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[54] **PROCESS FOR DEVELOPMENT OF TWO-COMPONENT DIAZOTYPE PHOTOSENSITIVE MATERIALS**

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[52] **U.S. Cl.** ..... **96/49,** 96/91 R

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[58] **Field of Search** ..... 96/91 R, 75, 49; 250/65 T; 117/36.7, 36.8, 36.9

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[57] **ABSTRACT**

A process for development of two-component diazotype photosensitive materials comprising exposing image-wise to light a photosensitive material having a two-component diazotype photosensitive layer comprising a photosensitive diazonium salt, a coupler capable of coupling with said diazonium salt and an acidic stabilizer, applying a small amount of an activating liquor to the photosensitive layer of the exposed photosensitive material and thereafter heating the activating liquor-applied photosensitive material according to need, said activating liquor being a solution or dispersion of a carboxylic acid salt selected from the group consisting of alkali metal carboxylates, alkaline earth metal carboxylates and mixtures thereof.

6 Claims, No Drawings

PROCESS FOR DEVELOPMENT OF TWO-COMPONENT DIAZOTYPE PHOTOSENSITIVE MATERIALS

This invention relates to a process for development of two-component diazotype photosensitive materials. More particularly, the invention relates to a process for development of two-component diazotype photosensitive materials comprising exposing image-wise to light a photosensitive material having a two-component diazotype photosensitive layer comprising a photosensitive diazonium salt, a coupler capable of coupling with said diazonium salt and an acidic stabilizer, applying a small amount of an activiating liquid to the photosensitive layer of the exposed photosensitive material and thereafter heating the activating liquor-applied photosensitive material according to need, said activating liquid being a solution or dispersion of a carboxylic acid salt selected from the group consisting of alkali metal carboxylates, alkaline earth metal carboxylates and mixtures thereof. A so-called dry development method using a gaseous mixture of ammonia and vapor has been broadly used in diazotype reproduction employing a two-component diazotype photosensitive material having a photosensitive layer comprising a photosensitive diazonium salt, a coupler and an acidic stabilizer. In this dry development method, since the contact of a gaseous mixture of ammonia and vapor acting as a developer with the photosensitive layer is a contact between the gas phase and the solid phase, it is necessary to supply the gaseous mixture in an amount such that the amount of ammonia is such greater than the amount required for coupling the coupler with the diazonium salt. As a result, excessive ammonia is discharged from the developing device and its nasty smell causes trouble.

As means for overcoming the above disadvantage of the dry development method, Japanese Patent Publication No. 39-8141/64 or No. 45-23515/70 has proposed a process comprising applying a small amount of an activating liquid comprising an organic amine such as mono-, di- and tri-ethanolamines to an light-exposed two-component diazotype photosensitive layer, and developing the photosensitive layer by or without heating.

This development method is advantageous in that the development can be accomplished, as in the dry development method, without substantial wetting of the diazotype photosensitive layer. However, this method has a fatal defect in the point that an organic amine which is highly irritative to skins and mucous membranes and which is readily absorbed in human bodies to give harmful effects thereto must be employed. For instance, ethanolamines, which are amines giving the least nasty smell among organic amines, are considered to give high irritation to skins and mucous membranes and exhibit high absorption in human bodies when they are heated. Therefore, according to The Food and Drug Administration of U.S.A., it is stipulated that in ethanolamines the tolerance should be 3 ppm or less. However, in the above known method comprising application of ethanolamines it is practically very difficult to control the ethanolamine concentration in the environment to less than 3 ppm during the development treatment.

In case a two-component diazotype photosensitive material is developed according to a so-called wet development method employing an aqueous solution of a non-volatile inorganic alkali, the above-mentioned defects can be overcome, but a copy sheet is obtained in the wet state, which results in handling inconveniences. Furthermore, this wet development method is defective in that contrast in the copied image is low and the remaining coupler is discolored by the alkali left on the whole surface of the copy sheet.

As described above, in all of known methods for developing two-component diazotype photosensitive materials the development is conducted with use of an aqueous solution containing a free organic amine or inorganic alkali or a salt forming a free amine or alkali under thermal decomposition. In short, it has been common in the art that the development of two-component diazotype photosensitive materials can be effected only in the presence of an organic amine or inorganic alkali.

We have now found to our surprise that when a solution or dispersion of an alkali metal salt or alkaline earth metal salt of a carboxylic acid is applied to a light-exposed two-component diazotype photosensitive material, copied images of high distinction and contrast can be obtained without the above-mentioned disadvantages and defects of the conventional techniques. The alkali metal salt or alkaline earth metal salt to be contained in the activating liquor to be used in this invention is a neutral salt (normal salt) and it is relatively stable at high temperatures, and in this point the activating liquid of this invention can be clearly distinguished from conventional aqueous solutions of organic amines or inorganic alkalis. Further, the mechanism of development by the activating liquor of this invention is quite different from the development mechanism in the conventional development methods.

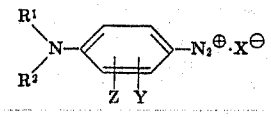
This invention will now be illustrated in detail.

Any of two-component diazotype photosensitive materials having a photosensitive layer comprising a photosensitive diazonium salt and a coupler capable of coupling with the diazonium salt may optionally be used in this invention. Such photosensitive materials are readily commercially available as dry diazotype photosensitive papers.

In general, the photosensitive layer of such two-component diazotype photosensitive material comprises as essential ingredients a light-decomposing diazonium salt, a coupler capable of coupling with said diazonium salt and an acidic stabilizer.

As the light-decomposing diazonium salt, any of diazonium salts which decompose under irradiation and are capable of coupling with a coupler under the developing conditions adopted may be used in the process of this invention. Typical instances of such diazonium salts are as follows:

Diazonium salts of N,N-disubstituted compounds of para-phenylene diamine expressed by the following general formula:



wherein X stands for an anion such as a halogen ion, a sulfuric ion or a fluoroboric ion, R^1 and R^2, which may be the same or different, designate an alkyl

group which may be substituted by a halogen atom or a hydroxyl or amino group, and Z and Y are substituents known in the art of dyestuffs as substituents on the benzene nucleus, e.g., hydrogen, halogens, alkyl groups and alkoxy groups.

Specific examples of compounds of this type are as follows:

4-Diazo-N,N-dimethylanilin (referred to simply as "MA salt")

4-Diazo-N,N-diethylaniline (referred to simply as "EA salt")

4-Diazo-N-ethyl-N-β-hydroxyethylaniline (referred to simply as "EH salt")

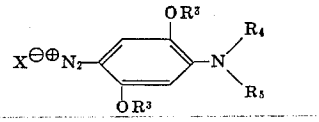
4-Diazo-N,N-bis-β-hydroxyethylaniline

4-Diazo-N-methyl-N-β-hydroxyethylaniline

4-Diazo-N-ethyl-N-β-hydroxypropylaniline

Other diazonium salts of para-phenylene di-amines N-mono- or N,N-di-substituted alkyl or hydroxyl-alkyl groups, such as 4-diazo-N-ethyl-N-(β-diethylamino)-ethylaniline, 4-diazo-2-chloro-N,N-diethylaniline, 4-diazo-2-methyl-N,N-diethylaniline, 4-diazo-2-iodo-N,N-diethylaniline, 4-diazo-N-ethyl-N-benzylaniline and 4-diazo-N-methyl-N-benzylaniline (referred to simply as "methylbenzyl")

Diazonium salts of the aminohydroquinone ether type expressed by the following general formula



wherein R^3, R^4 and R^5, which may be the same or different, stand for an optionally substituted alkyl or aryl group, and X is as defined above.

