United States Patent [19]

Matsukawa et al.

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[54] **DESENSITIZER COMPOSITION**

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[52] **U.S. Cl.** ..... **106/19;** 96/62; 106/22; 106/23; 106/24; 106/26; 106/27; 117/1.7; 117/36.7; 117/36.8; 260/37 EP; 260/38; 260/39 P; 260/42.21

[51] **Int. Cl.** **C09d 11/00**

[58] **Field of Search** 96/62; 106/2, 19–21, 106/22, 23, 24, 26, 27; 117/1.7, 36.7, 36.8

[56] **References Cited**

FOREIGN PATENTS OR APPLICATIONS

1,542,058 10/1968 France

Primary Examiner—Lorenzo B. Hayes

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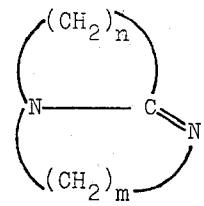
[57] **ABSTRACT**

In a desensitizer composition for desensitizing a developer to color a colorless color former, an amine of the formula



wherein *m* is an integer of 2–6, *n* is an integer of 2–11, and each ring can be substituted by one or more alkyl groups of 1–4 carbon atoms or a salt thereof, is incorporated as a desensitizing agent to exhibit a strong desensitization effect.

24 Claims, No Drawings

DESENSITIZER COMPOSITIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a desensitizer composition, more precisely, to a desensitizer composition which reduces or destroys the function of a developer to color a colorless color former.

2. Description of the Prior Art

Various methods are known of forming a developed color image utilizing the reaction of a color former, which is an almost colorless organic compound, and a developer. For example, such a color reaction has been utilized in recording materials as illustrated in U.S. Pat. Nos. 2,505,470; 2,505,489; 2,548,366; and 2,550,471, etc.; recording materials as illustrated in U.S. Pat. Nos. 2,712,507; 2,730,456; 2,730,457; and 3,293,060, etc.; recording materials as illustrated in U.S. application Ser. No. 40,732, British Pat. No. 825,354, etc.; and other recording materials for spirit printing, stencil printing, automatic ticket vending systems, fingerprinting system, letter writing systems, etc.

In these recording materials, the color reaction results from the contact of the color former and the developer, and it is desirable that the color reaction be prevented in parts which need not contain a developed color image, both from the view of the use of these materials and from the economical view-point. A desensitizer has heretofore been used for this purpose. For example, the following prior art discloses the use of desensitizers: U.S. Pat. No. 2,777,780 (high molecular primary alkylamines such as dodecylamine; quaternary ammonium salts such as dodecyltrimethylammonium chloride; alkyl or aryl amine acetates); Japanese Patent Publication No. 29546/71 (tertiary amines derived from a chemical bonding of a monoalkylamine, aralkylamine or ethanolamine and ethylene oxide); Japanese Patent Publication No. 3569/71 (precondensation products of urea resins); etc. (secondary alkylamines such as didodecylamine; tertiary alkylamines such as triethylamine; primary arylamines such as aniline; aralkylamines such as benzylamine; polyhydroxyl compounds such as polyethylene glycol and glycerin).

However, these desensitizers either have an insufficient desensitizing effect or, if the effect is sufficient, it is necessary to use a large amount of the agents in order to attain a practical effect. Thus, these agents have several faults. Some desensitizers color desensitized portions even if a large amount is used, and other desensitizers cause the same phenomenon unless a large amount thereof is used. In particular, these defects are apt to become great with improvements in color formers and developers.

For example, color formers containing a fluoran nucleus are especially difficult to desensitize, as compared with Crystal violet lactone, etc. In addition, these desensitizers are almost ineffective for developers such as phenol resins or metal salts of aromatic carboxylic acids. Therefore, limits on the few advantageous properties of these developers exist, e.g., the developed color image obtained using the same does not disappear in the presence of water.

Another defect of conventional desensitizers is that non-desensitized areas of a developer gradually color with the lapse of time (that is, fog occurs) when a color former is brought into contact with the desensitized developer using an encapsulation system.

In addition, conventional desensitizers are apt to yellow in contact with a developer, or since these desensitizers are used in large quantities, the drying speed is low and it is difficult to increase the coating (printing) speed.

SUMMARY OF THE INVENTION

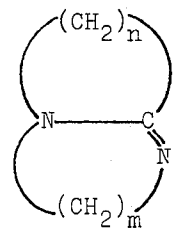
One object of the present invention is to provide a desensitizer composition having a strong desensitizing effect.

Another object of the present invention is to provide a desensitizer composition which has excellent coatability and which can be used for aqueous and oily materials.

Still another object of the present invention is to provide a desensitizer composition which does not harmfully affect a color former or a developer or a system containing both a color former and developer.

