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3,725,066

**DIAZO-TYPE MULTICOLOR REPRODUCTION PROCESS**

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No Drawing. Filed Aug. 31, 1970, Ser. No. 68,518  
Claims priority, application Japan, Sept. 1, 1969, 44/68,938

Int. Cl. G03c 5/34, 1/58

U.S. Cl. 96—49

8 Claims

**ABSTRACT OF THE DISCLOSURE**

A coloring material in use for the diazo-type multicolor reproduction which comprises a thermovolatilic or thermosublimative acid addition salt of a thermovolatilic or thermosublimative azo coupling component having an amino group, and a diazo-type multicolor reproduction process using such coloring material.

This invention relates to a coloring material useful in diazo-type multicolor reproduction. More detailedly, the invention relates to a coloring material useful in diazo-type multicolor reproduction comprising a thermovolatilic substance which can color portions of a photosensitive paper corresponding to predetermined portions of an original selectively to different hues without substantial mingling of colors.

We previously proposed a process for diazo-type multicolor reproduction based on the discovery that predetermined portions of an original can be reproduced into different hues regardless of difference or similarity of the light transmission in the original by conducting the steps of (A) exposing to light a diazo-type photosensitive material containing at least one diazonium salt (c) and (B) heating a layer of at least one thermovolatilic or thermosublimative coupler disposed in a face-to-face contact with the diazo-type photosensitive material at a portion corresponding to a predetermined portion of an original, the steps being carried out coincidentally or in an order of (A) to (B) or (B) to (A), and then developing the exposed photosensitive material in the pressure of a coupler (b) having a lower coupling rate under developing conditions than the thermovolatilic or thermosublimative coupler (a).

In this diazo-type multicolor reproduction process a thermovolatilic or thermosublimative coupler is applied to the back surface of one or more predetermined portions of a transparent or semi-transparent original.

This heat-transferable coupler is applied in the form of an ink-like composition, waxy composition or the like to the back surface of an original by coating, transferring or other procedures, but in general, thermovolatilic or thermosublimative couplers are chemically instable and tend to be easily discolored. When the coupler applied to the back surface of an original is discolored and the light transmission lowered, coloration is caused to occur in portions other than the portions corresponding to the predetermined portions of the original by the development treatment, with the result that a copied image excellent in distinctness cannot be obtained.

In the above-mentioned diazo-type multicolor reproduction process, the thermovolatilic or thermosublimative coupler is heat-transferred from the coupler layer applied to the back surface to a diazo-type photosensitive material. It has been experientially found that under some reproducing conditions only several multicolored copies can be obtained from one treated original.

It has now been found that the above defects can be overcome by using a thermovolatilic or thermosublimative

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acid addition salt of a thermovolatilic or thermosublimative acid addition salt of a thermovolatilic or thermosublimative azo coupling component containing an amino group.

Accordingly, a primary object of this invention is to provide a coloring material in use for the diazo-type multicolor reproduction process which is chemically stable by itself and accordingly is excellent in storage stability.

Another object of this invention is to provide a coloring material in use for the diazo-type multicolor reproduction process, which does not substantially damage the transparency or semi-transparency of the original when it is applied to the back surface of the original by coating, writing, transferring or bonding, and which can color only portions corresponding to the predetermined portions of the original and give multicolored copies having an image accurately corresponding to the image of the original.

Still another object of this invention is to provide a coloring material for use in diazo-type multicolor reproduction process which makes it possible to produce stably a great many multicolored copies from one original treated with a heat-transferable coupler.

The above-mentioned objects of this invention can be attained by a coloring material useful in diazo-type multicolor reproduction which comprises a thermovolatilic or thermosublimative acid addition salt of a thermovolatilic or thermosublimative azo coupling component containing an amino group.

Suitable thermovolatilic or thermosublimative azo coupling components containing an amino group may be selected from aminophenols, aromatic amines and amines containing active methylene groups. Typical examples of such azo couplers are as follows:

Aminophenols and benzene type amines:

Meta-aminophenol  
Para-aminophenol  
Ortho-aminophenol  
Meta-phenylenediamine  
Para-phenylenediamine  
2-amino-paracresol  
3-amino-orthocresol  
3-amino-paracresol  
5-amino-orthocresol  
Para-chloroaniline  
Meta-aminobenzoic acid  
3,4-diamino-paratoluene

Active methylene group-containing amino compounds:

1-phenyl-3-methyl-pyrazolone(5)  
1-phenyl-3-carboxypyrazolone  
3-methylpyrazolone  
Acetoacetic acid anilide  
Acetoacetic-o-chloroanilide  
Para-carboxyacetoacetoanilide

Any of the above-mentioned couplers may be used in this invention but it is preferable to use those having a melting point of 100–150° C. Among them particularly preferred are those whose thermovolatility or thermosublimativity is highly increased when converted to an acid addition salt. As typical instances of such coupling component there may be cited meta-aminophenol and phenyl-methylpyrazolone.

M.P. (° C.)

Meta-aminophenol	122
Meta-aminophenol hydrochloride	119
1-phenyl-3-methylpyrazolone(5)	127
1-phenyl-3-methylpyrazolone(5) hydrochloride	96

When the coloration tests were effected with use of the above-mentioned coupling components in combination with a diazo-type photosensitive material comprising

4-diazo-N,N-dimethylaniline chloride  $\frac{1}{2}\text{ZnCl}_2$  double salt and 2,7-dihydroxynaphthalene-3,6-disulfonic acid sodium salt, it was found that while free-meta-aminophenol can give 10-20 copies, its hydrochloride can give 30-40 copies under the same conditions, and that use of the hydrochloride salt of 1-phenyl-3-methylpyrazolone(5) can increase the number of copies by 20-30 sheets as compared with free 1-phenyl-3-methylpyrazolone(5).

In this invention, the above-mentioned couplers are used in the form of acid addition salts. Any acid is used for forming the acid addition salts of the coupling components, as long as the resulting salts are thermovolatilic or thermosublimative.

