducing limitations. Unless otherwise stated the parts are given by weight.

Example I

A coating solution was prepared by dissolving 10 grams of citric acid, 5.4 grams of thiourea, 1.6 grams of p-diethylaminobenzene diazonium chloride-zinc chloride double salt, and 2.7 grams of 2-methyl quinoline methomethyl sulfate, distilled water, and adjusting the volume to 100 cc. It was coated out on paper, exposed under a positive picture to ultra-violet light, and developed by gaseous ammonia. A blue-black print on a colorless background resulted.

Storage of the prints at 38° C. and 75% relative humidity for twenty hours prior to printing and developing induced no precoupling.

Example II

In place of the 2-methyl quinoline methomethyl sulfate in Example I, the following coupling components were used. The specific amounts of color component employed and the colors produced are set forth in the following table:

Coupler	Amount	Dye Color
	Grams	
2,6-Dimethylquinoline ethiodide	3.2	green-black.
2-Methyl-3-phenyl-4-quinazolone etho-p-toluene sulfonate.	3.5	brown.
2-Methyl-4,5-dihydrothiazole ethiodide	3.2	green.
2-Methyl-6-methoxy benzoselenazole ethiodide.	3.8	blue.
2-Methyl-benzoxazole ethiodide	3.6	brown.
2-Methyl-5,8-dimethoxyquinoline ethiodide.	3.6	Do.
2,6-Dimethylbenzothiazole ethiodide	3.2	blue-black.
2-Methyl-6-methoxyquinoline ethiodide	3.2	violet.
2-Methyl quinoline metho-p-toluene sulfonate.	3.8	green-black.

Example III

A melamine-formaldehyde resin solution was prepared by adding about 4 cc. of concentrated hydrochloric acid to a rapidly stirred suspension of ten grams a suitable melamine formaldehyde resin (such resins are described in U. S. Patents 2,291,079, 2,291,080 and 2,345,543) in 50 cc. of water at 50° C. After cooling, there was added 3.5 grams of 2-methyl quinoline ethiodide, 1.6 grams of p-diethylaminobenzene diazonium borofluoride and 10 grams of citric acid. The solution was made up to 100 cc. with water and coated on paper. After drying, the paper was exposed to ultra-violet light beneath a positive picture and developed with gaseous ammonia. An intense blue-black image on white background resulted.

Example IV

A coating solution was prepared from 10 grams of citric acid, 3.8 grams of 2-methyl-6-methoxybenzoselenazole ethiodide, 5.4 grams of thiourea, and 1.5 grams of naphthalene-2-diazo-1-oxide-5-sulfonic acid and water adjusted to total volume of 100 cc. This was coated on paper and upon printing and developing, as in Example I, gave a violet image on a white background.

Example V

A solution of 2.1 grams of 4-benzoylamino-2,5-diethoxy benzene diazonium chloride-zinc chloride double salt, 10 grams of citric acid, and 5.4 grams of thiourea was made up to 100 cc. with water. After coating on paper, prints were made under a positive picture and developed with a suspension prepared by making alkaline a solution of 3 grams of 2-methyl quinoline methomethyl sulfate in 60 cc. of water. Violet prints on a white background were obtained.

The coupling components of the present invention are in general best suited for use in aqueous diazotype two-component papers, since their salt-like character reduces their solubility in organic solvents. They possess the advantage of being easily water soluble, without possessing the disadvantage of conferring solubility upon the developed dye. The colors are brilliant and of excellent density.

I claim:

A light-sensitive diazotype photoprinting material comprising a suitable base carrying a light-sensitive layer containing a light-sensitive diazo

derivative of a p-diamino compound of the benzene series and as an azo coupling component a quaternary salt of 2-methyl-6-methoxy-benzoselenazole.

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