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3,576,631

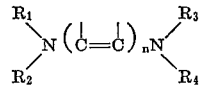
PHYSICAL DEVELOPMENT COMPOSITION AND PROCESS OF USING SAME

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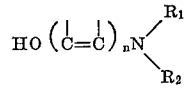
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Int. Cl. G03c 5/24
U.S. Cl. 96—48 20 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to a novel photographic physical development system comprising an acidic to neutral solution of reducing agent comprising a diamine compound and a hydroxylamine compound. The preferred diamine compound has the structure of:



and the preferred hydroxylamine compound has the structure of:



wherein n may be 0 or an integer from 1 to 10 and wherein R_1, R_2, R_3, and R_4 may be hydrogen, and substituted or unsubstituted alkyl, aryl, alkaryl, and aralkyl groups and wherein R_1, R_2, R_3, and R_4 may be the same or different. It will be understood that acid addition compounds of either the diamine compound or the hydroxylamine compound may also be used in this invention. This reducing agent solution may be combined with a solution of a readily reducible material which is at least as strong an oxidizing agent as cupric ion to form a unitary developer solution. A preferred embodiment, however, comprises the two separate solutions, i.e., the reducing solution and the solution of readily reducible material which is at least as strong an oxidizing agent as cupric ion, are used as separate solutions. These developer solutions may then be used in processes wherein physical developers are ordinarily used. Therefore the developer systems of this invention may be used to produce a visible image on a photosensitive copy medium which has been exposed to an image pattern of activating radiation. These developers may also be used for the intensification of developed images in these and like photographic systems. For example, these systems may be used to intensify chemically developed images in silver halide photographic systems.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to the field of liquid photographic developers and, more specifically, to the field of photographic physical development systems.

(2) Description of the prior art

Physical developers comprise two essential ingredients: the photographic reducing agent and readily reducible materials. Metal ions are a preferred class of readily reducible materials and include ions of the metals copper, silver, mercury, gold, platinum, and the like. The photographic reducing agents normally present in physical developers include compounds which can reduce these ions. Suitable reducing agents include hydroquinone or derivatives thereof, o- and p-aminophenol, p-methylaminophenol sulfate, p-hydroxyphenylglycine, o- and p-phenylenediamine, 1-phenyl-3-pyrazolidone and others which could be mentioned. Also, inorganic photographic reducing agents comprising ferrous, titanous and vanadous ions can be used. Oftentimes physical developers contain additional ingredients such as organic acids which can react with the metal ions to form complex metal anions. Further, the developers may contain alkali metal sulfites which serve primarily to retard oxidation of the reducing agents.

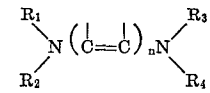
Physical development is distinguished from chemical development in that the metal or like colored material required for contrast formation in physical development is largely supplied from the developer, whereas in chemical development the metal required for contrast formation is derived only from the metal ions in the photosensitive layer on the film. Diffusion transfer developers, which contain metal complexing anions, are a form of physical developer.

SUMMARY OF THE INVENTION

It has been unexpectedly found that a photographic development system comprising an acidic to neutral solution of a reducing agent comprising a diamine compound and/or the acid addition compounds thereof and a hydroxylamine compound and/or the acid addition compounds thereof gives images having surprisingly high optical densities as compared with photographic developers utilizing either the diamine compound or the hydroxylamine compound separately. Thus when the total exposure ($E=It$) received by a photosensitive copy medium and the amount of time in the developer solutions are each held at a constant, it has been found that the optical density is markedly increased when a diamine compound are used in combination over what would be expected when said compounds are used alone. However, it is critical that the developer solutions of this invention be maintained in an acidic to neutral pH in order to obtain this unexpected effect. The preferred developer solutions of this invention are aqueous solutions having a pH of 3.0 to 7.0. The reducing agent comprising a diamine compound and a hydroxylamine compound may be used in combination with a solution of a readily reducible material, such as a metal ion, which is at least as strong an oxidizing agent as cupric ion, or the reducing agent solution may be separate from the solution containing said metal ion. The preferred physical developer of this invention comprises two separate solutions due to the increased stability of these solutions when separate. The process of recording an image pattern of activating radiation according to this invention is carried out by exposing a photosensitive copy medium to an image pattern of activating radiation and subsequently contacting the medium with a physical developer system comprising (1) a solution of metalions which is at least as strong an oxidizing agent as cupric ion, and (2) an acid to neutral reducing solution comprising a diamine compound and a hydroxylamine compound. This physical developer system can also be used to intensify images on previously developed photographic prints.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