The inventors found that the above and other objects can be attained by using at least one diaza-bicycloalkene, or a salt thereof, as the desensitizer component.

The diaza-bicycloalkene used are those represented by the following formula, and the salts thereof are fatty acid salts thereof or salts thereof with phenols:



wherein *m* is an integer of 2–6, *n* is an integer of 2–11, and each ring can be substituted by one or more alkyl groups of 1–4 carbon atoms, where all positions of the ring can be so substituted.

The desensitizer of the invention is a substance or compound capable of preventing the reaction of color formers and color developers which are coated on the same or different supports. More precisely, the desensitizer is a substance or compound capable of inactivating the color-formation property of color developers coating it on a layer thereof.

DETAILED DESCRIPTION OF THE INVENTION

Specific examples of the diaza-bicycloalkenes of the above formula used in the present invention are as follows:

1,5-diaza-bicyclo(4,2,0)octene-5
1,8-diaza-bicyclo(7,2,0)undecene-8
1,4-diaza-bicyclo(3,3,0)octene-4
3-methyl-1,4-diaza-bicyclo(3,3,0)octene-4
3,6,7,7-tetramethyl-1,4-diaza-bicyclo(3,3,0)octene-4
7,8,8-trimethyl-1,5-diaza-bicyclo(4,3,0)nonene-5
1,8-diaza-bicyclo(7,3,0)dodecene-8
1,7-diaza-bicyclo(4,3,0)nonene-6
1,5-diaza-bicyclo(4,4,0)decene-5
1,8-diaza-bicyclo(7,4,0)tridecene-8
1,8-diaza-bicyclo(5,3,0)decene-7
9-methyl-1,8-diaza-bicyclo(5,3,0)decene-7
1,8-diaza-bicyclo(5,4,0)undecene-7
1,6-diaza-bicyclo(5,5,0)dodecene-6

1,7-diaza-bicyclo(6,5,0)tridecene-7
1,8-diaza-bicyclo(7,5,0)tetradecene-8
1,10-diaza-bicyclo(7,3,0)dodecene-9
1,10-diaza-bicyclo(7,4,0)tridecene-9
1,14-diaza-bicyclo(11,3,0)hexadecene-13
1,14-diaza-bicyclo(11,4,0)hetadecene-13

The above diaza-bicycloalkenes are known, e.g., French Pat. No. 1,542,058 and Japanese Patents Publication Nos. 40553/**70** and 40554/**70**. The above specific examples are described merely for facilitating an easy understanding of the invention, and the present invention is not limited to the recited compounds.

As the acids used for the formation of salts of the diaza-bicycloalkenes, fatty acid or phenol type compound can be used.

Specific examples of the acids are, for example, saturated fatty acids such as acetic acid, propionic acid, butyric acid, caproic acid, caprylic acid, undecylic acid, lauric acid, tridecylic acid, myristic acid, palmitic acid, heptadecylic acid, stearic acid, etc.; unsaturated fatty acids such as acrylic acid, crotonic acid, undecylenic acid, oleic acid, sorbic acid, linoleic acid, linolenic acid, propiolic acid, etc; isoalkyl fatty acids such as 2-ethylhexanoic acid, etc.; hydroxy fatty acids, such as lactic acid, glycolic acid, ricinoleic acid, hydroxystearic acid, etc.

Specific examples of the phenols are, phenol, substituted phenols (such as cresol, xylenol, ethylphenol, propylphenol, butylphenol, nonylphenol, dodecylphenol, chlorophenol, cyclohexylphenol, phenylphenol, trimethylphenol, tetramethylphenol, naphthol, etc.), polyhydric phenols (such as resorcin, catechol, pyrogallol, hydroquinone, phloroglucinol, dihydroxymethylbenzene, naphthalenediol, etc.), phenol carboxylic acids (such as hydroxybenzoic acids, resorcylic acids, gallic acid, etc.), phenol sulfonic acids, nitrophenols and phenols such as biphenol, bicresol, dibenzylbiphenol, methylenebiphenol, bisphenol A, etc.

The salts of the above mentioned diaza-bicycloalkenes can be prepared merely by reacting the diaza-bicycloalkenes with the selected acid. In the preparation, the ratio of the respective reaction components can be equivalent, or excess diaza-bicycloalkenes can be used, or, excess acid component can be used. The formation of the salts easily proceeds at room temperature without any particular catalyst, but when solid acids are used, it is advantageous to use an inert volatile solvent such as benzene, toluene, xylene, hexane, heptane or the like.

The solvent used can easily be removed by any appropriate method after the completion of the reaction.