As acids preferably used in this invention there may be cited the following compounds:

Inorganic acids such as

hydrochloride,  
hydrobromic acid, and  
other hydrohalogenic acids;

Organic sulfonic acids such as

p-toluene sulfonic acid, and  
o-toluene sulfonic acid; and

Carboxylic acids such as

chloroacetic acid ( $\text{ClCH}_2\text{COOH}$ ),  
chloropropionic acid ( $\text{ClCH}_2\text{CH}_2\text{COOH}$ ),  
acetic acid ( $\text{CH}_3\text{COOH}$ ),  
salicylic acid ( $\text{C}_6\text{H}_4(\text{OH})(\text{COOH})$ ),  
2,6-dichlorobenzoic acid ( $\text{C}_6\text{H}_3\text{Cl}_2(\text{COOH})$ ),  
3,4-dimethylbenzoic acid ( $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{COOH}$ ),  
oxalic acid ( $(\text{COOH})_2$ ),  
oxalic acid hydrate ( $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ ),  
o-sulfobenzoic acid ( $\text{C}_6\text{H}_4(\text{CO}_2\text{H})(\text{SO}_3\text{H}) + 3\text{H}_2\text{O}$ ),  
trichloroacetic acid ( $\text{CCl}_3\text{COOH}$ ),  
formic acid ( $\text{HCOOH}$ ),  
benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ),  
methacrylic acid ( $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$ ), and  
butyric acid ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ ).

The preparation of acid addition salts of azo coupling components may be accomplished according to a customary method by mixing an azo coupling component with an acid such as cited above in a suitable medium.

In accordance with this invention, the acid addition salt of the azo coupling component is formed into a coating composition by dispersing the salt into a liquid, semi-solid or solid dispersion medium. The preparation of such coating composition will be described below by referring to some examples. The acid addition salt may be prepared in advance of the preparation of the coating composition, or it may be formed at the time of preparing the coating composition. In the latter case, it is possible to make an excess of the acid present in the composition.

#### (1) Ink-like composition:

Thermovolatilic acid addition salt of—	Percent
Heat-transferable coupler -----	5.0-25.0
Binder -----	0-5.0
Coloring material -----	0-3.0
Dispersing assistant -----	0-5.0
Dispersion medium -----	Balance

As the dispersion medium aliphatic alcohols such as dimethyl formamide, ethanol, n-propanol, isopropanol and isobutyl alcohol, aromatic solvents such as benzene, toluene and xylene, esters, OH-group-containing, neutral liquids having a boiling point of 100-240° C., such as water, high boiling point alcohols, e.g., n-hexyl alcohol, n-heptyl alcohol, 3-heptanol, 4-heptanol and octanol, and glycols, e.g., glycerin, ethylene glycol, propylene glycol, poly ethylene glycol, 1,3-butadiol may be used, 1,4-butadiol and 2,3-butadiol. These solvents may be used singly or in combination. As the thermovolatilic acid addition salt those which are mentioned above may be used. It

is possible to incorporate a coloring material so as to confirm the formation of a film of the composition, or to use a binder for the purpose of obtaining a good fixation of the coupler.

The composition of the above recipe is applied to the back surface of a portion of the original predetermined to have a different hue by means of a brush, an installed felt pen, a ball pen, a coating roller, a sprayer or a printing machine.

#### (2) Waxy composition:

Thermovolatilic acid addition salt of—	Percent
Heat-transferable coupler -----	5-25
Wax -----	85-15
Oil -----	10-40
Coloring material -----	0-20.0

The composition of the above recipe is shaped to have a crayon stick-like form or a chalk-like form, and the back surface of a portion of an original predetermined to have a different hue is painted therewith. It is also possible to form a pressure-sensitive transfer sheet by melting the above composition or dissolving it in a suitable solvent and coating the melt or solution on a substrate such as paper and plastic film. The so formed pressure-sensitive transfer sheet is overlapped on the back surface of an original sheet, and then pressing is effected thereon by means of a typewriter or other writing means to form a heat-transferable layer on the back surface of an image predetermined to have a different hue.

(3) Coupler-transferring sheet: The ink-like composition which is described in (1) or a composition obtained by incorporating a binder or an extender into such ink-like composition is coated on a transparent or semi-transparent sheet such as paper, plastic film or non-woven fabric. The so formed sheet for heat-transferring the coupler is cut into a desired size, if necessary, and then applied to the back surface of a portion of an original determined to have a different hue. It is possible to form a pressure-sensitive adhesive layer on the back surface of the coupler-transferring layer for preventing it from exfoliating from the original.

The original treated with the coloring material of this invention for the diazo-type multicolor reproduction is piled on a diazo-type photosensitive material containing at least one diazonium salt (c) and the assembly is subjected to the light exposure and the treatment for heat transferring the coloring material. The light-exposed and heat-transferred photosensitive material is then developed in the presence of a coupler (b) having a lower coupling rate than the coloring material under development conditions.

The multicolor reproduction with the use of the coloring material of this invention is performed by the following procedures.

At least one layer of the coloring material of this invention is applied to the back surface of one or more predetermined portions of a transparent or semi-transparent original to form an original for the multicolor reproduction. The so formed original for the multicolor reproduction is overlapped on a diazo-type photosensitive material containing at least one diazonium salt (c) in a manner such that the photosensitive surface of the photosensitive material will confront the heat-transferable coupler layer, and the light-exposure and heating are effected coincidentally or successively in this order or the reverse order. Thus, the heat-transferable coupler (a) is heat-transferred to the surface of the predetermined portion of the photosensitive material, and the light resolution of the diazonium salt (c) in the photosensitive material is caused to occur depending on the light transmission of the original. When the so exposed photosensitive material is developed by a method known per se, at the predetermined portion to which the coupler (a) of the coloring material has been heat-transferred, the diazonium salt (c) at the non-exposed area reacts selectively and

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preferentially with the coupler to form a dyestuff (c)-(a) and at other portion the diazonium salt (c) at the non-exposed area reacts with the coupler (b) having a lower coupling rate than the heat-transferable coupler (a) to form a dyestuff (c)-(b). Thus, there is obtained a multicolored reproductive copy in which the predetermined portion is colored in a hue different from that of the other portion.