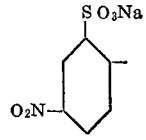
The diamine compounds useful in this invention are preferably those having the structure of:



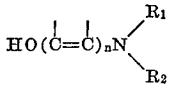
wherein n may be 0 or an integer from 1 to 10 and wherein R_1, R_2, R_3, and R_4 may be hydrogen and substituted or unsubstituted alkyl, aryl, alkaryl, and aralkyl groups and wherein R_1, R_2, R_3, and R_4 may be the same or dif-

ferent. Examples of this preferred group of diamine compounds are given in Table I below:

TABLE I

No.	Name	n	R_1	R_2	R_3	R_4
I	p-Phenylenediamine	2	H	H	H	H
II	N,N-dimethyl-p-phenylenediamine sulfate	2	$-CH_3$	$-CH_3$	H	H
III	N,N-diethyl-p-phenylenediamine sulfate	2	$-C_2H_5$	$-C_2H_5$	H	H
IV	N-methyl-p-phenylenediamine hydrochloride	2	$-CH_3$	H	H	H
V	N-(p-methoxyphenyl)-p-phenylenediamine hydrochloride	2		H	H	H
VI	4'-diethylamino acetanilide	2	$-OCCH_3$	H	$-C_2H_5$	$-C_2H_5$
VII	1,2,4-benzenetriamine dihydrochloride	1	H	H	H	H
VIII	2,4-diamino diphenylamine	1		H	H	H
IX	2-(p-aminoanilino)-5-nitrobenzene sulfonic acid, sodium salt	2		H	H	H
X	Hydrazine	0	H	H	H	H

The hydroxylamine compounds useful in this invention are preferably ones having the structure:



wherein R_1 and R_2 are as described above and include the acid addition salts of such hydroxylamine compounds. Examples of hydroxylamine compounds of the preferred structure are those such as listed in Table II below:

TABLE II

Name	n	R_1	R_2
Hydroxylamine	0	H	H
P-aminophenol	2	H	H
P-anilinophenol	4	H	H
P-methylaminophenol sulfate	2	$-CH_3$	H
P-benzylaminophenol hydrochloride	2		H
4-amino-2,6dibromophenol	2	H	H
4-amino-3-methylphenol	2	H	H

The acid addition compounds of the diamine and the hydroxylamine compounds are formed by mixing an acid with the particular diamine or hydroxylamine compound. Suitable acids are, for example, inorganic acids such as hydrochloric acid, sulfuric acid, and nitric acid and organic acids such as acelic acid and oxalic acid.

The photosensitive copy media to which the developer solutions of this invention may be applied are those media containing light-sensitive substances which upon exposure to activating radiation, electron beams, and like activating means, become activated and capable of causing chemical reaction on said media. The photosenstive substances useful in this photosensitive copy media are not limited to any group of compounds but may include organic and inorganic materials. Examples of such photosensitive materials are inorganic materials such as metals such as selenium (Se) and germanium (Ge), halides of silver or thallium, and compounds of a metal and a nonmetallic element of Group VI–A of the Periodic Table,[1] such as metal oxides, such as zinc oxide, titanium dioxide, antimony trioxide, aluminum oxide, zirconium dioxide, germanium dioxide, indium trioxide, hydrated potassium aluminum silicate ($K_2Al_6Si_6O_{22}\cdot 2H_2O$), tin oxide ($SnO_2$), bismuth oxide ($Bi_2O_3$), lead oxide (PbO), beryllium oxide (BeO), silicon dioxide (SiO_2), barium titanate ($BaTiO_3$), tantalum oxide (Ta_2O_5), tellurium oxide (TeO_2), and boron oxide (B_2O_3); metal sulfides such as cadmium sulfide (CdS), zinc sulfide (ZnS) and tin disulfide (SnS_2); metal selenides such as cadmium selenide (CdSe). Also useful as photosensitive materials are certain fluorescent materials. Such materials include, for example, compounds such as silver activated zinc sulfide, zinc activated zinc oxide, manganese activated zinc phosphate $Zn_3(PO_4)_2$, and admixture of copper sulfide, antimony sulfide (SbS) and magnesium oxide (MgO), cadmium borate and zinc-8-hydroxyquinoline. Photochromic materials such as the photochromic metal organic complexes, are also useful as photocatalysts in this invention. Such materials include photochromic complexes such as:

(1) $[Co(C_2H_4N_2H_4)_3]_2(S_2O_8)_3$
(2) $[Co(C_2H_4N_2H_4)_3]_2(C_2O_4)_3$
(3) $[Co(NH_3)_6]_2(SO_4)_2S_2O_8$
(4) $[Co(NH_3)_6]_2(C_2O_4)_3$
(5) $K_3[Fe(C_2O_4)_3]$
(6) $K_3[Mn(C_2O_4)_3]$

and

(7) $[Cr(C_2H_4B_2H_4)_3]_2(SO_4)_2S_2O_8$

In place of the ethylenediamine ($C_2H_4B_2H_4$) and ammonia of the above compounds, such coordinating groups as quanidine, azido and nitrito may be used. Other reducible anions which may be used in place of those of the above compounds include tetrathionate, selenate and perchlorate.