Specific examples of compounds of this type are as follows:

4-Diazo-2,5-dibutoxy-N,N-diethylaniline

4-Diazo-2,5-diethoxy-N-benzoylaniline (referred to simply as "BB salt")

4-Diazo-2,5-diethoxy-N-ethyl-N-benzoylaniline

4-Diazo-2,5-dibenzyloxy-N-benzoylaniline

4-Diazo-2-chloro-5-methoxy-N-benzoylaniline

4-Diazo-2,5-diethoxy-N-benzoylmethylaniline

Other 4-diazo-2,5-dihydroxyalkyl (or dihydroxyaryl)-N-alkyl (or aryl) compounds and derivatives thereof.

Diazonium salts of the aminodiphenyl or aminodiphenylamine type expressed by the following general formula $X^{-+}N_2\text{-}R^6\text{—}A\text{—}R^7$ or $X^{-+}N_2\text{—}R^6\text{—}A\text{—}R^7N_2{}^+X^-$

wherein R^6 and R^7, which may be the same or different, stand for an optionally substituted aryl group, especially a phenyl group, X is as defined above, and $R^6\text{—}A\text{—}R^7$ group stands for a diarylamino group (A = —NH—), a diphenyl group (A = direct bond), a diphenyloxide group (A = —O—), a diarylmethane group (A = $—CH_2—$), a stilbene group (A = —CH=CH—) or a diarylsulfide group (A = —S—).

Specific examples of compounds of this type are as follows:

Para-diazodiphenylamine

4-Diazo-2,5,4′-triethoxydiphenylamine

4-Diazo-2,5,4′-triethoxydiphenyl

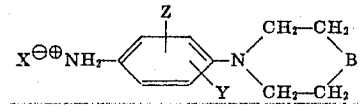
4,4′-Bis-diazo-2,2′,5,5′-tetrahydroxydiphenylmethane

Bis-diazo-3,3′-dichloro-5,5′-dimethoxybenzidine

4-Diazo-2,5-dimethoxyphenylethylsulfide

4-Diazo-2,5-diethoxy-4′-methyldiphenylsulfide

Diazonium salts of the heterocyclic amine type expressed by the following general formula



wherein X, Y and Z are as defined above, and B stands for —O— (morpholine type), —S— (thiomorpholine type), $—CH_2—$ (phenylpiperidine type) or a direct bond (phenylpyrolidine type).

Specific examples of compounds of this type are as follows:

4-Diazo-2,5-dibutoxy-N-phenylmorpholine

4-Diazo-2,5-diethoxy-N-phenylmorpholine

4-Diazo-2-methoxy-N-thiomorpholine

4-Diazo-N-phenylpiperidine

4Diazo-N-phenylpyrolidine

4-Diazo-2,5-di-n-butoxy-N-phenylpiperidine

Other 4-diazo-N-phenyl-heterocyclic amine derivatives

Diazonium salts of N,N-substituted ortho-phenylenediamines and diazonium salts of ortho-aminophenols. Specific examples of compounds of this type are as follows:

2-Diazo-4-methylmercapto-N,N-dimethylaniline

2-Diazo-5-benzoylamino-N,N-dimethylaniline

2-Diazo-1-naphthol-5-sulfonic acid

The above-mentioned diazo compounds are used in the form of relatively stable diazonium salts, such as sulfates or hydrochlorides. They may also be used in the form of double salts with zinc chloride, tin chloride, aluminum sulfate or the like. They may also be used in the form of diazotates stabilized by aryl sulfonates (diazonium salts of aromatic sulfonic acids) or diazosulfonates (diazonium salts of sulfonic acid acids or their alkali metal salts). These diazonium salts may be used singly, or mixtures of two or more of them may also be used.

As the coupler to be contained in the diazotype photosensitive material, any of couples capable of coupling with a diazonium salt such as exemplified above under development conditions adopted in this invention may be used. For instance, phenol derivatives, naphthol derivatives and active methylene group-containing compounds are used. Specific examples of such couplers are as follows:

Phenol derivatives such as pyrocatechol, resorcine, phloraglucinal, pyrogallol, resorcine monoglycol ether, meta-aminophenol, para-aminophenol, diethylaminophenol, 2,5,6-trimethylphenol, 2-hydroxymethylphenol, β-(2-hydroxyphenyl)-propionic acid, 2-(ω-phenylaminomethyl)-phenol, β-(4-methyl-2-hydrophenol)-glutaric acid, 2,5-dimethyl-6-(N-dimethylaminomethyl)-phenol, the 1,3-dimethyl ether of pyrogallol, α-resorcyclic acid ethanolamine, N-lauryl-para-aminophenol, β-resorcylic acid ethanolamine, N-acyl-meta-aminophenol, meta-hydroxyacetoanilide, ortho-N-hydroxydiphenol-monoguanidine, para-N-

hydroxydiphenyl-bi-guanidine, 2,5-dimethyl-4-morpholinomethylphenol, 2-methyl-5-isopropyl-4-morpholinomethylphenol, 4-morpholine-methylresorcinol monomethyl ether, 3,3',5-**trihydroxydiphenyl,** 3,3',5,5'-tetrahydroxydiphenyl, 2,2',4,4'-tetrahydroxydiphenyl, 2,4,4'-trihydroxydiphenyl-2'-sulfonic acid, 2,4,6,3',5'-pentahydroxydiphenyl, and 2,2',4,4'-tetrahydroxydiphenyl.

Hydroxynaphthalene derivatives such as 2,3-dihydroxynaphthalene, β-naphthol, α-naphthol, 1,6-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 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-dihydroxy-naphthalene-8-sulfonic acid, 1,8-aminonaphthol-5-sulfonic acid, 2,7-dihydroxy-3,6-disulfonic acid, 1,8-benzolyl-aminonaphthol-2-sulfonic acid, 1,8-dihydroxynaphthalene-6-sulfonic acid, 2-hydroxy-3-naphthonic-acid-N,N-bis-β-hydroxyethylamide, 8-hydroxy-2-naphthonic-acid-hydroxy-ethylamide, 1-(N-carboethoxymethylamino)-8-naphthol-4-sulfonic acid, 5-(para-nitro)-benzamide-1naphthol, 1-hydroxynaphthyl-7-phenylguanidine, 2-hydroxynaphthyl-8-biguanidine, 1-naphthol-3-(N-β-hydroxyethyl)-sulfonamide, 1-naphthol-3-(N-o-methoxyphenyl)-sulfonamide, bis-[5-hydroxy-7-sulfonaphthyl(2)]-amine, and N,N-bis-[1-hydroxy-3-sulfonaphthyl(6)]-thiourea.

Active methylene group-containing compounds such as 1-phenyl-3-methyl-pyrazolone (5), acetoacetic acid anilide, 1-phenyl-3-carboxypyrazolone, acetoacetic acid cyclohexylamide, acetoacetic acid benzylamide, cyanoacetoanilide, cyanoacetomorpholine, 1(3'-sulfonamide)-phenyl-3-methylpyrazolone-5, and 1-(4'-carboxy-ethylphenyl)-3-dodecyl-pyrazolone-5.