It is essential that among the thermovolatil or thermosublimative acid addition salt coupler (a) of the coloring material, coupler (b) and diazonium salt (c) to be used in this invention there should be established the following relations:

(I) Thermovolatil or thermosublimative coupler (a) has a higher coupling rate under developing conditions than coupler (b).

(II) Dyestuff (b)-(c), dyestuff (a)-(c), dyestuff (a')-(c) . . . formed at the development have hues different from one another.

As the coupling component (b) having a lower coupling rate than the coupler component (a) of the coloring material of this invention phenol derivatives, naphthols, active methylene group-containing compounds, heterocyclic compounds and other couplers usually used in the diazo-type photosensitive materials may be used. Specific examples of these couplers are as follows.

## Phenol derivatives:

2,5,6-trimethylphenol  
2-hydroxymethylphenol  
 $\beta$ -(2-hydroxyphenyl)-propionic acid  
2-( $\omega$ -phenylaminomethyl)-phenol  
 $\beta$ -(4-methyl-2-hydroxyphenyl)-glutaric acid  
2,5-dimethyl-6-(N-dimethylaminomethyl)-phenol  
1,3-dimethyl ether of pyrogallol  
 $\alpha$ -Resorcylic acid ethanalamine  
 $\beta$ -Resorcylic acid  
N-lauryl-p-aminophenol  
N-acyl-m-aminophenol  
Meta-hydroxy-acetoanilide  
Ortho-N-hydroxyphenyl-monoguanidine  
Para-N-hydroxyphenyl-biguanidine  
2,5-dimethyl-4-morpholinomethyl phenol  
2-methyl-5-isopropyl-morpholinomethyl phenol  
4-morpholinomethylresorcinol monomethyl ether  
3,3',5,5'-tetrahydroxydiphenyl  
3,3',5,5'-tetrahydroxydiphenyl  
2,2',4,4'-tetrahydroxydiphenyl  
2,4,4'-trihydroxydiphenyl-2'-sulfonic acid  
2,4,6,3',5'-pentahydroxydiphenyl  
2,2',4,4'-tetrahydroxydiphenyl sulfide

## Naphthols:

2,3-dihydroxynaphthalene-6-sulfonic acid  
2-naphthol-3,6-disulfonic acid  
2,7-dihydroxynaphthalene-3-sulfonic acid  
2,8-dihydroxynaphthalene-6-sulfonic acid  
1,8-dihydroxynaphthalene-8-sulfonic acid  
1,8-aminonaphthol-5-sulfonic acid  
2,7-dihydroxy-3,6-disulfonic acid  
1,8-benzoylaminonaphthol-2-sulfonic acid  
1,8-dihydroxynaphthalene-6-sulfonic acid  
2-hydroxy-3-naphthionic-N- $\beta$ -hydroxyethyl amide  
2-hydroxy-3-naphthionic-N,N-bis- $\beta$ -hydroxyl ether amide  
8-hydroxy-2-naphthionic-hydroxyethyl amide  
1-(N-carboethoxymethylamino)-8-naphthol-4-sulfonic acid  
5-(para-nitro)-benzamido-1-naphthol  
1-hydroxynaphthyl-7-phenyl-guanidine  
2-hydroxynaphthyl-8-biguanidine  
1-naphthol-3-(N- $\beta$ -hydroxyethyl)-sulfonic amide  
1-naphthol-3-(N-o-methoxyphenyl)-sulfonic amide  
Bis-[5-hydroxy-7-sulfo-naphthyl(2)]-amine  
N,N-bis[1-hydroxy-3-sulfo-naphthyl(6)]-thiourea

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## Active methylene group-containing compounds:

Acetoacetic acid cyclohexylamide  
Acetoacetic acid benzylamide  
Cyanoacetoanilide  
Cyanoacetomorpholine

## Heterocyclic compounds:

1-(3'-sulfoamide)-phenyl-3-methylpyrazolone-5  
1-(4'-carboxy-ethylphenyl)-3-dodecyl-pyrazolone-5  
8-hydroxy-1,2-naphthylimidazole  
2-methyl-4-hydroxybenzimidazole  
7-methyl-4-hydroxybenzothiazole  
1,7-dimethyl-4-hydroxy-benzotriazole  
3-hydroxythiophene-5-carboxylic acid  
1-3-4-cyclopentatriene

As the diazonium salt-containing diazo-type photosensitive material one-component photosensitive materials containing a diazonium salt and an optional assistant, and two-component photosensitive materials containing a diazonium salt, a coupler (b) and an optional assistant may be used. Suitable photosensitive materials are chosen depending on the developing method. These photosensitive materials are usually composed of a substrate such as paper, plastic film, fibrous textile, non-woven fabric, and metal foil, and coated thereon, a sensitizing composition. The preparation of such photosensitive material will now be described by referring to some examples.

## (A) Sensitizing composition for dry development:

	Percent
30 Azo coupling component (b) (having a lower coupling rate than heat-transferable coupling component (a) of the coloring material) -----	0.5-4
Diazo compound (c) -----	0.2-4
Non-volatile organic acid -----	0.1-5.0
35 Coloring matter -----	0-0.025
Development accelerator -----	1-10
Extender -----	0-2.5
Solvent -----	Balance

40 The sensitizing composition of the above recipe is coated on a substrate such as paper and plastic film, and dried to form a photosensitive sheet.

## (B) Two-component type sensitizing composition for wet development:

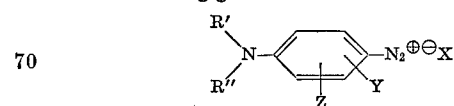
	Percent
45 Azo coupling component (b) (having a lower coupling rate than heat-transferable coupler component (a) of the coloring material) -----	0.5-4
Diazo compound (c) -----	0.2-4
Organic acid (non-volatile) -----	0.1-5.0
50 Extender -----	0-2.5
Coloring matter -----	0-0.025
Solvent -----	Balance

55 The sensitizing composition of the above recipe is coated on a substrate such as paper and plastic film, and dried to form a photosensitive sheet.