Most of these salts are colorless liquids free from any unpleasant odor, and are soluble in an aromatic type solvent as above and an alcohol, and, in addition they are easily dispersed or dissolved in water. All aromatic solvents and alcohols (aliphatic solvents such as methanol, ethanol, propanol, butanol or amyl alcohol) can be used to dissolve a solid acid in the reaction. The solvent is not limited so long as it does not react with the reaction components and products.

Summarizing the above material, the reactions of the amines and phenols or fatty acids are well known in the art, and briefly stated, all phenols and fatty acids can be used with success in the present invention. There is no substantial limitation thereon.

As mentioned above, the compounds of the present invention are effective for desensitization in small quantities, as compared with conventional desensitizers. For example, the present compounds display a sufficient desensitization effect in an amount of one-fifth (by weight) of conventional desensitizers. Of course, if the compound or compounds is/are used in an amount of more than one-fifth of conventional desensitizers, a stronger desensitization effect is attained, and the said weight value "one-fifth" is determined merely from economic advantages.

On the other hand, if the compound of the present invention is used in an amount less than one-fifth (weight amount) of conventional desensitizers, the effect thereof decreases with the decrease of the amount used, but it is to be noted that the compound of the present invention still displays an excellent effect over the same amount of a conventional desensitizer. On these grounds, it is apparent that the amount of the compounds of the present invention to be used is not specifically limited.

As stated above, the amount of the desensitizer of the present invention is not especially limited. However, in commercial use certain proportions will find greater acceptability than others, and usually at least about 1 weight percent to a maximum of 100 weight percent, based on the desensitizer composition weight, of the desensitizer of the present invention will be used, more preferably 5 to 30 weight percent. Generally, using from about 10 weight % to 20 weight % will provide excellent effects in almost cases. The maximum value set above is set purely for economic reasons, and it will be appreciated by one skilled in the art that little need exists to use such high proportions of desensitizer under normally encountered conditions.

The desensitizer composition of the invention contains the compound of the formula and generally an inorganic solid material and a binder. The inorganic solid material is used to provide a desired fluidity and whiteness to the composition, and the binder is used to carry the inorganic solid material. The amount of three components can be set in a wide range according to the desired purposes.

In the desensitizer composition of the present invention, it is sufficient that at least one of the above mentioned diaza-bicycloalkene or salts thereof is contained therein as the desensitizer component, and the other components can be any conventional ones.

The other components are the following components which are contained in conventional desensitizer compositions: Natural or synthesic high molecular weight compounds such as ketone resins, polyamide resins, maleic acid resins, fumaric acid resins, phenol resins, epoxy resins, alkyd resins, melamine resins, urea resins, acrylic resins, nitrocellulose, methyl cellulose, cellulose butyrate acetate, butyral resins, casein, gelatin, polyvinyl alcohol, etc. (in many cases, these are used as a binder, but the object thereof is not necessarily limited, for example, the binder can also function to prevent an ink from transferring to piled papers); pigments such as titanium dioxide, zinc oxide, barium sulfate, magnesium carbonate, calcium carbonate, barium carbonate, magnesium hydroxide, talc, etc. (these are to improve printability, whiteness and masking power), solvents such as glycols (e.g., ethylene glycol, diethylene glycol, glycerin, polyethylene glycol, polypropylene glycol, etc.), alcohols, e.g., as heretofore recited as salt-formation solvents, etc.; fats and oils such as paraffin, Japan wax, etc. (these are to improve abrasion resis-

tance); and drying oils (such as linseed oil, tung oil, bean oil), semidrying oils (such as cotton seed oil, sesame oil, corn oil, rape oil, rice bran oil).

In addition, the other conventionally known additives such as an off setting inhibitor (e.g., starch) as well as other desensitizers can optionally be incorporated in the composition of the present invention.

The composition of the present invention can be in any form as is commonly used in the art such as an aqueous solution, a solution in an organic solvent (e.g., alcohol solution), an aqueous dispersion, a paste or a solid. It is to be noted that the function of the composition of the present invention is not harmed in any manner due to the kind, amount or form of the other components contained therein, that is the function is present irrespective of the other additives used.

Expanding upon the above, it is to be specifically understood that in the desensitizer composition of the present invention the only "active" desensitizing component required is generally the one or more diazabicycloalkene compounds or the salts thereof. Thus, any other components can be freely and optionally selected and the proportion thereof freely varied in a manner known to the art.

The reason for this complete freedom in selecting other components is that these components do not per se affect the functioning the desensitizer composition. For instance, the high molecular weight compound merely serves, where rough handling is anticipated, to maintain the desensitizer composition in its desired position. Where such extra strength is not needed, the high molecular weight compound can be omitted.

The pigments, of course, improve commercial properties as recited above. Thus, in instances where such properties are not important, the pigments can be deleted.

