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[54] **TWO-COMPONENT DIAZO-TYPE PHOTOPRINTING MATERIAL FOR USE IN WET DEVELOPMENT**
7 Claims, No Drawings

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ABSTRACT: A two-component diazo-type photoprinting material which is developed with an alkaline aqueous solution containing no coupler, said photoprinting material comprising a supporting sheet and a light-sensitive layer provided on one face of said supporting sheet, said light-sensitive layer containing at least one aromatic diazo compounds and a coupler consisting of at least one aromatic compound adapted to couple to said diazo compound, said coupler being used with the ratio of 0.5–1.5 mols to 1 mol of said diazo compound.

TWO-COMPONENT DIAZO-TYPE PHOTOPRINTING MATERIAL FOR USE IN WET DEVELOPMENT

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a two-component diazotype photoprinting material for use in wet development, said development being conducted by the use of an alkaline aqueous solution containing no coupler.

2. Description of the Prior Art

Conventional diazotype photoprinting materials for use in wet development were of the "one-component diazotype," or more specifically, the light-sensitive layer of such a photoprinting material of the prior art contained only a diazo compound. It has been commonly known that such a photoprinting material, after being exposed to light, is developed by the use of a developing liquid containing, dissolved therein, a coupler which is adapted to produce an azo dyestuff image as the result of its being coupled to the aforesaid diazo compound in the stage of development. The photoprinting materials of the aforesaid prior type had the following shortcoming. Specifically, the coupler contained in the developing liquid was susceptible to being oxidized from contact with ambient air while in use or during storage, and such oxidized coupler constituted a tinting component which made the developing liquid turbid. Therefore, the developing liquid could not be stored for an extended period of time. Furthermore, an exposed photoprinting material which was developed with such a spoiled developing liquid did not produce an unstained, clear print. As a result, the user was required to replace the developing liquid with a fresh liquid as frequently as once every several days.

On the other hand, the so-called "two-component diazotype" photoprinting materials of the prior art were intended for dry development which was conducted by the use of ammonia gas. In case copying was performed by the use of photoprinting materials of this prior type, it was necessary that the color-development reaction had to be perfectly complete by the time that the photoprinting material passed through the developer tank which contained ammonia gas. For this reason, in order to obtain a print having a satisfactory image density, it was necessary that the light-sensitive layer of the photoprinting material of said prior type contain a coupler to an extent of at least four to six times the amount, by mol, of the diazo compound contained therein.

For example, with a photoprinting material whose light-sensitive layer contained a coupler in as small an amount as 0.5–2.0 mols per 1.0 mol of the diazo compound, the color-development reaction showed hardly any progress in one process of development with ammonia vapor. Even after several repeated development operations, there still remained some unreacted diazo compound which hindered obtaining a satisfactory image of print.

SUMMARY OF THE INVENTION

The present invention concerns a novel "two-component" diazotype photoprinting material for use in wet development, and more specifically, it relates to a diazotype photoprinting material which is of an improved shelf life and a superior printing ability due to the fact that the light-sensitive layer of this photoprinting material contains a small amount of coupler relative to the content of the diazo compound.

The diazotype layer of the present invention contains a coupler in such a small amount as 0.5–1.5 mols to 1 mol of the diazo compound which is the principal component of the light-sensitive layer. However, the photoprinting material of the present invention is featured by the fact that it provides a satisfactory image of print when the photoprinting material is developed. The aforesaid range of coupler content is optimal in practice. Although the color-development velocity exhibited by the photoprinting material of the present invention is slightly smaller than that obtained from the conventional photoprinting materials for use in wet development, such a small retardation constituted no problem in the practical use.

More specifically, the photoprinting material of the present invention is intended for development by the use of an alkaline aqueous solution containing no coupler, and therefore, the photoprinting material remains wet with the liquid in an alkaline state for some while after being developed. This insures that the coupling reaction is allowed to make a complete progress during such period, and that as a result, a very clear image of print is formed.

Furthermore, the aforesaid small content of coupler in the photosensitive layer of the photoprinting material of the present invention permits the employment of a coupler which has an increased coupling velocity, since there occurs practically no coupling reaction between the coupler and the diazo compound during storage, and thus the photoprinting material remains extremely stable for an extended period of time.

The aromatic couplers which are used in the present invention can include those which have been used in the developing liquids of the conventional wet development process. They include, for example, 1-naphthol-4-sulfonic acid sodium salt, 2-naphthol-3,6-disulfonic acid sodium salt, 2-hydroxy-3-naphthoic acid-hydroxyethylamide, 2-hydroxy-3naphthoic acid diethylaminoethylamide, 2-hydroxy-3-naphthoic acid morpholinoethylamide, resorcinol, 1-morpholinoacetylamino-7-naphthol, α-resorcylic acid, resorcinol monosulfonic acid sodium salt, α-naphthol, 1-biguanidino-7-naphthol, β-hydroxy naphthoic acid morpholinopropyl amide and β-hydroxy naphthoic acid dimethylaminopropylamide.