Any of conventional photo-resoluble diazonium salts may be used in the above-mentioned composition, as long as it is capable of coupling with the heat-transferable coupling component (a) of the coloring material and the coupler (b) having a lower coupling rate than the coupling component (a), under development conditions.

60 Examples of such diazonium compounds are as follows:

© Para-phenylene-diamine-N,N-substituted compounds of the following general formula:



75 wherein X stands for an anion, R' and R'' each are aliphatic groups, and Z and Y denote groups which can be introduced into the benzene nucleus.

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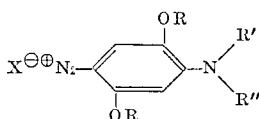
Specific examples of the compounds of this type are as follows:

- 4-diazo-N,N-dimethyl aniline (referred to simply as "MA salt")  
 4-diazo-N,N-diethyl aniline (referred to simply as "EA salt")  
 4-diazo-N-ethyl-N-β-hydroxyethyl aniline (referred to simply as "EH salt")  
 4-diazo-N,N-bis-β-hydroxyethyl aniline  
 4-diazo-N-methyl-N-β-hydroxyethyl aniline  
 4-diazo-N-ethyl-N-β-hydroxypropyl aniline

Other diazonium salts of p-phenylene diamines N,N-substituted with alkyl or hydroxy-alkyl groups

- 4-diazo-N-ethyl-N-(β-diethylamino)-ethyl aniline  
 4-diazo-2-chloro-N,N-diethyl aniline  
 4-diazo-2-methyl-N,N-diethyl aniline  
 4-diazo-2-iodo-N,N-diethyl aniline  
 4-diazo-2-trifluoromethyl-N,N-diethyl aniline  
 4-diazo-N-ethyl-N-benzyl aniline  
 4-diazo-N-methyl-N-benzyl aniline (referred to simply as "methyl benzyl")

⊙ Aminohydroquinone ether-type compounds of the following general formula:



wherein R, R' and R'' are alkyl or aryl groups and X stands for an anion.

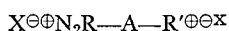
Specific examples of the compounds of the above type are as follows:

- 4-diazo-2,5-dibutoxy-N,N-diethyl aniline  
 4-diazo-2,5-diethoxy-N-benzoyl aniline (referred to simply as "BB salt")  
 4-diazo-2,5-diethoxy-N-ethyl-N-benzoyl aniline  
 4-diazo-2,5-dibenzoyloxy-N-benzoyl aniline  
 4-diazo-2-chloro-5-methoxy-N-benzoyl aniline  
 4-diazo-2,5-diethoxy-N-benzoyl-methyl aniline  
 4-diazo-2,5-diethoxy-N-benzoyloxy-methyl aniline  
 Other 4-diazo-2,5-dioxyalkyl (or dioxyaryl)-N-alkyl (or aryl) compounds and derivatives thereof

⊙ Aminodiphenyl compounds, aminodiphenyl amine compounds and their analogues of the following general formulas:



and



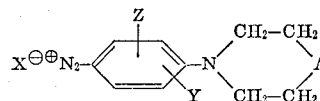
wherein X is an anion, R is a divalent aryl group, R' is a monovalent or divalent aryl or alkyl group, A is a divalent group or a direct bond and examples of the R—A—R' are diarylamine (A; —NH—), diphenyl (A; direct bond), diphenyl oxide (A; —O—), diaryl methane (A; —CH₂—), stilbene (A; —CH=CH—) and diaryl or dialkyl sulfide (A; —S—).

Specific examples of the compounds of the above type are as follows:

- Para-diazophenyl amine  
 4-diazo-2,5,4'-triethoxydiphenyl amine  
 4-diazo-2,5,4'-triethoxydiphenyl  
 4,4'-bis-diazo-2,2',5,5'-tetrahydroxydiphenyl methane  
 Bis-diazo-8,8'-dichloro-5,5'-dimethoxy benzidine  
 4-diazo-2,5-dimethoxyphenylethyl sulfide  
 4-diazo-2,5-diethoxy-4'-methyl-diphenyl sulfide

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⊙ Heterocyclic amine derivatives of the following general formula:



wherein X stands for an anion, Y and Z are groups which can be introduced into the benzene nucleus, and A is a direct bond (phenylpyrrolidine) or a divalent group such as —O— (morpholine), —S— (thiomorpholine) and methylene (phenyl piperidine).

Specific examples of the compounds of this type are as follows:

- 4-diazo-2,5-dibutoxy-N-phenyl morpholine  
 4-diazo-2,5-diethoxy-N-phenyl morpholine  
 4-diazo-2-methoxy-N-thio morpholine  
 4-diazo-N-phenyl piperidine  
 4-diazo-N-phenyl pyrrolidine  
 4-diazo-2,5-di-n-butoxy-N-phenyl piperidine  
 Other derivatives of 4-diazo-N-phenyl heterocyclic amines.

⊙ N,N-substituted ortho-phenylene diamine derivatives and orthoamino-phenol derivatives.

Specific examples of the compounds of this type are as follows:

- 2-diazo-4-methylmercapto-N,N'-dimethyl aniline  
 2-diazo-5-benzoylamino-N,N'-dimethyl aniline  
 2-diazo-1-naphthol-5-sulfonic acid

The above-mentioned diazonium compounds may be used in the form of a relatively stable salt with sulfuric acid or hydrochloric acid. They may be also used in the form of a double salt with zinc chloride, tin chloride, aluminum sulfate or the like. Further, they may be used in the state stabilized by an aryl sulfonate (in the form of a diazonium salt of an aromatic sulfonic acid), a diazo-sulfonate or the like. These diazonium salts may be used either singly or in the form of a mixture of two or more of them.

As the organic acid in the sensitizing composition citric acid, tartaric acid, oxalic acid, sulfamic acid, boric acid, phosphoric acid, etc. may be used. As the extender there dextrin, gum arabic, colloidal silica, etc. may be used. As the stabilizers 1,3,6-naphthalene, sodium trisulfonate and other aryl sulfonic acids may be used. Polyhydric alcohols such as glycerin and ethylene glycol are used as a development accelerator. Coloring matters are used for indicating the photosensitive face and increasing the whiteness of the background, and blue dyestuffs such as Methylene Blue and Patent Blue are used for this purpose. As the solvents water and organic solvent such as alcohols, acetone, toluene, xylene and esters may be used.