The solvents, of course, are merely for improving coatability, as are the fats and oils. Thus, where coatability is not an important factor, these components can be omitted.

In short, the types and proportions of the components recited above are established on a case by case basis, and these materials can, in fact, be omitted in theory. However, in practice, since we are concerned with commercial embodiments, these materials generally are present to perform their art recognized functions.

Thus, the desensitizer composition of the present invention can easily be prepared by those skilled in the art, and can be supplied to a developer by means of various methods such as relief printing or photogravure printing, spraying, hand writing as a crayon or in the form of an eraser, or the like.

The developers to which the desensitizer composition of the present invention can be applied are electron acceptors, which are well known in this technical field. They are generally electron-accepting solid acids. Examples thereof are the clay minerals such as terra alba, attapulgite etc.; organic acids such as tannic acid, gallic acid, propyl gallate, etc.; acid polymers such as phenol-formaldehyde resins, phenolacetylene condensation resins, etc.; metal salts of aromatic carboxylic acids such as zinc salicylate, tin salicylate, zinc 2-hydroxynaphthoate, zinc 3,5-di-tert.butyl-salicylate, etc.; or mixtures thereof. Such developers are disclosed in U.S. Pat. Nos. 2,972,547; 3,455,721; 3,427,180; 3,516,845; 3,634,121; and 3,672,935 and in U.S. Ser. Nos. 183,647 and 192,594. Other developers are disclosed in the literature discussed under the prior art at an earlier part of this specification.

The developer is applied on a support such as a paper, plastic film laminated paper or the like, together with a binder such as styrene-butadiene latex.

Binders for color developers can be classified into two types. One is a water-insoluble high molecular weight compound in the form of latex such as a styrene-methylmethacrylate copolymer latex, a styrene-ethylmethacrylate copolymer latex, a styrene-butadiene copolymer latex, a butadiene-methylmethacrylate copolymer latex, a butadiene-ethyl methacrylate copolymer latex, a polyvinyl acetate latex, a polyvinylidene chloride latex, a polymethylmethacrylate latex, a polyethylmethacrylate latex, etc. The other is a water-soluble high molecular weight compound such as starch, casein, polyvinyl alcohol, styrene-maleic anhydride copolymer, etc.

On the other hand, the color formers reacted with the developers at color forming are almost colorless organic compounds which are electron donors, and are, for example, triazolemethane type compounds, diphenylmethane type compounds, xanthene type compounds, thiazine type compounds, spiropyran type compounds, etc. Examples these compounds are as follows:

Triazolemethane type compounds:

3,3-bia(p-dimethylaminophenyl)-6-dimethylaminophthalide or Crystal violet lactone (hereunder referred to as CVL), 3,3-bis(p-dimethylaminophenyl)phthalide, 3-(p-dimethylaminophenyl)-3-(1,2-dimethylindol-3-yl)phthalide, 3-(p-dimethylaminophenyl)-3-(2-methylindol-3-yl)phthalide, 3-(p-dimethylaminophenyl)-3-(2-phenylindol-3-yl)phthalide, 3,3-bis-(1,2-dimethylindol-3-yl)-5-dimethylaminophthalide, 3,3-bis-(1,2-dimethylindol-3-yl)-6-dimethylaminophthalide, 3,3-bis-(9-ethylcarbazol-3-yl)-5-dimethylaminophthalide, 3,3-bix-(2-phenylindol-3-yl)-5-dimethylaminophthalide, 3-p-dimethylaminophenyl--
-bis-(-(1-methylpyrrol-2-yl)6-dimethylaminophthalide, etc.

Diphenylmethane type compounds:

4,4'-bis-dimethylaminobenzhydryl benzylether, N-halophenylleucoauramine, N-2,4,5-trichlorophenylleucoauramine, etc.

Xanthene type compounds:

Rhodamine-B-anilinolactam, rhodamine-(p-nitroanilino)lactam, rhodamine-B-(p-chloroanilino)lactam, 7-dimethylamino-2-methoxyfluoran, 7-diethylamino-2-methoxyfluoran, 7-diethylamino-3-methoxyfluoran, 7-diethylamino-3-chlorofluoran, 7-diethylamino-3-chloro-2-methylfluoran, 7-diethylamino-2,3-dimethylfluoran, 7-diethylamino-(3-acetylmethylamino)fluoran, 7-diethylamino-(3-methylamino)fluoran, 3,7-diethylaminofluoran), 7-diethylamino-3-(dibenzylamino)fluoran, 7-diethylamino-3-(methylbenzylamino)fluoran, 7-diethylamino-3-(chloroethylmethylamino)fluoran, 7-diethylamino-3-(diethylamino)fluoran, etc.