These couplers may be used singly, or mixtures of two or more of these compounds may be used.

Non-volatile or difficulty volatile, organic or inorganic acids are generally used as the acidic stabilizer (precoupling inhibitor) to be contained in the diazotype photosensitive material to be used in this invention. As such non-volatile or difficulty volatile acid there are mentioned, for example, citric acid, tartaric acid, oxalic acid, maleic acid, malic acid, succinic acid, sulfamic acid, boric acid, phosphoric acid, etc.

In this invention, such composition constituting the photosensitive layer of the diazotype photosensitive material to be used in this invention may further comprise an extender for improving the bondability of the composition to the substrate, the coating uniformity and water resistance. It is also possible to incorporate into such photosensitive composition additives orginarily used in the art, such as development promotors and coloring materials.

As the extender there may be employed, for example, dextrin, polyvinyl alcohol, gum arabic, colloidal silica, and polyvinyl borate emulsion. As the development promotor there may be used, for example, glycerine, ethyleneglycol and other polyhydric alcohols. In general, coloring materials are used for the purpose of indicating the surface to be exposed to light and increasing the whiteness of the background. As such coloring material there may be preferably used blue dyes such as Methylene Blue, Patent Blue, etc. Water and organic solvents such as alcohols, e.g., methanol and ethanol, ketones, e.g., acetones and methylethylketone, aromatic hydrocarbons, e.g., toluene and xylene, and esters, e.g., ethyl acetate and butyl acetate are used for dissolving the above ingredients of the photosensitive composition constituting the photosensitive layer.

Two-component diazotype photosensitive compositions suitable for attaining the objects of this invention generally contain ingredients at ratios illustrated below, through the scope of this invention is not at all limited by such illustration:

Diazonium salt	0.1 – 4 % by weight, preferably 0.7 – 2 % by weight
Coupler	0.5 – 5 % by weight, preferably 2 – 4 % by weight
Acidic stabilizer	0.1 – 5 % by weight, preferably 1.5 – 3 % by weight
Coloring material	0 – 0.025 % by weight, preferably 0.01 – 0.02 % by weight
Development promotor	0 – 10 % by weight, preferably 3 – 8 % by weight
Extender	0 – 5 % by weight, preferably 3 – 5 % by weight
Solvent	balance

The above photosensitive composition is coated on a substrate such as paper, plastic film, woven fabric, non-woven fabric or metal foil, whereby a two-component diazotype copying material is formed.

In accordance with this invention, a two-component diazotype photosensitive material having a photosensitive layer formed by application of the above-mentioned two-component diazotype photosensitive composition is exposed image-wise to light emitted from a known light source used in the diazotype reproduction, such as from a fluorescent lamp, tungsten lamp, mercury lamp, arc lamp, xenon lamp, sun-light, etc. through an original having opaque image areas and transparent or semi-transparent non-image areas; whereby a pattern consisting of a latent image composed of the undecomposed diazonium salt and a background is formed on the photosensitive layer. The above operation can be accomplished by means known in the art.

According to the process of this invention, an activating liquor composed of a solution or dispersion of an alkali metal or alkaline earth metal salt of a carboxylic acid is applied to the photosensitive layer having a latent image consisting of the undecomposed diazonium salt.

Alkali metal and alkaline earth metal salts of organic compounds having at least one carboxyl group are used as far as they are soluble or dispersible in solvents to be used, and it does not matter whether they are volatile or not. In some cases, however, it is preferred that carboxylic acids are volatile and carboxylic acid salts are soluble in water. As the alkali metal for forming a salt with such carboxylic acid, there may be mentioned, for instance, potassium, sodium, lithium and rubidium, and use of sodium and potassium is especially preferred. As the alkaline earth metal there may be exemplified magnesium, calcium, barium, beryllium and strontium, and use of magnesium and calcium is especially preferred.

Examples of alkali metal and alkaline earth metal salts of carboxylic acids to be used in this invention are as follows:

a. Alkali metal and alkaline earth metal salts, e.g., sodium salts, potassium salts, lithium salts, Rochelle salts, magnesium salts, calcium salts and barium

salts, of aliphatic monocarboxylic acids expressed by the following general formula

$$RCOOM_{1/n}$$

wherein R is a saturated or unsaturated, straight, branched or cyclic mono-valent aliphatic groups which may have such substituents as halogen, hydroxyl, amino or sulfonic groups, M is an alkali metal or alkaline earth metal, and n is 1 or 2 indicating the valency of M;

such as alkali metal and alkaline earth metal salts of such aliphatic monocarboxylic acids as formic acid, acetic acid, propionic acid, acrylic acid, aconic acid, acetoacetic acid, valdric acid, crotonic acid, butyric acid, undecanoic acid, butyric acid, capric acid, caprylic acid, chloroacetic acid, bromoacetic acid, trichloroacetic acid, chlorofumaric acid, cyclobutane-carboxylic acid, quinic acid, sulfoacetic acid, sorbic acid, tiglic acid. tetrolic acid, vinylacetic acid, pyruvic acid, methacrylic acid, levulinic acid, caproic acid, isovaleric acid, pelargonic acid, palmitic acid, lauric acid, myristic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, erucic acid, tridecanoic acid, morganic acid, behenic acid, stearclic acid, glycolic acid, citric acid, tartaric acid, adipic acid, arabonic acid, alloxanic acid, saccharic acid, isovanillic acid, hydroxybutyric acid, glyceric acid, gluconic acid, diglycolic acid, citramanic acid, thioglycolic acid, desoxalic acid, lactic acid, racemic acid, mannonic acid, malic acid, leucic acid, glycine, alanine, leucine, serine, threonine, cysteine, lysine and arginine.

Sodium and potassium salts of formic acid and acetic acid are especially preferably among the above-mentioned alkali metal or alkaline earth metal salts of carboxylic acids.

b. Alkali metal and alkaline earth metal salts, e.g., sodium salts, potassium salts, lithium salts, magnesium salts, calcium salts, and barium salts, of aliphatic polycarboxylic acids expressed by the following general formula

$$R'(COOM_{1/n})_m$$

wherein R' is a saturated or unsaturated, straight, branched or cyclic poly-valent aliphatic group which may have such substituents as halogen, hydroxyl, amino or sulfonic groups, m is the valency of the aliphatic group, and M and n are as defined above;

such as alkali metal and alkaline earth metal salts of such carboxylic acids as malonic acid, acetonedicarboxylic acid, citraconic acid, oxalic acid, acrylmalonic acid, isocamphoronic acid, ethylmalonic acid, glutaric acid, succinic acid, camphoric acid, sebacic acid, pimelic acid, brassylic acid, maleic acid, muconic acid, mesaconic acid, adipic acid, azelaic acid, suberic acid, aspartic acid aconitic acid, and glutamic acid.