The so formed photosensitive sheet is piled on an original, on the back surface of one or more predetermined portions of which the above-mentioned coloring material has been applied in advance, in a manner such that the coloring material-treated back surface of the original will confront the photosensitive layer of the photosensitive sheet. When the assembly is subjected to the light exposure and heating, the coupling component (a) of the coloring material is heat-transferred on the portions of the photosensitive sheet corresponding to the predetermined portions of the original and the light resolution of the diazonium salt (c) is caused to occur depending on the light transmission of the original. The so treated photosensitive sheet is developed in the presence of a coupler (b) having a lower coupling rate than the coupling component (a) contained in the coloring material by a method known per se. The coupler (b) having a relatively low coupling rate may be incorporated in the photosensitive material in advance or may be contained in a developing liquid.

The developing may be conducted by either the dry method or the wet method. In the dry method, the devel-

opment can be accomplished by exposing the heated and exposed photosensitive sheet to a mixed gas of ammonia and steam. In the case of a one-component type photosensitive paper for the wet development, a liquid developer having, for instance, the following recipe;

	Percent
Coupler (b) (having a lower coupling rate than the heat-transferable coupling component (a) of the coloring material) -----	0.2-1.5
Alkaline agent -----	0.5-20
Reducing agent -----	0-20
Surfactant -----	0-0.5
Water -----	Balance

is applied to the heated and exposed photosensitive sheet by a customary method such as dipping, roller coating, and spray coating methods. In the case of a two-component photosensitive sheet, the development is accomplished by contacting the heated and exposed photosensitive sheet with an aqueous liquid developer containing an alkaline agent.

In accordance with this invention, by employing the thermovolatil or thermosublimate coupler (a) in the form acid addition salt, it is possible to prevent effectively the coloring material used multicolor reproduction from being discolored during storage or after its application to an original and to overcome the defect of the conventional product that the light transmission of the portion of the original treated with the coloring material is lowered because of the contamination of the treated original. Thus, this invention can provide distinct multicolored reproductive copies in which portions corresponding to predetermined portions of the original are colored selectively in different hues.

Further, in accordance with this invention, it is possible to obtain from one treated original many copies, e.g., 30-100 distinct copies.

Examples of the preparation of ink-like compositions for treating the back surface of an original:

#### EXAMPLE 1

An ink-like composition of the following recipe is prepared as a yellow color-forming agent for treating the back surface of an original:

Acetoacetic acid anilide acetate salt -----	g-- 25
Ethylene glycol -----	g-- 15
Alkyd resin -----	g-- 5
Ethanol -----	ml-- 100

The above composition is directly used as a material to be coated on the back surface of a portion of the original desired to be reproduced in yellow by means of a brush, a coating roller or a sprayer, or after it has been charged in a felt pen or a ball pen, it is used as a material for treating the back surface of a portion of the original desired to be reproduced in yellow.

#### EXAMPLE 2

An ink-like composition of the following recipe is prepared as a red color-forming agent for treating the back surface of an original:

1-phenyl-3-methylpyrazolone(5) -----	g-- 20
Hydrochloric acid (36%) -----	ml-- 10
Glycerin -----	g-- 10
Ethanol -----	ml-- 50
Water -----	ml-- 50

The above composition is directly used as a material to be coated on the back surface of a portion of the original to be reproduced in red by means of a brush, a coating roller or a sprayer, or after it has been charged in a felt pen or a ball pen, it is used as a material for treating the back surface of a portion of the original to be reproduced in red.

#### EXAMPLE 3

An ink-like composition of the following recipe is prepared as a brown color-forming agent for treating the back surface of an original:

5 Meta-aminophenol hydrochloride -----	g-- 30
Ethylene glycol -----	g-- 15
Vinyl acetate resin -----	g-- 5
Methanol -----	ml-- 100

10 The above composition is directly used as a material to be coated on the back surface of a portion of the original desired to be reproduced in brown by means of a brush, a coating roller or a sprayer, or after it has been charged in a felt pen or a ball pen, it is used as a material for treating the back surface of a portion of the original desired to be reproduced in brown.

#### EXAMPLE 4

20 A yellowish brown color-forming agent is prepared by using meta-phenylene diamine hydrochloride instead of meta-aminophenol hydrochloride in the composition of Example 3.

#### EXAMPLE 5

25 A yellow color-forming agent is prepared by using 3-amino-o-cresol hydrochloride instead of meta-aminophenol hydrochloride in the composition of Example 3.

Examples of the preparation of waxy agents for treating the back surface of an original:

#### EXAMPLE 6

A waxy composition to be used as a yellow color-forming agent for treating the back surface of an original is prepared by heat melting

35 Metaphenylene diamine hydrochloride -----	G. 30
Stearic acid -----	100
Paraffin -----	50
Terra abla -----	50
40 Diatomaceous earth -----	20

and solidifying the melt.

The above composition is molded into a crayon stick-like form and is used as a material to be coated on the back surface of a portion of the original desired to be reproduced into a different hue.

#### EXAMPLE 7

A waxy composition to be used as a brown color-forming agent for treating the back surface of an original is prepared by heat melting

50 Meta-aminophenol hydrochloride -----	G. 40
Paraffin -----	50
55 Terra abla -----	70
Haze wax -----	20
Stearic acid -----	100
Magnesium carbonate -----	20

and solidifying the melt.

60 The so formed composition is molded into a crayon stick-like or chalk-like form and is used as a material for coating the back surface of a portion of an original desired to be reproduced in a different hue.

#### EXAMPLE 8

A waxy composition of the following recipe is prepared as a red color-forming agent for treating the back surface of an original:

70 1-phenyl-3-methylparazolone(5) hydrochloride ---	G. 20
Stearic acid -----	100
Paraffin -----	50
Diatomaceous earth -----	30
75 Haze wax -----	20

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The above composition is molded into a crayon stick-like or chalk-like form and is used as a material for coating the back surface of a portion of the original desired to be reproduced in a different hue.

