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PHLOROGLUCIDE CONTAINING DIAZO PHOTOPRINTING MATERIAL

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6 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-diaminotriphenyl-methane 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 dye

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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 usually necessary to limit the selection of the diazo compound to the diazo salts 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 components, thus reducing the keeping quality of the coated carrier.

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.

Diazo sulfonates will not couple with a coupling component in the absence of strong actinic light. However, they may be employed in a photoprinting process as follows. A solution of a diazo sulfonate and a coupling component is coated upon a carrier, dried, and exposed to strong actinic light under an original. The portions of the diazo sulfonate which are exposed to the actinic light are decomposed to form a diazo compound which will couple with the coupling component to give an azo dye image. By this method, a positive is obtained from a negative, and a negative is obtained from a positive.

The coupling components must be stable, fast to light and insensitive to alkali. They should be soluble in water or in an organic solvent, yet the dyestuff produced therefrom should be water insoluble. Only few serviceable compounds are available as coupling components, such as phenols, amines, aminophenols, pyrazolones, carbazoles, sultones, naphthols, acetoacetic acid esters and acetanilides.

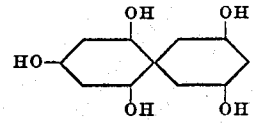
An object of the present invention is to provide new photoprinting material containing a coupling component which will couple with an undecomposed diazonium salt in the density areas after exposure to light and upon development in an alkaline medium to give an azo dye image.

Another object is to provide photoprinting material which contains a coupling component which will couple with the decomposed diazo sulfonate in the high-light areas upon exposure to light to give an azo dye image.

A further object is to provide a process of producing such photoprinting material.

I have discovered that a valuable photoprint-

ing material may be obtained when phloroglucide, an ester of phloroglucide, an ether of phloroglucide, or a salt of phloroglucide is employed as a coupling component. Phloroglucide is believed to have the formula



As examples of esters of phloroglucide there may be mentioned the formate, acetate, propionate, butyrate, benzoate, naphthionate and anthranilate. As examples of ethers of phloroglucide, there may be mentioned the methyl, ethyl, propyl, amyl, butyl, hexyl, phenyl, benzyl, naphthyl, and the like, ethers. As examples of salts of phloroglucide, there may be mentioned the sodium, potassium, calcium, barium, magnesium, copper, and the like, salts. These compounds may be further substituted for example by COOH, SO_3H, NO_2, NH_2, Cl, alkoxy, aryloxy and benzyl groups in which case, however, at least one nuclear position should be unsubstituted.

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 phloroglucide or its derivatives, 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 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 or other suitable alkaline materials.

The coupling components of the present invention are particularly suited to non-aqueous coatings, such as those obtained from resinous solutions. Organic solutions of high volatility such as alcohols, ethers and ketones, may also be employed in the place of water. Such diluents may 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 coupling component necessary to combine with the undecomposed diazonium salt to form a dye 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, color intensifiers and light-sensitive intensifiers.

The colors produced by this process are intensely dark, and are similar to those obtained when phloroglucinol is employed as the coupling component. However, unlike phloroglucinol, the two-component diazotype coatings using phloroglucide or its derivatives as the coupling component produce a diazotype photoprinting material which will not precouple during long storage prior to use. Undesirable background color in the prints subsequently made from such diazotypes is accordingly eliminated.

The following examples illustrate methods of carrying out the present invention, but it is to be understood that these examples are given by way of illustration and not of limitation.

Example 1

A solution of 0.6 gram phloroglucide in 70 cc. of ethanol was coated on paper and dried. The paper was then coated with a solution of 1.6 grams of p-diethylaminobenzenediazonium chloride-zinc chloride double salt, 10 grams citric acid, and 5.4 grams thiourea in 100 cc. aqueous solution. Upon exposure to ultraviolet light under a positive picture and development with ammonia vapors, an intense violet image on a white background was obtained.

Storage of the above unexposed paper for 20 hours at 38° C. and 75% relative humidity, followed by exposure and development, gave prints whose backgrounds showed no appreciable discoloration.