Sodium and potassium salts of oxalic acid and malonic acid are especially preferred among these alkali metal and alkaline earth metal salts of carboxylic acids.

c. Alkali metal and alkaline earth metal salts, e.g., sodium salts, potassium salts, lithium salts, magnesium salts, calcium salts and barium salts, of aromatic mono- and poly-carboxylic acids expressed by the following general formula

$$Ar(COOM_{1/n})_p$$

wherein Ar stands for a mono-valent or polyvalent aryl or aliphatic groups which may have such substituents as halogen, amino, hydroxyl, mercapto, alkyl, alkenyl, hydroxyalkyl, acyl and sulfonic groups, p is the valency of the Ar group, and M and n are defined above;

such as alkali metal and alkaline earth metal salts of such aromatic carboxylic acids as benzoic acid, phthalic acid, terephthalic acid, trimellitic acid, salicylic acid, acetophenone-carboxylic acid, anisic acid, aminobenzoic acid, aminocinnamic acid, propylbenzoic acid, hydroxyphthalic acid, hydroxyphenylacetic acid, cinnamic acid, chlorobenzoic acid, chlorophthalic acid, dimethoxyphthalic acid, sulfosalicylic acid, thiosalicylic acid, toluic acid, truxillic acid, tropic acid, naphthalic acid, vanillic acid, biphenyl-carboxylic acid, phenyl-acetic acid, phenylsuccinylacetic acid, phenyl-lactic acid, benzenetetracarboxylic acid, phenylbutyric acid, benzoylbenzoic acid, benzoylglucolic acid, benzoylacetic acid, homophthalic acid, mandelic acid, phenylalanine and tryosine.

Sodium and potassium salts of benzoic acid and salicylic acid are especially preferred among the above-mentioned alkali metal and alkaline earth metal salts of aromatic carboxylic acids.

d. Alkali metal and alkaline earth metal salts of heterocyclic mono- and poly-carboxylic acids such as sodium, potassium, lithium, magnesium, calcium and barium salts of 2,4-dimethyl-3-furancarboxylic acid, thiophenecarboxylic acid, terpenylic acid, paraconic acid, furanacarboxylic acid, alginic acid, coumarinic acid, and pyridine-carboxylic acid.

In the activating liquor to be used in this invention, one or more of the above-mentioned carboxylic acid salts need not be completely dissolved, but a dispersion (or suspension) of such salt may also be used. Water is most preferred as a medium for dissolving such carboxylic acid salt, but it is also possible to use aqueous mixtures of water-miscible organic solvents such as polyhydric alcohols, e.g., methanol, ethanol and propanol, ketones, e.g., acetone and methylethylketone, and polyhydric alcohols, e.g., ethylene glycol and glyceral. Still in addition, organic solvents capable of dispersing therein carboxylic acid salts can be used in this invention. As such solvent there may be exemplified alcohols such as methanol, ethanol and propanol, ketones such as acetone and methylethylketone, aromatic hydrocarbons such as toluene and xylene, esters such as ethyl acetate and butyl acetate, ethers such as butyl ether, propyl ether, dioxane and trioxane, and halogenated hydrocarbons such as chloroform and carbon tetrachloride.

The activating liquor to be used in this invention contains the alkali metal or alkaline earth metal salt of a carboxylic acid at a concentration generally ranging from 5 to 60 percent by weight, preferably 10 to 40 percent by weight, based on the amount of the activating liquor. The above-mentioned alkali metal or alkaline earth metal carboxylates may be used either singly or in the form of mixtures of two or more of them. In case mixtures of two or more salts are used, it is preferred that the total amount of the salts be within the

above-mentioned range. Since the activating liquor is applied to the two-component diazotype photosensitive material, it is important that the activating liquor should not contain a coupler. In addition to the above-mentioned carboxylic acid salt, the activating liquor may further comprise small amounts of assistants as optional components. Examples of such assistants include dye-insolubilizing agents such as disclosed in Japanese Patent Publication No. 45-27680/70, e.g., quaternary ammonium compounds and amines; penetrants such as mono- and poly-hydric alcohols, or non-ionic surface active agents; and extenders such as dextrin, starch, and polyvinyl alcohol. In order to improve the visual whiteness of the background, it is possible to incorporate in the activating liquor a whitening agent such as fluorescent dyes and blue dyes.

A typical instance of the composition of an activating liquor to be used preferably in this invention is as follows:

Alkali metal or alkaline earth metal carboxylate	5 – 60 % by weight, especially 10 – 40 % by weight
Penetrant	0 – 20 % by weight, especially 2 – 5 % by weight
Dye-insolubilizing agent	0 – 15 % by weight, especially 1 – 3 % by weight
Extender	0 – 20 % by weight, especially 2 – 5 % by weight
Whitening agent	0 – 0.5 % by weight, especially 0.01 – 0.1 % by weight
Solvent	balance

In accordance with this invention, a small amount of the activating liquor is applied to the exposed two-component diazotype photosensitive material, and it is preferred that the activating liquor is applied uniformly to the light-exposed photosensitive layer. In this invention, it is sufficient that the amount of the activating agent is such that the photosensitive layer is wetted with the activating liquor, and it is generally unnecessary to drench the photosensitive layer with the activating liquor. Of course, it is possible to apply a considerable amount of the activating liquor to the photosensitive layer, but any particular advantage is not attained by application of the activating liquor in a great amount. Further, when a diazonium salt or coupler contained in the photosensitive layer is readily soluble in water, use of a great amount of the activating liquor results frequently in such defects as flow and blot of a copied image.

The amount applied of the activating liquor liquor varies considerably depending on the kind of the carboxylic acid salt contained in the activating liquor, but generally speaking, it is preferred that the activating agent is applied in an amount of 1 to 15 g, especially 4 to 10 g, per square meter of the photosensitive layer.

Application of the activating liquor can be accomplished by means known per se, for instance, roller coating, spraying and other liquid-applying methods. For instance, when the application of the activating liquid on the two-component diazotype photosensitive layer is carried out by employing a roll, the abovementioned amount of the activating liquor is at first applied on the coating roll and then a thin layer of the activating liquor on the coating roll is transferred onto the photosensitive layer. As such coating roll, there may be employed, for instance, a smooth metal roll, a mesh roll, a rubber roll, a sponge roll and the like.

In the two-component diazotype photosensitive material which has been exposed to light and on which a small amount of the activating liquor has been applied, a latent image formed on the photosensitive layer can be developed into a visible image without any particular heating (namely allowing it to stand still at temperatures approximating room temperature). In such case, however, it takes time to develop the latent image into a visible image. Therefore, in general, heating is used to develop the latent image consisting of the undecomposed diazonium salt and coupler and obtain a copy sheet in the dry state. The heating temperature varies greatly depending on the kind of the activating liquor or combination of the diazonium salt and coupler. In general, however, it is desired that the heating is effected at 50° to 250°C., preferably 60° to 200°C., especially 70° to 120°C. To conduct the development at such elevated temperatures is advantageous in that development is accomplished instantaneously and a dry copy sheet is obtained. In case the activating liquor is free of water, it is important that the heating is effected with use of steam or the photosensitive layer is wetted with water by some means prior to heating.

The heating of the photosensitive material can be conducted with ease by optional heating means, for instance, a heating roll, infrared irradiation, hot air, heated steam or the like.

Reasons why the alkali metal or alkaline earth metal carboxylate promotes development in the two-component diazotype photosensitive material in this invention have not been completely elucidated. However, in view of the fact that the alkali metal or alkaline earth metal carboxylate is a neutral salt and is stable at high temperatures, it is readily presumed that the carboxylate or its thermal decomposition product may neutralize the acidic stabilizer in the two-component diazotype photosensitive composition and initiate coupling of the diazonium salt with the coupler. We construe that the reason why the alkali metal or alkaline earth metal carboxylate enables coupling of the diazonium salt with the coupler at relatively low temperatures is not that the carboxylate acts on the acidic stabilizer but that the carboxylate activates the diazonium salt by synergetic activity with the heat thereby initiating initiate coupling of the diazonium salt with the coupler regardless of the presence of the acidic stabilizer.