It is needless to say that the couplers which can be applied to the present invention are not restricted to those enumerated above. In case these couplers are used in photoprinting materials intended for dry development, the amount of the coupler used must be three to four times that of the coupler used in the photoprinting material of the present invention in order to obtain a satisfactory image of print. In case a coupler is used in such a great amount in a photoprinting material, there arises a severe precoupling phenomenon, and as a result, the photoprinting material cannot be stored for an extended period of time and, accordingly, it is not qualified for being used for practical purposes. More specifically, these couplers have an increased coupling velocity, and therefore, they cannot be used in the so-called two-component photoprinting materials of the prior art. In the present invention, however, there is used, jointly with such a coupler as has been described, an aromatic diazo compound which, when present side-by-side with such coupler, would not give rise to precoupling phenomenon and which easily produce azo dyestuff image when brought into contact with an alkaline aqueous solution and which, as a result, provides the formation of an image of print of a high density. Those aromatic diazo compounds which give satisfactory results include, for example, 1-diazo-4-benzoylamino-2,5-diethoxybenzene·zinc chloride double salt, 1-diazo-4-(4'-methoxy) benzoylamino-2,5-diethoxybenzene·zinc chloride double salt, 1-diazo-4-(4'-methoxy) benzoylamino-2,5-dimethoxybenzene·zinc chloride double salt, 1-diazo-4-(4'-methyl) benzoylamino-2,5-diethoxybenzene·zinc chloride double salt, 4-diazo-2,5-dibutoxyphenylmorpholine·zinc chloride double salt, 4-diazo-2,5-diethoxyphenylmorpholine·zinc chloride double salt, 4-diazo-1-benzylmethylamino-2,5-diethoxybenzene·zinc chloride double salt, and 4-diazo-benzylmethylamino benzene·zinc chloride double salt. It should also be noted that the aromatic diazo compounds which are applied to the present invention are not restricted thereto. While the light-sensitive layer of the present invention is the so-called "two-component" type layer, this light-sensitive layer of the present invention cannot be developed by the dry development process which utilizes ammonia vapor. On the other hand, the light-sensitive layer of the present invention permits a colored image to be obtained in an alkaline aqueous solution which contains no coupler. From these points of view, it may be said that the light-sensitive layer of the present invention is of an intermediate nature between the dry type and the wet type.

With respect to the alkali components for use in the developing liquids of the present invention, there are, for ex-

ample, potassium carbonate, potassium hydroxide, sodium carbonate, potassium metaborate and potassium tetraborate which are used either independently or in combination. A pH of the developing liquid in the range of the order from 11.5 to 12.0 leads to best color development. The light-sensitive layer of the present invention can contain 1 to 3 percent by weight of thiourea, cadmium sulfate, cadmium sulfide or the like to prevent the occurrence of the running of ink. The light-sensitive layer of the present invention further can contain an inorganic or organic acid such as oxalic acid, sulfuric acid, tartaric acid, citric acid and maleic acid, either independently or in appropriate combination. In addition, by incorporating 0.5 to 1 percent by weight of boric acid in the light-sensitive layer, there can be provided a photoprinting material having a further improved shelf life.

The photoprinting material of the present invention has a shelf life which is superior to that of the conventional commercial photoprinting materials intended for dry development process and almost equal to that of the commercial photoprinting materials of the wet development type.

Another feature of the photoprinting material of the present invention lies in the fact that there remains very little unreacted coupler at the time of the copying operation owing to the very small content of the coupler present in the light-sensitive layer. Accordingly, there is hardly noted any phenomenon that the surface of the photoprinting material becomes stained due to the coupler being oxidized during storage of an extended period of time. It has been the accepted idea that the prints made with the photoprinting materials of the wet development type in general have a rather great tendency for color-fading and that, therefore, they are not suitable for copy prints which are to be preserved for a long time. In contrast to these, the copies obtained by the use of the photoprinting materials of the present invention withstand storage of a prolonged period of time.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

EXAMPLE 1

A solution for use in the formation of a light-sensitive layer and consisting of the following components was prepared:

Water	1 liter
Conc. sulfuric acid	4 cc.
Citric acid	20 g.
Boric acid	5 g.
Thiourea	10 g.
Cadmium sulfate	10 g.
Caffeine	10 g.
2-hydroxy-3-hydroxyethylumido naphthoate·HCl	3 g.
4-diazo-2, 5-dibutoxyphenylmorpholine·½$ZnCl_2$	7 g.
Methylene Blue	0.05 g.
Saponin	1 g.