Thiazine type compounds:

Benzoyl-leucomethylene blue, p-nitrobenzyl-leucomethylene blue, etc.

Spiro type compounds:

3-methyl-spiro-dinaphthopyran, 3-thyl-spiro-dinaphthopyran, 3,3'-dichloro-spiro-dinaphthopyran, 3-benzyl-spiro-dinaphthopyran, 3-methyl-naphtho-(3-methoxy-benzo)-spiropyran, 3-propyl-spiro-dibenzopyran, etc.

The color former is coated on a support by dissolving the same into a synthetic or natural oil such as chlorinated diphenyl, chlorinated terphenyl, alkylated diphenyl, alkylated terphenyl, chlorinated paraffin, chlorinated naphthalene, alkylated naphthalene, kerosene, paraffin, naphthene oil or the like, and applying the resulting solution to the support together with a binder, or encapsulating a color former solution according to the method as described, for example, U.S. Pat. No. 2,800,457. The color former solution may, if desired, be applied only to limited parts of the paper to be coated, which is another embodiment. The color former and the developer can be used in an manner for pressure-sensitive recording papers, heat-sensitive copying papers and the like.

Basically speaking, any encapsulation method of the prior art can be used in the present invention. The Greene et al patent cited above is merely exemplary, as this is a landmark patent in the field of complex coacervation. Any other encapsulation technique can be used without restriction.

The present invention will now be explained in more detail in the following examples, and the excellent merits of the present invention will be self-explanatory therefrom.

The developer sheets, color former sheets and desensitizer ink used in the following examples to confirm the effect of the desensitizers of the present invention were prepared as follows: ("part" means "part by weight" hereinunder).

Unless otherwise indicated, all developer sheets were prepared at room temperature (about 25°C). There is no substantial limitation upon the temperature of developer sheet formation. Further, unless otherwise indicated, all reactions and processing sequences were at atmospheric pressure.

Preparation of Developer Sheet A

After 100 parts of terra alba treated with sulfuric acid were disposed in 280 parts of water containing 10 parts of 20% caustic soda using a homogenizer, 10 parts of a 10% aqueous solution of methyl vinyl ether-maleic anhydride copolymer sodium salt (trade name: GANTREZ-AN-119 manufactured By General Aniline and Film Corporation) and 37 parts of styrene-butadiene latex (trade name: Dow Latex by Dow Chemical Company) were added thereto, the system was applied to a base paper (weight: 50 g/m²) by air-knife coating and dried to form a developer sheet, the coated solids content being 10 g/m².

Preparation of Developer Sheet B

170 parts of para-phenylphenol, 70 parts of a 37% aqueous form-aldehyde solution and 50 parts of water were condensed at 160°C in the presence of concentrated hydrochloric acid (catalyst), and then cooled to form a phenol resin powder.

To 50 parts of the phenol resin powder there were added 10 parts of polyvinyl alcohol (trade name; PVA-205 by Kurare Co.) and 500 parts of water, and the resulting mixture was milled in a ball mill for 10 hours to obtain a coating solution (Coating Solution B).

The thus prepared coating solution was applied to a base paper (weight: 50 g/m²) and dried to obtain a developer sheet (Developer Sheet B). The coated solids content was 2 g/m².

Preparation of Developer Sheet C

4 parts of caustic soda were dissolved in 200 parts of water, and 25 parts of 3,5-di-tert-butyl-salicylic acid were dissolved therein while stirring.

While further stirring, a solution of 7 parts of zinc chloride in 100 parts of water was gradually added thereto. 50 parts of a 10% aqueous solution of polyvinyl alcohol (trade name: PVA-205 by Kurare Co.) were further added thereto, and the resulting mixture was milled in a ball mill for 10 hours to prepare a coating solution (Coating Solution C).

The thus prepared coating solution was applied to a base paper (weight: 50 g/m²) and dried to form a developer sheet (Developer Sheet C), the coated solids content being 2 g/m².

Preparation of Developer Sheet D

35 parts of the above Coating Solution B, 50 parts of the above Coating Solution C and 15 parts of pyrophyllite clay were milled in a ball mill for 10 hours to prepare a coating solution. The resulting solution was applied to a base paper (weight: 50 g/m²) and dried to form a developer sheet (Developer Sheet D), the coated solids content being 2 g/m².

Preparation of Color Former Sheet A

10 parts of an acid treated gelatin having an isoelectric point of 8.0 and 10 parts of gum arabic were dissolved in 60 parts of water at 40°C, and 0.2 part of sodium alkylbenzene sulfonate was added thereto as an emulsifier, and then 50 parts of a color former oil were emulsified therein.