## EXAMPLE 9

To the composition of Example 8 100 g. of mineral oil, 50 g. oleic acid and 20 g. of Permanent Red are added, and the mixture is kneaded in a bowl mill to disperse additional components uniformly. Then, the kneaded mixture is coated on a substrate such as paper to obtain a pressure-sensitive copy sheet. The so formed copy sheet is overlapped on the back surface of an original and the pressing is effected thereon by means of a typewriter or other writing means. Thus, the sheet is used as a material for forming a layer of the waxy agent on the back surface of an image of the original to be reproduced in a different hue.

Examples of the preparation of coupler-transferring sheets for treating the back surface of an original:

## EXAMPLE 10

A composition of the following recipe is prepared as a brown color-forming agent for treating the back surface of an original:

Meta-aminophenol hydrochloride	g	30
Triacetate resin	g	10
Methanol	ml	50
Acetone	ml	50

The above composition is coated on a transparent or semi-transparent sheet such as polyester film by means of a rod coater and dried at a relatively low temperature (40–50° C.) to form a sheet for heat-transferring the coupler. After being cut into a desired size according to need, the sheet is used as a material to be applied to the back surface of a portion of an original desired to be reproduced in a different hue.

## EXAMPLE 11

A composition to be used as a red color-forming agent for treating the back surface of an original is prepared by using 1-phenyl-3-methylpyrazolone(5) hydrochloride instead of meta-aminophenol hydrochloride in Example 10. From this composition a sheet for heat-transferring the coupler capable of forming a red color is formed.

## APPLICATION EXAMPLE 1

Multicolor-forming diazo-type photosensitive paper in use for dry development

A solution of the following recipe is prepared:

4 - diazo - N - ethyl-N-hydroxyethylaniline chloride	G.
$\cdot \frac{1}{2} \text{ZnCl}_2$	15
Diethylene glycol	60
Citric acid	20
2,3-dihydroxynaphthalene-6-sulfonic acid	7
Zinc chloride	50
Thiourea	25
Patent Blue	0.1
Water	Balance
Total—1 liter.	

The solution is coated on a base paper by a customary coating procedure such as using an air knife coater and dried to form a photosensitive sheet.

The sheet is overlapped on an original in which the back surface of a portion is treated with the ink-like composition prepared in Example 1 and the back surface of another portion is treated with the ink-like composition prepared in Example 2. Then, the assembly is heated at 70–100° C. and exposed to light by means of a mercury lamp to form a latent image of the diazonium salt.

Next, the so treated sheet is subjected to development with gasified ammonia and steam. Thus, a clear multi-

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color copy is obtained in which at a portion corresponding to the portion treated with the ink of Example 1 the diazonium salt is colored in a yellow color, at a portion corresponding to the portion treated with the ink of Example 2 the diazonium salt is colored in red and at another portion corresponding to the untreated portion the diazonium salt is colored in bluish violet. The resulting copy is very clear and excellent in color distinction.

## APPLICATION EXAMPLE 2

When Application Example 1 is repeated by using instead of 4-diazo-N-ethyl-N-hydroxyethyl-aniline chloride  $\cdot \frac{1}{2} \text{ZnCl}_2$ , 4 - diazo - N,N - dimethylaniline chloride  $\cdot \frac{1}{2} \text{ZnCl}_2$ , a multicolor reproductive copy similar to that of Application Example 1 is obtained.

## APPLICATION EXAMPLE 3

Multicolor-forming photosensitive paper in use for dry development

A solution of the following recipe is prepared:

4-diazo-N,N-diethyl-aniline chloride $\cdot \frac{1}{2} \text{ZnCl}_2$	G.	15
Ethylene glycol		50
Citric acid		20
2,7-dihydroxynaphthalene-3,6-disulfonic acid sodium salt		8
Zinc chloride		20
Thiourea		100
1,3,6-naphthalene-trisulfonic acid sodium salt		20
Patent Blue		0.1
Water		Balance
Total—1 liter.		

By a customary coating method such as using an air knife coater, a photosensitive paper is prepared from the above solution. The photo-sensitive paper is overlapped on an original in which a portion of the back surface is treated with the ink-like composition prepared in Example 2 and another portion of the back surface is treated with the composition prepared in Example 3. The assembly is exposed to light and heated by means of a mercury lamp. Then, the so treated sheet is subjected to development with gasified ammonia and steam. Thus, a clear three-color reproductive copy is obtained in which a portion corresponding to the portion of the original treated with the composition of Example 2 is colored in red, a portion corresponding to the portion treated with the composition of Example 3 is colored in brown, and another portion corresponding to the untreated portion of the original is colored in blue. The copy is very clear and excellent in color distinction.

## APPLICATION EXAMPLE 4

Multicolor-forming photosensitive paper for dry development

A solution of the following recipe is prepared:

4-diazo-N,N-diethylaniline chloride $\cdot \frac{1}{2} \text{ZnCl}_2$	g	20
Diethylene glycol	g	50
Citric acid	g	3
Bis-[5-hydroxy-7-sulfonaphthyl(2)]amine	g	14
Zinc chloride	g	30
Thiourea	g	25
Hydrochloric acid (36%)	ml	10
Patent Blue	g	0.1
Water		Balance
Total—1 liter.		

By a customary coating method such as using an air knife coater, the above solution is applied to a substrate of a photosensitive paper and dried. The so formed photosensitive paper is piled on an original, a portion of the back surface of which is treated with the waxy composition prepared in Example 7 and another portion of the back surface of which is treated with the waxy com-

position obtained in Example 8. Then the assembly is heated and printed by means of a mercury lamp, followed by development with gaseous ammonia and steam. Thus a clear three-color reproductive copy in which a portion corresponding to the portion treated with the treating agent of Example 7 is colored in brown, another portion corresponding to the portion corresponding to the portion treated with the treating agent of Example 8 is colored in red and the remaining portion corresponding to the untreated portion is colored in dark blue. The copy is very clear and excellent in color distinction.