In the process of this invention, since the ingredient of the activating liquor is a salt stable. even at high temperatures, one obvious advantage is that development can be accomplished easily without formation of a nasty or irritative decomposition gas. Further, since the ingredient of the activating liquor to be applied on the two-component diazotype photosensitive material is a non-volatile salt, it is sufficient that the activating liquor is applied only in a very small amount. Accordingly, the process of this invention is advantageous also from the economical viewpoint, and any special operation need not be effected to dry a copy sheet. Still further, even when the ingredient of the activating liquor applied to the two-component diazotype photosensitive material is left on the photosensitive layer, since the alkali metal or alkaline earth metal carboxylate is a neutral salt which is stable of itself, it exhibits no tendency of discoloring the coupler remaining in the photosensitive layer unlike conventional free organic amines or inorganic alkalis. In fact, copy sheets obtained accord-

ing to the process of this invention, as copy sheets obtained by the dry development method using a gaseous mixture of ammonia and steam, are characterized in that distinction of the non-exposed areas is very high (whiteness of the background is excellent) and discoloration hardly occurs even when copy sheets are stored for a long period of time.

As compared with the dry developing method, the process of this invention is generally advantageous in that copy sheets excellent in the image density and water resistance can be obtained. For instance, in the case of a combination of dihydroxynaphthalene sulfonic acid and a diazonium salt, which is most commonly used in two-component diazotype photosensitive copying papers for the dry development, copied images are relatively faintly blue and poor in water resistance when the development is conducted by the dry development method using a gaseous mixture of ammonia and vapor. In contrast, if the activating liquor of this invention, for instance, an aqueous solution of sodium acetate is applied to such photosensitive papers, images of a dense violet color excellent in water resistance can be obtained.

The process of this invention can be effectively applied not only to ordinary diazotype reproduction processes but also to multi-color reproduction processes such as disclosed in German Patent Application Laid-Open Specification No. 2,007,690.

This invention will now be detailed by reference to Examples, from which effects and advantages of this invention will readily be understood.

EXAMPLE 1

A composition of the following recipe was coated on a substrate paper for a photosensitive copying sheet by means of an ordinary coating device such as an air knife coater, and dried to form a two-component diazotype photosensitive paper for heat development:

4-Diazo-N,N-dimethylaniline chloride·½$ZnCl_2$	15 g
Diethyleneglycol	60 g
Citric acid	40 g
Sodium 2,7-dihydroxynaphthalene-3,6-disulfonate	20 g
Zinc chloride	50 g
Thiourea	50 g
Patent Pure Blue	0.1 g
Water	balance
Total	1 liter

The so formed photosensitive copying sheet was overlapped with an original sheet having an image thereon, and the assembly was exposed to light emitted from a mercury lamp disposed above the assembly thereby to form a latent image of the diazonium salt. Then, an activating liquor of the following recipe was applied uniformly onto the surface of the copying sheet in an amount of about 8 g per square meter of the copying sheet surface by means of a coating roll:

Sodium acetate	150 g
Diethyleneglycol	50 g
Water	balance
Total	1 liter

Then, the activating liquor-applied copying sheet was allowed to have an instantaneous contact with a heating roll of the heat transfer type maintained at about 80°C. to effect the development. A copy sheet having an image of a clear blue was obtained.

Example 2

A composition of the following recipe was coated on a substrate paper for a photosensitive copying sheet by means of an ordinary coating device such as air knife coater, and dried to form a two-component diazotype photosensitive paper for heat development:

4-Diazo-N-ethyl-N-hydroxyethylaniline·½$ZnCl_2$	15 g
Glycerine	50 g
Tartaric acid	50 g
Sodium 2,3-dihydroxy-6-sulfonate	30 g
Zinc chloride	40 g
Thiourea	50 g
Patent Blue	30 g
Water	0.1 g
Total	balance
	1 liter

The so formed photosensitive copying sheet was overlapped with an original sheet having an image thereon, and the assembly was exposed to light emitted from a light source such as a mercury lamp or fluorescent lamp disposed above the assembly thereby to form a latent image of the diazonium salt. Then, an activating liquor of the following recipe was applied onto the surface of the copying sheet in an amount of about 8 g per square meter of the copying sheet surface by means of a coating roll:

Lithium acetate	150 g
Ethyleneglycol	50 g
Dye-insolubilizing agent of polyamine type (Mōrin Fix PA Conc manufactured by Mōrin Chemical Industries, Inc.)	10 g
Water	balance
Total	1 liter

The activating liquor-applied sheet was instantaneously heated at about 100°C. by means of infrared irradiation. A copy sheet having an image of a clear blue color was obtained.

Example 3

A composition of the following recipe was coated on a substrate paper in the same manner as in Example 1 and dried to obtain a diazotype photosensitive copying sheet for heat development and black coloration:

4-Diazo-N,N-diamethylaniline chloride·½$ZnCl_2$	20 g
Diethylene glycol	50 g
Tartaric acid	50 g
Sodium 2,7-dihydroxynaphthalene-3,6-disulfonate	25 g
Resorcinal	4 g
Acetoacetoanilide	3 g
Zinc chloride	15 g
Thiourea	50 g
Sodium 1,3,6-naphthalene-trisulfonate	30 g
Patent Blue	0.1 g
Water	balance
Total	1 liter

The so formed copying sheet was overlapped with an original sheet having an image thereon, and the assembly was exposed to light emitted from a mercury lamp disposed above the assembly thereby to form a latent image of the diazonium salt thereon. Then, an activating liquor of the following recipe was applied on the copying sheet by spray coating in an amount of about 5 g per square meter of the copying sheet surface:

Sodium formate	80 g
Sodium tartrate	100 g
Water	balance
Total	1 liter

The activating liquor-applied copying sheet was instantaneously contacted with a heating roll maintained at 80° – 90°C. A copying sheet having a black image was thus obtained.

Example 4

A composition of the following recipe was applied on a substrate for a copying sheet in the same manner as in Example 1 and dried to obtain a two-component diazotype copying sheet for heat development and red coloration:

4-Diazo-N-methyl-N-hydroxyethylaniline chloride·½$ZnCl_2$	15 g
Diethyleneglycol	75 g
α-Resorcylic acid ethanolamine	8 g
Citric acid	40 g
Zinc chloride	50 g
Thiourea	25 g
Patent Blue	0.1 g
Water	balance
Total	1 liter

The so formed copying sheet was exposed to light in the same manner as in Example 1 to form a latent image of the diazonium salt, and an activating liquor of the following recipe was coated thereon by a coating roll in an amount of about 8 g per square meter of the copying sheet surface:

Potassium formate	50 g
Sodium oleate	100 g
Water	balance
Total	1 liter

The activating liquor-applied copying sheet was instantaneously contacted with heated steam (maintained at about 100°C.) thereby to obtain a copy sheet having a copied image of a red color.