The color former oil was prepared by dissolving in an oil consisting of 4 parts of diisopropylphenyl and 1 part of kerosene, 2.5% by weight of Crystal violet lactone and 2.0% by weight of benzoyl leucomethylene blue.

When the emulsified drops grew to 8 μ on an average, 100 parts of water at 40°C were added to the emulsion to control the emulsification.

While continuing stirring, 210 parts of water at 30°C were further added to the system which was at 40°C and 20% hydrochloric acid was then added to adjust the pH of the system to 4.4, the system being maintained at 30°–40°C. While continuing stirring at this temperature the solution was cooled to 8°C, and then 1.5 parts of 20% glutaraldehyde were added thereto.

Next, 30 parts of a 10% aqueous carboxymethyl starch solution were successively poured into the resulting solution, 25% caustic soda was added dropwise to adjust the pH value thereof to 8.5, and then the temperature of the solution was elevated from 8°C to 30°C to thereby form microcapsules having hardened walls.

Into the resulting solution were dispersed 10 parts of a cellulose flock and the resulting dispersion was applied on a paper-sheet (weight: 40 g/m²) to obtain a color former sheet (Color Former Sheet A), the coated solids content being 6 g/m².

Preparation of Color Former Sheet B

To an oil consisting of 1 part of diisopropylnaphthalene, 1 part of diisopropyl-biphenyl and 2 parts of 1-(dimethylphenyl)-1-phenylethane were dissolved 1%

by weight of crystal violet lactone, 4% by weight of 3-diethylamino-7-diethylaminofluoran, 4% by weight of 3-diethylamino-7-phenylaminofluoran, 3% by weight of 3-diethylamino-7,8-benzofluoran, 0.5% by weight of 3,6-bis-methoxyfluoran and 2% by weight of benzoyl-leucomethylene blue, to prepare a color former oil. Using 50 parts of resulting oil, a color former sheet (Color Former Sheet B) was prepared according to the procedure of preparing Color Former Sheet A.

Preparation of Desensitization Ink

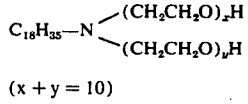
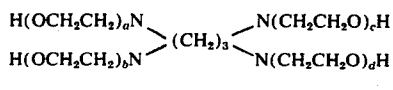
60 parts of desensitizer as shown in the following Table, and, as a binder, 30 parts of rosin-modified maleic acid resin (trade name: Hitalac X24M, by Hitachi Chemical Industries Co.) were heated and melted to form a varnish. 10 parts of titanium dioxide were added to the resulting varnish and kneaded in a three-roll mill, and then 2 parts of polyethylene glycol (average molecular weight 400) were added thereto to prepare an ink.

The resulting ink was applied to each of the above mentioned developer sheets in an amount of 2 g/m², and printed as described below.

Test Method

On each of the developer sheets there was printed desensitizer which was optionally and freely prepared, and the desensitized part was put face to face with a color former sheet, whereupon the coloring operation was carried out under an electric charge of 600 kg/cm².

The desensitization effect was evaluated from the reflection visible density value (Vis. D), obtained by measuring the density of the sheet with a microdensitometer after it was left to stand for 1 full day.

Ex. No.	Desensitizer	Desensitization effect (Vis.-D) Color Former Sheet A: Developer Sheet A	Developer Sheet B	Developer Sheet C	Developer Sheet D	Color Former Sheet B: Developer Sheet A
1	1,8-diazabicyclo(5,4,0) undecene-7	0.01	0.01	0.01	0.01	0.01
2	1,8-diazabicyclo(5,4,0) undecene-7 (3 mols)-oleic acid (1 mol) reaction product	0.01	0.02	0.02	0.01	0.02
3	reaction product of 1,8-diazabicyclo-(5,4,0)undecene-7 (3 mols) and phenol (1 mol)	0.01	0.02	0.01	0.02	0.02
4	reaction product of 1,5-diazabicyclo (4,3,0)nonene-5 (3 mols) and p-cresol (1 mol)	0.01	0.015	0.02	0.02	0.02
5	reaction product of 1,4-diazabicyclo (3,3,0)octene-4 (3 mols) and 2-ethyl-hexanoic acid (1 mol)	0.01	0.01	0.02	0.02	0.02
6	1,5-diaza-bicyclo(4,2,0) octene-5	0.01	0.01	0.01	0.01	0.01
7	3-methyl-1,4-diaza-bicyclo(3,3,0)octene-4	0.01	0.01	0.01	0.01	0.01
8	reaction product of 1,6-diaza-bicyclo-(5,5,0)dodecene-6 (3 mols) and stearic acid (1 mol)	0.01	0.02	0.02	0.02	0.02
9	1:1 mixture of 1,8-diaza-bicyclo(5,4,0)-undecene-7 and  $(x + y = 10)$	0.02	0.02	0.02	0.02	0.03
10	1:1 mixture of 1,8-diaza-bicyclo(5,4,0)undecene-7 and  $(a + b + c + d = 30)$	0.01	0.02	0.02	0.02	0.02
Comparative Example 1	Without Desensitization	1.08	1.05	0.94	1.04	1.05
Comparative Example 2	Desensitizer $C_{12}H_{25}NH_2$	0.35	0.40	0.45	0.35	0.40