When an equivalent amount of phloroglucinol was substituted for the phloroglucide in the above paper, and the coated paper stored under the same conditions as above upon exposure and development, there were obtained prints having badly discolored backgrounds indicating that a high degree of coupling had taken place during storage.

When methyl 2,4,6-trihydroxybenzoate (as disclosed in U. S. P. 2,286,656) is used instead of phloroglucide, and the coated paper stored under the same conditions, the results are similar to those experienced with phloroglucinol.

Example 2

In the process of Example 1, 1.5 grams of naphthalene-2-diazo-1-oxide-5-sulfonic acid is substituted for the 1.6 grams of p-diethylaminobenzenediazonium chloride-zinc chloride. Similar intense violet images on excellent clear white backgrounds are obtained.

Storage of the unexposed paper of this example for twenty hours at 38° C. and 75% relative humidity, followed by subsequent exposure and development, gave prints whose backgrounds showed no appreciable discoloration.

Example 3

A coating solution of 0.3 gram of phloroglucide, 5 grams maleic acid, and 0.7 gram of p-diethylaminobenzenediazonium borofluoride (in 3 cc. formic acid) was dissolved in 50 cc. of a 12% acetone solution of cellulose acetate butyrate. This solution was coated onto cellulose acetate foil and onto paper. Upon exposure to ultraviolet light under a suitable positive and development with ammonia vapors, intense, almost black prints, on colorless background were obtained.

Storage under the conditions in Example 1, exposing and developing, gave pictures in which the whites were clear and showed no appreciable staining resulting from precoupling.

When phloroglucinol was substituted for the phloroglucide in the same papers, prints were obtained, after similar storage as above, in which the unexposed portions could scarcely be distinguished from the exposed surfaces.

Phloroglucide acetate gives the same good results as are obtained from phloroglucide.

Example 4

Paper was coated with a solution of 2.1 grams of 4 - benzoylamino - 2,5 - diethoxy - benzenediazonium chloride-zinc chloride double salt, 10 grams citric acid, and 5.4 grams thiourea in 100 cc. of water. The dried coating was exposed to ultraviolet light and sponged with a solution of 2 grams phloroglucide dissolved in 100 cc. of water made alkaline with sodium hydroxide. Dark prints on a white background were obtained.

Example 5

A solution of 10 grams of citric acid, 5.4 grams of thiourea, and 1.5 grams of p-phenylaminobenzenediazonium sulfate in 98 cc. of water was added to a solution of 0.6 gram phloroglucide in 4 cc. of dimethylformamide. The solution was coated on paper and when exposed and developed as in Example 1, gave excellent intense pictures.

Storage of the unexposed paper of this example for twenty hours at 38° C. and 75% relative humidity, followed by exposure and development, gave prints whose backgrounds were not appreciably discolored.

When phloroglucinol was substituted for phloroglucide in the coating solution of this example and the coated paper stored under the above conditions, then exposed and developed, the prints obtained had badly discolored backgrounds.

In any of the foregoing examples, any of the esters, ethers or salts of pholoroglucide, such as phloroglucide acetate, monomethyl ether of phloroglucide and sodium phloroglucide, can be substituted for the phloroglucide to produce the same results as are obtained when using phloroglucide. Diazosulfonates may also be substituted for the diazo compounds when negative prints are desired. A typical diazo sulfonate coating solution contains 3.5 grams of 4-benzoylamino-2,5-dimethoxybenzene diazo sulfonate and 2 grams of the monomethyl ether of phloroglucide in 100 cc. of a 1% sodium hydroxide solution. After drying such a coating on a suitable base, exposing under a negative to ultraviolet light and developing with ammonia gas, an excellent positive picture can be obtained.

I claim:

1. A photoprinting material containing a light-sensitive diazo compound and a phloroglucide compound as the azo dye component.

2. A photoprinting material containing a light-sensitive diazo compound and phloroglucide.

3. A photoprinting material containing a light-sensitive diazo compound and an ester of phloroglucide.

4. A photoprinting material containing a light-sensitive diazo compound and an ether of phloroglucide.

5. A photoprinting material containing a light-sensitive diazo compound and phloroglucide acetate.

6. A photoprinting material containing a light-sensitive diazo compound and phloroglucide methyl ether.

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