Example 5

A composition of the following recipe was coated on a substrate paper for a copying sheet in the same manner as in Example 1 and dried to obtain a two-component diazotype phososensitive copying sheet for heat development:

4-Diazo-2,5-dibutoxy-N-phenyl-morpholine·½$ZnCl_2$	15 g
Tartaric acid	30 g
Diethylene glycol	50 g
β-Hydroxynaphthoic acid aminoethylamine	7 g
Zinc chloride	25 g
Thiourea	25 g
Patent Blue	0.1 g
Water	balance
Total	1 liter

A latent image of the diazonium salt was formed on the copying sheet in the same manner as in Example 1, and an activating liquor having the following recipe was applied on the copying sheet in an amount of about 6 g per square meter of the copying sheet surface by a coating roll:

Sodium potassium tartrate	150 g
Potassium acetate	50 g
Water	balance
Total	1 liter

Then, the activating liquor-applied copying sheet was instantaneously contacted with a heating roll maintained at about 100°C. to obtain a copy sheet having a copied image of a blue color.

Example 6

A solution of the following recipe was coated on a semi-transparent tracing paper and dried to obtain a two-component diazotype copying sheet for heat development and for formation of a second original:

4-Diazo-N-ethyl-N-hydroxyethylaniline chloride ½$ZnCl_2$	25 g
Tartaric acid	40 g
Ethyleneglycol	50 g
Resorcinal	100 g
Phloroglucinol	2 g
Zinc chloride	40 g
Boric acid	10 g
Water	balance
Total	1 liter

The so formed photosensitive copying sheet was overlapped with an original sheet having an image and the assembly was exposed to light emitted from a mercury lamp disposed above the assembly to form a latent image of the diazonium salt. Then, an activating liquor of the following recipe was applied to the copying sheet in an amount of about 5 g per square meter of the copying sheet surface by means of a coating roll:

Sodium monochloroacetate	100 g
Sodium formate	50 g
Water	balance
Total	1 liter

The activating liquor-applied copying sheet was instantaneously contacted with a heating roll maintained at 110°C. to obtain a copy sheet having a brown-colored image which could be used as a second original.

Example 7

A solution of the following recipe was coated on a substrate paper for a photosensitive copying sheet according to a customary coating method using an air knofe coater and dried at a relatively low temperature (80°– 90°C.) to obtain a two-component diazotype photosensitive sheet for heat development:

4-Diazo-N,N-dimethylaniline·½$ZnCl_2$	15 g
Tartaric acid	5 g
Sodium 2,3-dihydroxynaphthalene-6-sulfonate	40 g
Urea	20 g
Thiourea	25 g
Saponin	0.1 g
Methylene Blue	0.1 g
Water	balance
Total	1 liter

The so formed copying sheet was overlapped with a semi-transparent original sheet having an image thereon and the assembly was exposed to light emitted from a mercury lamp disposed above the assembly to form a latent image of the diazonium salt on the copy-

ing sheet. An activating liquor of the following recipe was applied on the copying sheet by means of a coating roll in an amount of about 5 g per square meter of the copying sheet surface:

Sodium benzoate	150 g
Polyvinyl alcohol	5 g
Diethyleneglycol	50 g
Water	balance
Total	1 liter

The activating liquor-applied copying sheet was instantaneously contacted with a heating roll maintained at about 100°C. thereby to obtain a copy sheet having a blue-colored image.

Example 8

A composition of the following recipe was coated on a polyester film by means of a rod coater and dried by hot air maintained at about 100°C. to obtain a two-component diazotype photosensitive film for heat development:

4-Diazo-2,5-dibutoxy-N-phenylmorpholine·½$ZnCl_2$	15 g
Tartaric acid	8 g
β-Hydroxynaphthoic acid ethanolamine	8 g
Butylated urea resin	4 g
Oil Blue	0.2 g
Methanol	balance
Total	1 liter

The so formed photosensitive copying sheet overlapped with an original sheet having an image thereon, and the assembly was exposed to light emitted from a mercury lamp disposed above the assembly to form a latent image of the diazonium salt on the copying sheet. An activating liquor of the following recipe was applied to the copying sheet by means of a coating roll in an amount of about 3 g per square meter of the copying sheet surface:

Sodium formate	100 g
Sodium oleate	50 g
Methanol	80 g
Water	balance
Total	1 liter

The activating liquor-applied copying sheet was instantaneously contacted with heated steam maintained at about 100°C. thereby to obtain a copy sheet having a blue-colored image.

Example 9

A solution of the following recipe was coated by means of an air knife coater on a substrate paper which had been treated in advance with a 20 percent solution of a butadiene-methyl methacrylate copolymer resin emulsion, and dried to obtain a two-component diazotype photosensitive copying sheet for heat development and multi-color reproduction:

4-Diazo-N,N-dimethylaniline chloride·½$ZnCl_2$	15 g
Diethyleneglycol	40 g
Tartaric acid	100 g
Sodium 2,7-dihydroxynaphthalene-3,6-disulfonate	8 g
Zinc chloride	10 g
Thiourea	40 g
Patent Blue	0.1 g
Water	balance
Total	1 liter

The photosensitive copying sheet was overlapped with an original sheet in which a portion of the back surface of an image had been treated with a red-color-forming liquor of the following recipe containing a thermovolatile coupler and another portion of the back surface of the image had been treated with a yellow-color-forming liquor of the following recipe containing a thermovolatile coupler, in such a manner that the treated surface of the original sheet confronted the photosensitive layer of the copying sheet:

Red-Color-Forming Liquor

1-Phenyl-3-methylpyrazolone(5)	20 g
Polyvinyl acetate resin emulsion (50 %)	5 g
Thiourea	5 g
Methanol	balance
Total	100 ml

Yellow-Color-Forming Liquor

Resorcinol	50 g
Thiourea	4 g
Methanol	balance
Total	1 liter

The above assembly of the copying sheet and original was heated and exposed to light by means of a light source installed with a mercury lamp and an infrared irradiator and disposed above the assembly. Thus, a latent image of the diazonium salt was formed on the copying sheet and at the same time the thermovolatile couplers were transferred to the copying sheet at parts corresponding with the treated portions of the original sheet. An activating liquor of the following recipe was applied to the copying sheet in an amount of about 7 g per square meter of the copying sheet surface:

Sodium trichloroacetate	150 g
Dextrin	20 g
Dye-insolubilizing agent (Mōrin Fix Conc 2 R manufactured by Mōrin Chemical Industry, Inc.)	10 g
Water	balance
Total	1 liter

The activating liquor-applied copying sheet was instantaneously contacted with a heating roll maintained at about 120°C. to obtain a three-color copy sheet in which the part corresponding with the portion of the original treated with the red-color-forming liquor was colored red, the part corresponding with the portion of the original treated with the yellow-color-forming liquor was colored yellow and the part corresponding with the untreated portion of the original was colored blue.