Said solution for use in the formation of a light-sensitive layer was applied onto the precoat layer formed on a surface of a supporting sheet, said precoat layer being formed by applying, on the surface of a sheet form, a solution containing 10 g. of colloidal silica having a grain size ranging from 1 to 5μ, 100 g. of corn starch having a grain size of 5μ, and 60 g. of vinyl acetate emulsion (solid matter being 50 percent); and then the treated supporting sheet was dried, with the result that a diazotype photoprinting material for wet development was obtained. A suitable original was placed on the light-sensitive layer of the photoprinting material, and the assembly was exposed to light in a copying apparatus using a 60 w. fluorescent lamp. The exposed photoprinting material was then developed in an aqueous solution of 5.0 percent of potassium metaborate. The result was that a highly dense, excellent blue image of print was obtained. The obtained copy was placed in a file and the file was stored for 6 months in an atmosphere at 30° C. and a relative humidity of 80 percent, but there was noted no occurrence of any stained surface of the copy.

EXAMPLE 2

Water	1 liter
Oxalic acid	20 g.
Thiourea	10 g.
Cadmium chloride	10 g.
1-biguanidino-7-naphthol·HCl	8.5 g.
1-diazo-4-(4'-methoxy) benzoylamino 2,5-dimethoxybenzene·½$ZnCl_2$	18 g.
Saponin	1 g.
Patent pure Blue	0.1 g.

A solution consisting of the foregoing components for the formation of a light-sensitive layer was applied onto a surface of a white supporting sheet and dried, with the result a diazotype photoprinting material for wet development was obtained.

An original was placed on the light-sensitive layer of the photoprinting sheet thus obtained, and they were exposed to high-pressure mercury lamp. Thereafter, the exposed photoprinting material was subjected to development with an alkaline aqueous solution containing 2 percent by weight of potassium carbonate and 2 percent by weight of potassium tetraborate. The result was that a well-contrasted blue-violet image of print was obtained.

EXAMPLE 3

A solution containing 20 g. of colloidal silica having a grain size ranging from 1 to 5μ and 40 g. of vinyl acetate emulsion (solid matter being 50 percent) in 1 liter of water was prepared, and this solution was precoated on a surface of a white sheet. Thus, a supporting sheet for use in the preparation of a photoprinting material was produced.

On said precoated face of said supporting sheet was applied a solution for the formation of a light-sensitive layer, consisting of the following components:

Water	1 liter
Sulfuric acid	5 cc.
Boric acid	5 g.
Resorcinol monosulfonic acid sodium salt	3 g.
4-diazo-2,5-diethoxyphenyl morpholine·½$ZnCl_2$	10 g.
Methylene Blue	0.06 g.
Saponin	1 g.

and was dried, with the result that a diazotype photoprinting material for wet development was obtained. By subjecting this photoprinting material to an operation and treatment in a manner similar to those described in connection with example 1, to obtain a copy, a brown highly dense image of print was formed.

EXAMPLE 4

A solution for forming a light-sensitive layer having the same composition with the solution for forming a light-sensitive layer in example 1, with the only exception that 2-hydroxy-3-naphthoic acid hydroxyethylamide·HCl was replaced by 4 g. of 2-hydroxy-3-naphthoic acid morpholinoethylamide·HCl was prepared. Also, a solution for forming a light-sensitive layer was prepared in the same way as that in example 1 with the only exception that 4 g. of 2-hydroxy-3-naphthoic acid diethylaminoethylamide was used, with the remainder being exactly of the same composition with the solution in said example.

These two types of solutions for forming light-sensitive layers were subjected to treatment in the same way as described in the preceding examples, to obtain two types of diazotype photoprinting materials for wet development. These photoprinting materials were subjected to copying operations and were developed with the same developing liquid as the one used in example 1. The result was that very clear images of print were formed. Also, the resulting copies had a durability in the same degree as that of the copy obtained in example 1.

EXAMPLE 5

A solution for forming a light-sensitive layer was prepared in the same way as that described in example 1, with the only exception that the 4-diazo-2,5-dibutoxyphenyl morpholine·½$ZnCl_2$ was replaced by 7 g. of 4-diazo-benzyl-methylamino-2,5-diethoxybenzene·½$ZnCl_2$ was used, the remainder being the same in composition with the solution of example 1.

This solution was subjected to treatment in exactly the same way as that described in example 1, and a diazotype photoprinting material for wet development was obtained. Also, a copy was taken in exactly the same way as that in example 1, and the result was that a very clear sky-blue image of print was formed. While the color-development velocity at the time of the development process was slightly smaller than that of the photoprinting material of example 1, this delay was practically negligible in nature.