Ex. No.	Desensitizer	Desensitization effect (Vis.-D) Color Former Sheet A Developer Sheet A	Developer Sheet B	Developer Sheet C	Developer Sheet D	Color Former Sheet B Developer Sheet A
Comparative Example 3	$C_{18}H_{35}-N(CH_2CH_2O)_xH(CH_2CH_2O)_yH$ (x + y = 10)	0.05	0.10	0.15	0.12	0.11
Comparative Example 4	urea-formaldehyde resin precondensation Product	0.24	0.42	0.39	0.36	0.45
Comparative Example 5	$(C_2H_5)_3N$	0.33	0.40	0.42	0.39	0.42
Comparative Example 6	$HO(CH_2CH_2O)_xH$ (x = 10)	0.28	0.35	0.37	0.36	0.34

Examples 9 and 10 above show the compound of this invention used in combination with a conventional desensitizer.

The merits of the compounds of the present invention are apparent from the above Table. In the Table, the numerical values show the desensitization effect, that is, the smaller the value the greater the effect, and a difference of 0.05 or more shows a remarkable desensitization effect.

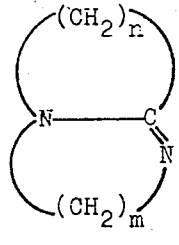
The compositions of the present invention are effective to desensitization about 100 times a composition not containing any desensitizer (COmparative Example 1), and about 35 times as effective as a conventional desensitizer (Comparative Example 2-6).

Among the conventional desensitizers, the compound of Comparative Example 3 is more effective than the other compounds, but the desensitization effect thereof varies depending upon the kind of color former used. On the contrary, the desensitizers of the present invention are effective for desenstization in any case, and further, the desensitization effect is always great irrespective of the kinds of the used color formers. Thus, the present desensitizers are extremely advantageous.

While the invention has been described in detail and with reference to specific embodiments thereof, will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. In a desensitizer composition for desensitizing a developer against coloring a colorless color former, which comprises an inorganic pigment, a resin binder and a desensilizing agent; the improvement comprising, as said agent at least about 1 weight percent, based on the composition weight, of an amine of the folllowing formula or a salt thereof:



wherein *m* is an integer of 2–6, *n* is an integer of 2–11, and each ring can be substituted by one or more alkyl groups of 1–4 carbon atoms.

2. The desensitizer composition as claimed in claim **1** wherein said amine is selected from the group consisting of 1,5-diaza-bicyclo(4,2,0)octene-5; 1,8-diaza-bicyclo(7,2,0)-undecene-8; 1,4-diaza-bicyclo(3,3,0)-octene-4; 3-methyl-1,4-diaza-bixyclo(3,3,0)octene-4; 3,6,7,7-tetramethyl-1,4-diaza-bicyclo(3,3,0)octene-4; 7,8,8-trimethyl-1,5-diaza-bicyclo(4,3,0)nonene-5; 1,8-diaza-bixyclo(7,3,0) dodecene-8; 1,7-diaza-bicyclo(4,3,0)nonene-6; 1,5-diaza-bixyclo(4,4,0) decene-5; 1,8-diaza-bicyclo(7,4,0)tridecene-8; 1,8-diaza-bicyclo(5,3,0)-decene-7; 9-methyl-1,8-diaza-bicyclo(5,3,0)decene-7; 1,8-diaza-bicyclo(5,4,0)undecene-7; 1,6-diaza-bixyclo(5,5,0)dececene-6; 1,7-diaza-bicyclo(6,5,0)tridecene-7; 1,8-diaza-bicyclo(7,5,0-etradecene-8; 1,10-diaza-bicyclo(7,3,0)dececane-9; 1,10-diaza-bicyclo(7,4,0)tridecene-9; 1,14-diaza-bixyclo(11,3,0)hexadecene-13 and 1,14-diaza-bicyclo(11,4,0)heptadecene-13.

3. The desensitizer composition as claimed in claim **1** wherein said salt is a salt with a member selected from the group consisting of a fatty acid and a phenol compound.

4. The desenstizer composition as claimed in claim **3** wherein said fatty acid is selected from the group consisting of a saturated fatty acid, unsaturated fatty acid, isoalkyl fatty acid and hydroxy fatty acid.