## APPLICATION EXAMPLE 5

Multicolor-forming photosensitive paper in use for dry development

A solution of the following recipe is prepared:

4-diazo-N,N-dimethylaniline chloride · ½ ZnCl <sub>2</sub> -----	G. 20
Diethylene glycol -----	50
Tartaric acid -----	20
2,7-dihydroxynaphthalene-3,6-disulfonic acid sodium salt -----	8
Resorcinol monoethyl ether -----	3
Zinc chloride -----	10
Thiourea -----	50
1,3,6-naphthalene-trisulfonic acid sodium salt -----	20
Patent Blue -----	0.1
Water -----	Balance
Total—1 liter.	

In the same manner as in Example 1, a photosensitive paper is prepared from the above solution by coating and drying. The photosensitive paper is piled on an original, a portion of the back surface of which is treated with the coupler-heat-transferring sheet prepared in Example 10 and another portion of the back surface of which is treated with the treating agent obtained in Example 11. Then the assembly is heated and light-exposed by means of a mercury lamp, followed by development with gaseous ammonia and steam. Thus there is obtained a clear three-color reproductive copy in which a portion corresponding to the portion treated with the treating agent of Example 10 is colored in yellowish brown, another portion corresponding to the portion corresponding to the portion treated with the treating agent of Example 11 is colored in red and the remaining portion corresponding to the untreated portion is colored in black. The copy is clear and distinct without mingling of colors.

## APPLICATION EXAMPLE 6

Multicolor-forming photosensitive paper for dry development

A solution of the following recipe is prepared:

4-diazo-N,N-dimethylaniline chloride -----	G. 30
Tartaric acid -----	20
Ethylene glycol -----	50
2,4,2',4'-tetrahydroxydiphenyl sulfide -----	11
Thiourea -----	25
Zinc chloride -----	50
Patent Blue -----	0.1
Water -----	Balance
Total—1 liter.	

The above solution is coated on a semi-transparent paper such as tracing paper and dried to form a photosensitive paper. The photosensitive paper is piled on an original, a portion of the back surface of which is treated with the ink-like composition prepared in Example 2 in a manner such that the treated surface of the original confronts the photosensitive layer of the photosensitive paper. Then the assembly is heated and light-exposed by means of a mercury lamp, followed by development with gaseous ammonia and steam. Thus a clear two-color reproductive

copy is obtained usable as the intermediate in which a portion corresponding to the portion of the original treated with the composition of Example 2 is colored in red and another portion corresponding to the untreated portion of the original is colored in yellowish brown. The intermediate is clear and excellent in color distinction.

## APPLICATION EXAMPLE 7

Multicolor-forming sensitive paper in use for either dry or wet development

A solution of the following recipe is prepared:

4-diazo-2,5-dibutoxy-N-phenylmorpholine · ½ ZnCl <sub>2</sub> -----	G. 15
Citric acid -----	30
Diethylene glycol -----	40
β-Hydroxynaphthoic acid aminoethyl amine hydrochloride -----	7
Thiourea -----	40
Zinc chloride -----	30
Patent Blue -----	0.1
Water -----	Balance
Total—1 liter.	

From the above solution, a photosensitive paper is prepared by conducting the coating and drying in the same manner as in Application Example 1. The so formed photosensitive paper is piled on an original, a portion of the back surface of which is treated with the ink-like composition prepared in Example 1 and another portion of the back surface of which is treated with the treating material prepared in Example 2, in a manner such that the treated surface of the original confronts the photosensitive layer of the photosensitive paper. Then the assembly is heated and light-exposed by means of a mercury lamp, followed by development with gaseous ammonia and steam or with an alkaline liquid developer of the following recipe:

Postassium carbonate -----	G. 20
Sodium thiosulfate -----	40
Sodium bicarbonate -----	30
Potassium tetraborate -----	5
Water -----	Balance
Total—1 liter.	

Thus a clear three-color reproductive copy without any substantial mingling of colors is obtained, in which a portion corresponding to the portion of the original treated with the composition of Example 1 is colored in yellow, a portion corresponding to the portion of the original treated with the composition of Example 2 is colored in red and the remaining portion corresponding to the untreated portion of the original is colored in blue.

## APPLICATION EXAMPLE 8

Multicolor-forming photosensitive paper in use for wet development

A solution of the following recipe is prepared:

4-diazo-2,5-diethoxy-N-benzoylaniline · ½ ZnCl <sub>2</sub> -----	G. 15
Citric acid -----	10
Dextrin -----	20
Methylene Blue -----	0.1
Water -----	Balance
Total—1 liter.	

The above solution is coated on a base paper of a photosensitive paper by a customary method using an air knife coater or the like and dried. The so formed photosensitive paper is piled on an original, the back surface of a portion of which is treated with the waxy composition prepared in Example 8, in a manner such that the photosensitive layer of the photosensitive paper confronts the treated surface of the original. Then the assembly is



heated and light exposed by means of a mercury lamp and a liquid developer having the following recipe

	G.
NW acid -----	15
Potassium carbonate -----	80
Sodium bicarbonate -----	30
Sodium thiosulfate -----	50
Borax -----	10
Water -----	Balance
Total—1 liter.	

is applied to the heated and light-exposed photosensitive paper by roll coating or spraying to develop the photosensitive paper. Thus a two-color copy of a clear color distinction is obtained in which the portion corresponding to the portion of the original treated with the composition of Example 8 is colored in red and other portion corresponding to the untreated portion of the original is colored in bluish violet.