Reducible image forming materials having at least the oxidizing power of cupric ion include preferably readily reducible metal ions such as, for example, $Ag+$, Hg^{+2}, Pb^{+4}, Au^{+3}, Pt^{+4}, Ni^{+2}, Sn^{+2}, Pb^{+2}, Cu^{+1}, and Cu^{+2}. Other suitable reducible image forming materials are MnO_4-ion, various leuco dye materials, and the like.

It will also be understood that the developer solutions of this invention can be used for diffusion transfer reversal processing where the positive image is formed by physical development and for purposes of intensifying already developed images in manners known in the physical developer art. For example, physical developers have been used to intensify chemically developed images in silver halide photographic systems.

Solvents useful in the development systems of this invention are preferably polar solvents such as water, alcohol and the like. Water is preferred because of its economy and availability.

The physical development system of this invention preferably comprises a diamine compound present in the amount of 0.001 to 1.0 moles of diamine compounds per mole of hydroxylamine compound. However, it is to be understood that the concentration of the developer solutions of this invention can be varied according to the various needs of the particular photographic system to which the developer system is to be applied.

[1] Periodic Table from Lange's Handbook of Chemistry, 9th edition, pp. 56–57, 1956.

It will be understood that the developer solutions of this invention may contain additives such as, for example, stabilizing agents such as disclosed in U.S. Pat. 3,157,502 which discloses improved physical developer systems obtained by the use therein of ionic surfactants. In addition, this patent discloses in detail fashion the ingredients of physical developers as well as many of the prior solutions and is therefore incorporated herein by reference.

The invention described herein is exemplified as follows: A photosensitive copy medium composed of a cellulose triacetate support coated with a finely-divided titanium dioxide dispersed in gelatin is exposed to an xenon flash source of an image pattern of activating radiation for $\frac{1}{1000}$-second duration, thereby giving an exposure of 7.4 meter candle seconds. This thus-exposed substrate is immersed for 15 seconds in 3 N silver nitrate solution, then developed in one of the following aqueous test developers for 25 seconds, and fixed for 1 minute in an aqueous sodium thiosulfate solution. The gross transmission density of each thus-developed photosensitive medium is measured with a photoelectric transmission densitometer. The net density is then determined by subtracting the sum of base and fog densities of an unexposed portion of said medium from the gross density of an exposed portion of said medium. The diamine compound used is designated by a Roman numeral which refers back to Table I and the respective diamine compound associated with the Roman numeral.

EXAMPLE 9

A zinc oxide-coated substrate is exposed to an image pattern of activating radiation. The thus-exposed substrate is then developed by dipping for 15 seconds in a solution comprising silver nitrate and Metol (p-methylaminophenol sulfate) at pH of about 3.8. A second zinc oxide-coated substrate is exposed for an identical duration to a similar image pattern of activating radiation and then dipped for 15 seconds in an aqueous solution of silver nitrate and p-phenylenediamine at pH of about 3.8. A third similar zinc oxide-coated substrate is similarly exposed to an image pattern of activating radiation and then dipped in an aqueous solution of silver nitrate, Metol (p-methylaminophenol sulfate) and p-phenylenediamine at pH of about 3.8. The net transmission density as determined in Examples 1–8 showed a marked increase with respect to the photosensitive medium developed in the developer solution containing both Metol and p-phenylenediamine as compared with the optical density of the substrates developed in either of the other two solutions.