Example 10

A solution of the following recipe was coated on a substrate paper in the same manner as in Example 1 and dried to obtain a photosensitive copying sheet for heat development and for two-color reproduction:

4-Diazo-N-methyl-N-hydroxyethylaniline chloride ½$ZnCl_2$	12 g
2-Diazo-1-naphthol-5-sulfonic acid	30 g
Tartaric acid	80 g
Diethyleneglycol	40 g

-Continued

Zinc chloride	50 g
Thiourea	25 g
Sodium 1,3,6-naphthalene-trisulfonate	30 g
Water	balance
Total	1 liter

The so formed photosensitive copying sheet was overlapped with an original sheet on which an image was drawn with a drafting ink and a pencil of a relatively faint color, and the assembly was exposed to light emitted from a mercury lamp disposed above the assembly to form a latent image of the diazonium salt. Then, an activating liquor of the following recipe was applied uniformly on the copying sheet in an amount of about 5 g per square meter of the copying sheet surface:

Potassium acetate	50 g
Sodium salicylate	80 g
Polyvinyl alcohol	10 g
Glycerine	10 g
Water	balance
Total	1 liter

The activating liquor-applied copying sheet was instantaneously contacted with a heating roll maintained at about 110°C. to effect the development. A two-color copy sheet in which the part corresponding with the image portion drawn with the drafting ink was colored blue and the part corresponding with the image portion drawn with the pencil colored red was thus obtained.

Example 11

A solution of the following recipe was coated on an ordinary substrate paper for a copying sheet by means of an air knife coater and dried to obtain a two-component diazotype photosensitive copying sheet for heat development:

4-Diazo-N-ethyl-N-hydroxyethylaniline·½$ZnCl_2$	15 g
Glycerine	50 g
Tartaric acid	30 g
Sodium 2,3-dihydroxy-6-sulfonate	40 g
Zinc chloride	50 g
Thiourea	30 g
Patent Blue	0.1 g
Water	balance
Total	1 liter

The so formed copying sheet was overlapped with an original sheet having an image thereon, and the assembly was exposed to light emitted from a mercury lamp, a fluorescent lamp or other light source disposed above the assembly to form a latent image of the diazonium salt on the copying sheet. Then, an activating liquor of the following recipe was applied on the copying sheet by means of a coating roll in an amount of about 8 g per square meter of the copying sheet surface:

Calcium acetate	150 g
Ethyleneglycol	50 g
Dye-insolubilizing agent of polyamine type (Mōrin Fix PA Conc manufactured by Mōrin Chemical Industry, Inc.)	10 g
Water	balance
Total	1 liter

The activating liquor-applied copying sheet was instantaneously heated at about 100°C. by infrared irradiation thereby to obtain a copy sheet having an image of a clear blue color.

EXAMPLE 12

A solution of the following recipe was coated on a substrate paper in the same manner as in Example 11:

4-Diazo-2,5-dibutoxy-N-phenylmorpholine·½$ZnCl_2$	15 g
Tartaric acid	30 g
Diethyleneglycol	50 g
β-Hydroxynaphthoic acid aminoethylamine	7 g
Zinc chloride	25 g
Thiourea	25 g
Patent Blue	0.1 g
Water	balance
Total	1 liter

The so formed two-component diazotype photosensitive copying sheet was overlapped with an original sheet and the assembly was exposed to light in the same manner as in Example 11 thereby to form a latent image of the diazonium salt on the copying sheet. Then, an activating liquor of the following recipe was applied on the copying sheet by means of a coating roll in an amount of about 6 g per square meter of the copying sheet surface:

Magnesium tartrate	150 g
Calcium acetate	50 g
Water	balance
Total	1 liter

The activating liquor-applied copying sheet was instantaneously contacted with a heating roll maintained at about 100°C. thereby obtaining a copy sheet having a blue-colored image.

EXAMPLE 13

A solution of the following recipe was coated on a substrate paper for a copying sheet by a customary coating method employing an air knife coater and dried at a relatively low temperature (80° – 90°C.) to obtain a two-component diazotype photosensitive copying sheet for heat development:

4-Diazo-N,N-dimethylaniline·½$ZnCl_2$	15 g
Tartaric acid	5 g
Sodium 2,3-dihydroxynaphthalene-6-sulfonate	40 g
Trichloroacetic acid	50 g
Urea	20 g
Thiourea	25 g
Saponin	0.1 g
Methylene Blue	0.1 g
Water	balance
Total	1 liter

The so formed photosensitive copying sheet was overlapped with a semi-transparent original sheet having an image thereon, and the assembly was exposed to light emitted from a mercury lamp disposed above the assembly to form a latent image of the diazonium salt. An activating liquor of the following recipe was coated on the copying sheet by means of a coating roll in an amount of about 5 g per square meter of the copying sheet surface:

Magnesium benzoate	150 g
Polyvinyl alcohol	5 g
Diethylene glycol	50 g
Water	balance
Total	1 liter

The activating liquor-applied copying sheet was instantaneously contacted with a heating roll maintained at about 100°C. thereby to form a copy sheet having a blue-colored image.

In order to illustrate excellent effects attained by conducting the heat development with use of an activating liquor containing an alkali metal or alkaline earth metal carboxylate according to the process of this invention, the following experiments were carried out.

Experimental Procedures

Two-component diazotype photosensitive copying sheets were prepared by coating on substrate papers by means of an air knife coater a photosensitive composition of the following recipe that is most customarily used in the art and drying it:

4-Diazo-N-ethyl-N-hydroxyethylaniline chloride·½$ZnCl_2$	15 g
Glycerine	50 g
Tartaric acid	30 g
Sodium 2,3-dihydroxy-6-sulfonate	40 g
Zinc chloride	50 g
Thiourea	25 g
Saponin	0.3 g
Patent Blue	0.1 g
Water	balance
Total	1 liter.

Each of the so formed photosensitive copying sheets was overlapped with an original having an image thereon and exposed to light, following which the development was carried out by either of the following development methods.

1. Development Process of This Invention

An activating liquor of the following recipe was coated on the above light-exposed copying sheet by means of a coating roll in an amount of about 8 g per square meter of the copying sheet surface:

Sodium acetate	150 g
Diethyleneglycol	50 g
Dextrin	5 g
Dye-insolubilizing agent (Mōrin Fix PA Conc manufactured by Mōrin Chemical Industry, Inc.)	15 g
Water	balance
Total	1 liter

The so treated copying sheet was instantaneously contacted with a heating roll maintained at about 120°C. to effect the development.

2. Development Process Using Gaseous Mixture of Ammonia and Steam

The above light-exposed copying sheet was contacted with a gaseous mixture of ammonia and steam according to a customary method to effect the development.

3. Development Process Using Nitrogen-Containing Organic Base

In accordance with the teachings of Japanese Patent Publication No. 39-8149/64, a liquid developer of the following recipe was coated on the above light-exposed copying sheet by means of a coating roll in an amount of about 10 g per square meter of the copying sheet surface:

Triethanolamine	10 g
Water	100 ml

The so treated copying sheet was instantaneously contacted with a heating roll maintained at about 150°C. to effect the development.

4. Development Process Using Aqueous Solution of Alkali

In accordance with the teachings of Japanese Patent Publication No. 43-13815/68, an aqueous solution of the following recipe was coated on the above light-exposed copying sheet by means of a coating roll in an amount of about 7 g per squre meter of the copying sheet surface:

Potassium carbonate	5 g
Water	balance
Total	100 ml

With respect to each development process, the development efficiency was evaluated by the following procedures.