#### APPLICATION EXAMPLE 9

##### Multicolor-forming film

A solution of the following recipe is prepared:

4 - diazo-2,5 - dibutoxy - N - phenyl morpholine ·½ZnCl <sub>2</sub> -----	g-- 15
Citric acid -----	g-- 10
β-Hydroxynaphthoic acid ethanol amine -----	g-- 7
Triacetate resin -----	g-- 15
Oil Blue -----	g-- 0.2
Acetone -----	ml-- 400
Methanol -----	ml-- 700

The solution is coated on a polyester film by a rod coater and dried at a relatively low temperature (40–50° C.) by warm air to form a photosensitive film. The film is piled on an original in which a part of the back surface of an original image is treated with the ink-like composition prepared in Example 1 and another part of the back surface of the original image is treated with the ink-like composition prepared in Example 2. The assembly is heated and exposed to light by a mercury lamp. The photosensitive film containing a latent image of the diazonium salt is developed with gasified ammonium and steam. Thus, a clear three-color reproductive copy without any substantial mingling of colors is obtained, in which a portion corresponding to the part treated with the treating composition of Example 1 is colored in yellow, a portion corresponding to the part treated with the treating composition of Example 2 is colored in red, and another portion corresponding to the untreated part of the original is colored in blue.

What we claim is:

1. A process for multicolor reproduction, which comprises (A) exposing imagewise to actinic light an assembly of (i) an original sheet having opaque image areas and transparent non-image areas on one surface and a layer of at least one thermovolative or sublimable azo coupler (a) contiguous with pre-selected opaque image areas, said thermovolative or sublimable azo coupler (a) being a thermovolative or sublimable acid addition salt of a thermovolative or sublimable azo coupling component containing an amino group, selected from the group consisting of aminophenols, aromatic amines and active methylene group-containing amines, and (ii) a diazo-type photosensitive material having a photosensitive layer containing at least one photosensitive diazonium salt (c), an acidic stabilizer and an azo coupler (b) having a substantially lower rate of coupling with the diazonium salt (c) under the developing conditions that that of the azo coupler (a), said original sheet (i) being superposed on said diazo-type photosensitive material (ii) so that the layer of the azo coupler (a) comes into face-to-face contact with the photosensitive layer; (B) heating said assembly thereby to heat-transfer said layer of the coupler (a) to the corresponding position on the surface of said

photosensitive layer, said steps (A) and (B) being performed simultaneously or in the sequence of (A) to (B) or (B) to (A); and (C) contacting the exposed photosensitive material with a mixture of ammonia and steam or an alkali-containing aqueous liquid developer to thereby develop said photosensitive material, whereby in the unexposed latent image area of the portion to which the coupler (a) has been heat-transferred, a dye (c)–(a) having a certain hue or color is formed by the selective reaction between the heat-transferred coupler (a) and the diazonium salt (c) and at the same time, in the unexposed latent image areas to which the coupled (a) has not been heat-transferred, a dye (c)–(b) having a different hue or color from said dye (c)–(a) is formed by the reaction of the coupler (b) with the diazonium salt (c), thus producing a multi-colored copied image.

2. The process of claim 1 wherein said thermovolative or sublimable azo coupler has a melting point of 100–150° C.

3. The process of claim 1 wherein said thermovolative or sublimable acid addition salt is a salt of a thermovolative or sublimable azo coupling component containing an amino group with an acid selected from the group consisting of hydrohalogenic acids, organic sulfonic acids, chloroacetic acid, chloropropionic acid, acetic acid, salicylic acid, 2,6-dichlorobenzoic acid, 3,4-dimethylbenzoic acid, oxalic acid, oxalic acid hydrate, o-sulfobenzoic acid, trichloroacetic acid, formic acid, methacrylic acid and butyric acid.

4. The process of claim 1 wherein said thermovolative or sublimable acid addition salt of a thermovolative or sublimable azo coupling component is selected from the group consisting of metaaminophenol hydrochloride and 1-phenyl-3-methyl-pyrazolone(5) hydrochloride.

5. A process for multicolor reproduction, which comprises (A) exposing imagewise to actinic light an assembly of (i) an original sheet having opaque image areas and transparent non-image areas on one surface and a layer of at least one thermovolative or sublimable azo coupler (a) contiguous with pre-selected opaque image areas, said thermovolative or sublimable azo coupler (a) being a thermovolative or sublimable acid addition salt of a thermovolative or sublimable azo coupling component containing an amino group, selected from the group consisting of aminophenols, aromatic amines and active methylene group-containing amines, and (ii) a diazo-type photosensitive material having a photosensitive layer containing at least one photosensitive diazonium salt (c), said original sheet (i) being superposed on said diazo-type photosensitive material (ii) so that the layer of the azo coupler (a) comes into face-to-face contact with the photosensitive layer; (B) heating said assembly thereby to heat-transfer said layer of the coupler (a) to the corresponding position on the surface of said photosensitive layer, said steps (A) and (B) being performed simultaneously or in the sequence of (A) to (B) or (B) to (A); and (C) contacting the exposed photosensitive material with an alkali-containing aqueous liquid developer containing an azo coupler (b) having a substantially lower rate of coupling with the diazonium salt (c) under the developing conditions that that of the azo coupler (a), to thereby develop said photosensitive material, whereby in the unexposed latent image area of the portion to which the coupler (a) has been heat-transferred, a dye (c)–(a) having a certain hue or color is formed by the selective reaction between the heat-transferred coupler (a) and the diazonium salt (c) and at the same time, in the unexposed latent image areas to which the coupler (a) has not been heat-transferred, a dye (c)–(b) having a different hue or color from said dye (c)–(a) is formed by the reaction of the coupler (b) with the diazonium salt (c), thus producing a multicolored copied image.

6. The process of claim 5 wherein said thermovolative or sublimable azo coupler has a melting point of 100–150° C.



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7. The process of claim 5 wherein said thermovolatilable or sublimable acid addition salt is a salt of a thermovolatilable or sublimable azo coupling component containing an amino group with an acid selected from the group consisting of hydrohalogenic acids, organic sulfonic acids, chloroacetic acid, chloropropionic acid, acetic acid, salicylic acid, 2,6-dichlorobenzoic acid, 3,4-dimethylbenzoic acid, oxalic acid, oxalic acid hydrate, o-sulfobenzoic acid, trichloroacetic acid, formic acid, methacrylic acid and butyric acid.

8. The process of claim 5 wherein said thermovolatilable or sublimable acid addition salt of a thermovolatilable or sublimable azo coupling component is selected from the group consisting of metaaminophenol hydrochloride and 1-phenyl-3-methyl-pyrazolone(5) hydrochloride.

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U.S. Cl. X.R.

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