5. The desensitizer composition as claimed in claim **4** wherein said fatty acid is selected from the group consisting of acetic, propionic, butyric, caprylic, caproic, undecylic, lauric, tridecyclic, myristic, palmitic, heptadecyclic, stearic, acrylic, crotonic, undecylenic, oleic, sorbic, linoleic, linolenic, propiolic, 2-ethylhexanoic, lactic, glycolic, ricinoleic and hydroxy stearic acid.

6. The desensitizer composition as claimed in claim **3** wherein said phenol compound is selected from the group consisting of phenol, cresol, xylenol, ethylphenol, propylphenol, butylphenol, nonylphenol, dodecylphenol, chlorophenol, cyclohexylphenol, phenylphenol, trimethylphenol, tetramethylphenol, napthol, resorcin, catechol, pyrogallol, hydroquinone, phloroglucinol, dihydroxymethylbenzene, napthalenediol, hydroxybenzoic acid, resorcylic acid, gallic acid, phenol sulfonic acid, nitrophenol, biphenol, bicressol, dibenzylbiphenol, methylenebiphenol and bisphenol A.

7. The desensitizer composition of claim **1** in combination with an electron accepting developer.

8. The desensitizer composition as claimed in claim **7** wherein said electron accepting developer is selected

from the group consisting of a clay mineral, an organic acid, an acid polymer, a metal salt of an aromatic carboxylic acid and a mixture thereof.

9. The desensitizer composition as claimed in claim **8** wherein said electron accepting developer is selected from the group consisting of terra alba, attapulgite, tannic acid, gallic acid, propyl gallate, a phenolformalin resin, a phenol acetylene condensation resin, zinc salicylate, tin salicylate, zinc 2-hydroxynaphthoate, zinc 3,5-di-tert-butyl-salicylate and mixture thereof.

10. The desensitizer composition as claimed in claim **1** in combination with a color former which is a colorless, electron donating organic compound.

11. A desensitizer composition as claimed in claim **10** where said color former is selected from the group consisting of a triazolemethane, diphenylemethane xanthene, thiazine or and spiropyran compound.

12. The desensitizer composition as claimed in claim **1** in combination with an electron accepting developer and a color former which is a colorless, electron donating organic compound.

13. The desensitizer composition as claimed in claim **1,** wherein said binder is selected from the group consisting of ketone, polyamide, maleic acid, fumaric acid, phenol, epoxy, alkyd, melamine, urea, acrylic, nitrocellulose, methyl cellulose, cellulose butyrate acetate, butyral, casein, polyvinyl alcohol and gelatin and

the pigment is selected from the group consisting of titanium dioxide, zinc oxide, barium sulfate, magnesium carbonate, calcium carbonate, barium carbonate, magnesium hydroxide and talc.

14. The desensitizer composition as claimed in claim **1,** which further comprises a solvent.

15. The desenstizer composition as claimed in claim **14,** where the solvent is selected from the group consisting of a glycol or alcohol.

16. The desensitizer composition as claimed in claim **1,** which further comprises a fat.

17. The desensitizer composition as claimed in claim **1,** which further comprises an oil.

18. The desensitizer composition as claimed in claim **1,** which further comprises a drying oil selected from the group consisting of linseed oil, tung oil, and bean oil.

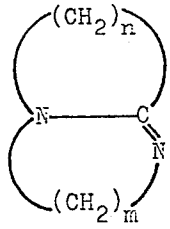
19. The desensitizer composition as claimed in claim **1,** which further comprises a semi-drying oil selected from the group consisting of cotton seed oil, sesame oil, corn oil, rape oil and rice bran oil.

20. The desensitizer composition as claimed in claim **1,** which further contains an off-setting inhibitor.

21. The desenstizer composition as claimed in claim **1,** which further comprises a desensitizer, which desensitizer is different from said amine.

22. The desensitizer composition as claimed in claim **1, 2h343in** from 5 to 30 weight percent of daid desnsitizer is present, based on the desensitizer composition weight.

23. In a method for desensitizing a developer, which developer produces a colored reaction product upon reaction with a colorless color former, which comprises applying thereto a desensitizer composition comprising an inorganic pigment, a resin binder and a desensitizing agent; the improvement comprising, as said agent, at least about 1 weight percent, based on the composition weight, of an amine of the following formula or a salt thereof:



wherein *m is an integer of* 2–6, *n* is an integer of 2–11, and each ring can be substituted by one or more alkyl groups of 1–4 carbon atoms.

24. The method of claim **23** wherein from 3 to 30 percent by weight of said desensitizer is present, based on the desensitizer composition weight.

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