METHODS OF MEASUREMENT OF DEVELOPMENT EFFICIENCY

a. Image Density

With respect to the copy sheets obtained by the above development processes, the Y value of the unexposed area of the copied image was measured by means of a color-difference meter of type No. 4 manufactured by Nippon Denshoku Co., Ltd., and the image density was expressed in terms of the value of $(-\log Y)$.

b. Coloring Rate

The coloring state was visually evaluated with respect to each of the above development processes.

c. Discoloration of Copied Image (Photoresistance)

Unexposed and completely exposed portions of the sample copying sheet were developed by either of the above development processes, and then exposed to light emitted from a mercury lamp of 800 W disposed 30 cm apart from the copy sheet surface for 3 hours. L, a and b values according to UCS chromatocity were measured by means of a color difference meter (manufactured by Nippon Denshoku) and the discoloration was expressed in terms of the color difference of the so treated copying sheet (ΔE) from the untreated sample copying sheet calculated by the following formula:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

d. Water Resistance of Copied Image

An image of the unexposed portion developed by either of the above development processes was dipped in flowing water maintained at 18°C. for 5 minutes, and then dried. The dye concentration $(-\log Y)$ was measured with respect to the so treated copy and the untreated copy by means of a color difference meter of ND-4 type (manufactured by Nippon Denshoku), and the dye residual ratio was calculated by the following equation:

Dye residual ratio = Remaining dye concentration of treated copy/Dye concentration fo untreated copy

e. Flow of Image at Development

With respect to each of the above development processes, the state of flow of the image was visually examined.

Results of these tests are shown in Table given below.

From the test results shown in the Table, it is seen that the development process of this invention is not

substantially different from the conventional dry development method using a gaseous mixture of ammonia and water with respect to the development efficiency and the process of this invention is superior to the said conventional dry development method with respect to the water resistance of the copied image. It is also seen that the process of this invention is superior to the conventional method employing a nitrogen-containing organic base in that the concentration of the colored image is higher in the process of this invention and such fatal effects of the conventional method as contamination and discoloration of the copied image are prominently overcome in the process of this invention. Further, in the method employing an aqueous alkali solution it can be seen that, the flow of the image was extreme with the copy lacking accuracy. Clearly, there is no comparison with such process and the process of the instant invention.

Table

Test Items	Development Processes: Process of this invention	Process Using Gaseous Mixture of Ammonia and Water	Process Using Nitrogen-Containing Organic Base	Process Using Aqueous Solution of Alkali
Colored Image Density (−log Y)	1.1079	1.1872	0.7852	0.7167
Coloring Rate	almost simultaneously with heating	instantaneously	high temperature required; rate was low at 150°C.	very low
Discoloration of Copy (ΔE) (photoresistance)				
image portion	6.8	7.8	18.4	flow of image was extreme and image lacked accuracy
non-image portion	7.2	5.2	20.1	
Water Resistance of Image (%)	89.2	83.5	87.3	
Flow of Image at Development	hardly observed	—	considerably observed	

What we claim is:

1. In a process for wet developing two-component diazotype photosensitive materials comprising exposing image-wise to actinic light a photosensitive material having a two-component diazotype photosensitive layer consisting essentially of a photosensitive diazonium salt, a coupler capable of coupling with the diazonium salt and an acidic stabilizer, and developing said photosensitive material by applying a small amount of an activating liquid to the photosensitive layer of the exposed photosensitive material, the improvement characterized in that the activating liquid consists essentially of:

a. an alkali metal carboxylate and/or an alkaline earth metal carboxylate 5–60% by weight;
b. a penetrant 0–20% by weight;
c. a dye-insolubility agent 0–15% by weight;
d. an extender 0–20% by weight;
e. a whitening agent agent 0–0.5% by weight; and
f. water to 100 percent of the activating liquid; with development carried out by heating the activating liquid applied to the photosensitive material at a temperature in the range of from 70° to 120°C.

2. A process set forth in claim **1,** wherein the carboxylic acid is one selected from the group consisting of aliphatic monocarboxylic acids, aliphatic polycarboxylic acids, aromatic monocarboxylic acids, aromatic polycarboxylic acids, heterocyclic monocarboxylic acids and heterocyclic polycarboxylic acids.

3. A process set forth in claim **2,** wherein the aliphatic monocarboxylic acid is one selected from the group consisting of formic acid, acetic acid, propionic acid, acrylic acid, aconic acid, acetoacetic acid, valerianic acid, crotonic acid, butyric acid, undecanoic acid, enanthic acid, capric acid, caprylic acid, chloro-acetic acid, bromacetic acid, trichloracetic acid, chlorofumaric acid, cyclobutane-carboxylic acid, quinic acid, sulfoacetic acid, sorbic acid, tiglic acid, tetrolic acid, vinylacetic acid, pyruvic acid, methacrylic acid, levulimic acid, caproic acid, isovaleric acid, pelargonic acid, palmitic acid, lauric acid, myristic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, erucic acid, tridecanoic acid, margaric acid, behenic acid, stearolic acid, glycolic acid, citric acid, tartaric acid, aconitic acid, adipic acid, arabonic acid, alloxanic acid, saccharic acid, isovanillic acid, hydroxybutyric acid, glyceric acid, gluconic acid, diglycolic acid, citramanic acid, thioglycolic acid, desoxalic acid, lactic acid, racenic acid, mannonic acid, malic acid, leucic acid, glycine, alanine, leucine, serine, threonine, cysteine, methionine, lysine and arginine.

4. A process set forth in claim **2,** wherein the aliphatic polycarboxylic acid is one selected from the group consisting of malonic acid, acetone-dicarboxylic acid, citraconic acid, oxalic acid, acrylmalonic acid, isocamphoronic acid, ethylmalonic acid, glutaric acid, succinic acid, camphoric acid, sebacic acid, pimelic acid, brassylic acid, maleic acid, muconic acid, mesaconic acid, adipic acid, axelaic acid, suberic acid, aspartic acid and glutamic acid.

5. A process set forth in claim **2,** wherein the aromatic mono- or poly-carboxylic acid is one selected from the group consisting of benzoic acid, phthalic acid, terephthalic acid, trimellitic acid, salicylic acid, acetophenone-carboxylic acid, anisic acid, aminobenzoic acid, aminocinnamic acid, propylbenzoic acid, hydroxy-phthalic acid, hydroxyphenylacetic acid, cinnamic acid, chlorobenzoic acid, chlorophthalic acid, dimethoxyphthalic acid, sulfosalicylic acid, thiosalicylic acid, toluic acid, truxillic acid, tropic acid, naphthalic acid, vanillic acid, biphenyl-carboxylic acid, phenyl-acetic acid, phenylsuccinylacetic acid, phenyllactic acid, benzene tetracarboxylic acid, phenylbutyric acid, benzoylbenzoic acid, benzoylglucolic acid, ben-

zoylacetic acid, homophthalic acid, mandelic acid, phenylalanine and tyrosine.

6. A process set forth in claim 2, wherein the heterocyclic mono- or poly-carboxylic acid is one selected from the group consisting of 2,4-dimethyl-3-furancarboxylic acid, thiophenecarboxylic acid, terpenylic acid, paraconic acid, furancarboxylic acid, alginic acid, coumarinic acid and pyridine-carboxylic acid.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,820,996 Dated June 28, 1974

Inventor(s) Nihyakumen, et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claim 1, subparagraph "e", delete "agent" in the second instance.

Claim 3, line 6, delete "chloro-acetic", insert -- chloroacetic--

Claim 3, line 7, delete "bromacetic", insert -- bromoacetic --

Claim 3, line 7, delete "trichloracetic", insert

-- trichloroacetic --

Claim 4, line 8, delete "axelaic", insert -- azelaic --

Signed and sealed this 8th day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

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