EXAMPLE 6

A solution for forming a light-sensitive layer was prepared in exactly the same way as that in example 2, with the only exception that 1-biguanidino-7-naphthol·HCl was replaced by 10 g. of 1-naphthol-4-sulfonic acid sodium salt was used, the remainder being of the same composition with the solution of example 1. This solution was subjected to treatment in the same way as that described in example 2, and a diazotype photoprinting material for wet development was obtained. The photoprinting material thus obtained was subjected to copying operation in exactly the same way as that described in example 2, and a clear violet image of print was obtained.

EXAMPLE 7

A solution for forming a light-sensitive layer was prepared in the same way as that in example 1 with only the exception that 2-hydroxy-3-naphthoic acid hydroxyethylamide·HCl was replaced by a mixture of 3 g. of 2-hydroxy-3-naphthoic acid morpholinoethylamide/and 1 g. of 1-biguanidino-7-naphthol, the remainder being the same in composition with the solution of example 1. This solution was subjected to treatment in the same way as that in example 1, and a diazotype photoprinting material for wet development was obtained. Also, the resulting photoprinting material was subjected to copying operation in the same way as that in example 1, and the result was that a clear blue-violet image of print which was greater in image density than that obtained in example 1 was obtained.

What is claimed is

1. A two-component diazotype photoprinting material for wet development by an aqueous alkaline solution free of coupler, said material comprising a supporting sheet and a light-sensitive layer on one surface of said sheet, said layer containing

A. at least one diazo compound selected from the group consisting of 4-diazo-2,5-dibutoxyphenylmorpholine zinc chloride double salt, 4-diazo-2,5-diethoxyphenyl-morpholine zinc chloride double salt, 4-diazo-1-benzyl-methylamino-2,5-diethoxybenzene zinc chloride double salt; and

B. at least one coupler selected from the group consisting of 1-naphthol-4-sulfonic acid sodium salt, 2-naphthol-3,6-disulfonic acid sodium salt, 2-hydroxy-3-naphthoic acid hydroxyethylamide, 2-hydroxy-3-naphthoic acid diethylaminoethylamide, 2-hydroxy-3-naphthoic acid morpholinoethylamide, resorcinol, 1-morpholinoacetylamino-7-naphthol, α-resorcylic acid, resorcinol monosulfonic acid sodium salt, α-naphthol, 1-biguanidino-7-naphthol, β-hydroxy naphthoic acid morpholinopropylamide, and β-hydroxy naphthoic acid dimethylaminopropylamide

the coupler being mixed with said diazo compound in an amount in the range of from 0.5 to 1.5 mols of said coupler to 1 mol of said diazo compound.

2. A two-component diazotype photoprinting material for wet development according to claim 1, wherein said light-sensitive layer further contains an acid stabilizer and an agent adapted to prevent the running of ink.

3. A two-component diazotype photoprinting material for wet development according to claim 2, wherein said acid stabilizer is a substance selected from the group consisting of oxalic acid, sulfuric acid, tartaric acid, citric acid, maleic acid and boric acid, and said agent adapted to prevent the running of ink is a substance selected from the group consisting of thiourea, cadmium sulfate and cadmium chloride.

4. A two-component diazotype photoprinting material for wet development according to claim 1, wherein said supporting sheet has a precoated surface.

5. A method of making photoprints, which comprises the steps of

1. exposing to actinic radiation a two-component diazotype photoprinting material comprising a supporting sheet and a light-sensitive layer on one surface of said sheet, said layer containing

A. at least one diazo compound selected from the group consisting of 4-diazo-2,5-dibutoxyphenylmorpholine zinc chloride double salt, 4-diazo-2,5-diethoxyphenyl-morpholine zinc chloride double salt, 4-diazo-1-benzyl-methylamino-2,5-diethoxybenzene zinc chloride double salt; and

B. at least one coupler selected from the group consisting of 1-naphthol-4-sulfonic acid sodium salt, 2-naphthol-3,6-disulfonic acid sodium salt, 2-hydroxy-3-naphthoic acid hydroxyethylamide, 2-hydroxy-3-naphthoic acid diethylaminoethylamide, 2-hydroxy-3-naphthoic acid morpholinoethylamide, resorcinol, 1-morpholinoacetylamino-7-naphthol, α-resorcyclic acid, resorcinol monosulfonic acid sodium salt, α-naphthol, 1-biguanidino-7-naphthol, β-hydroxy naphthoic acid morpholinopropylamide, and β-hydroxy naphthoic acid dimethylaminopropylamide

the coupler being mixed with said diazo compound in an amount in the range of from 0.5 to 1.5 mols of said coupler to 1 mol of said diazo compound; and then

2. treating the material with an aqueous alkaline solution free of coupler to develop an image.

6. A method according to claim 5, in which the aqueous alkaline solution is selected from the group consisting of aqueous solutions of potassium carbonate, potassium hydroxide, sodium carbonate, potassium metaborate and potassium tetraborate.

7. A method according to claim 5, in which the pH of the aqueous alkaline solution is in the range of about 11.5 to 12.0.