EXAMPLE 10

Three silver halide prints which have been exposed to an image pattern of activating radiation and chemically developed to form visible images are each treated in a manner as described above in Example 9 in an attempt to intensify the images. The silver halide prints which are dipped in the solution containing both Metol and p-phenylenediamine show markedly greater intensifica-

	Diamine		Metol (p-methylaminophenol sulfate), moles	pH	Anti-oxidant, moles	Net transmission density
	Compound	Moles				
Example 1A			0.09	4.8		1.41
Example 1B	I	0.01		4.8		0.50
Sum of A and B						1.91
Example 1C	I	0.02	0.09	4.8		2.82
Example 2A			0.09	4.2		1.36
Example 2B	II	0.01		4.2		0.46
Sum of A and B						1.82
Example 2C	II	0.01	0.09	4.2		3.7
Example 3A			0.09	3.5	0.006	0.64
Example 3B	IV	0.001		3.5	0.006	Zero
Sum of A and B						0.64
Example 3C	IV	0.001	0.09	3.5	0.006	0.72
Example 4A			0.09	4.3	0.006	0.99
Example 4B	V	0.004		4.3		0.40
Sum of A and B						1.39
Example 4C	V	0.004	0.09	4.3	0 .006	3.8
Example 5A			0.09	4.3	0.006	2.19
Example 5B	VI	0.01		4.3		Zero
Sum of A and B						2.19
Example 5C	VI	0.01	0.09	4.3	0.006	3.0
Example 6A			0.09	3.6	0.006	0.64
Example 6B	VII	0.001		3.6	0.006	Zero
Sum of A and B						0.64
Example 6C	VII	0.001	0.09	3.6	0.006	0.74
Example 7A			0.09	3.8		1.41
Example 7B	VIII	0.001		3.8		Zero
Sum of A and B						1.41
Example 7C	VIII	0.001	0.09	3.8		1.70
Example 8A			0.09	3.9		1.42
Example 8B	IX	0.001		3.9		Zero
Sum of A and B						1.42
Example 8C	IX	0.001	0.09	3.9		2.36

In each of the above examples the density obtained with the pair of developing agents is greater than the sum of the densities obtained when they are used alone.

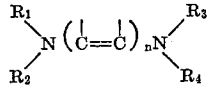
tion than the prints developed in either of the other two solutions.

EXAMPLE 11

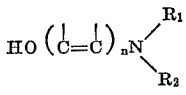
A substrate coated with a gelatino silver halide emulsion is exposed to an image pattern of activating radiation and developed in the developers of Example 2. The optical density obtained with developer 2C is greater than the sum of those obtained with developers 2A and 2B.

What is claimed is:

1. In a photographic physical development composition comprising an acid to neutral solution of a readily reducible material which is at least as strong an oxidizing agent as cupric ion and a reducing agent for the readily reducible material, the improvement comprising utilizing in said developer composition a reducing agent comprising a diamine compound which has the structure of:



and a hydroxylamine compound which has the structure of:



wherein n may be 0 or an integer from 1 to 10 and wherein R_1, R_2, R_3, and R_4 may be hydrogen and substituted or unsubstituted alkyl, aryl, alkaryl, and aralkyl groups, and wherein R_1, R_2, R_3, and R_4 may be the same or different, and wherein either or both of the diamine compound and the hydroxylamine compound may be the acid addition salt compound thereof.

2. A physical development composition as in claim 1 wherein the pH of the development composition is between about 3.0 and 7.0.

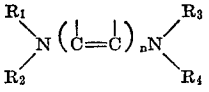
3. A physical development composition as in claim 1 wherein the diamine compound is present in the amount of 0.001 to 1.0 mole of diamine compound per mole of hydroxylamine compound.

4. A physical development composition as in claim 3 wherein the diamine compound is selected from the group consisting of p-phenylenediamine, N,N-dimethyl-p-phenylenediamine, N,N-diethyl-p-phenylenediamine, N-methyl-p-phenylenediamine, N - (p-methoxyphenyl)-p-phenylenediamine, 4'-diethylamino acetanilide, 1,2,4-benzenetriamine, 2,4-diamino diphenylamine, 2-(p-aminoanilino)-5-nitrobenzene sulfonic acid sodium salt, hydrazine, and the acid addition compounds thereof, and wherein the hydroxylamine compound is selected from the group consisting of hydroxylamine, p-aminophenol, p-anilinophenol, p-methylaminophenol, p-benzylaminophenol, 4-amino-2,6-dibromophenol, 4-amino-3-methylphenol, and the acid addition salt compounds thereof.

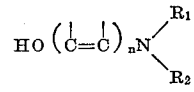
5. A physical development composition as in claim 4 wherein the diamine compound is N, N-dimethyl-p-phenylenediamine sulfate and the hydroxylamine compound is p-methylaminophenol sulfate and the metal ion is at least one member selected from the group consisting of silver, copper, mercury, gold, and platinum ion in an aqueous solution.

6. A physical development composition as in claim 1 wherein the solution of readily reducible material which is at least as strong an oxidizing agent as cupric ion is an aqueous solution of at least one metal ion and forms a separate solution from the reducing agent.

7. A photographic development composition comprising acidic to neutral solution of a diamine compound which has the structure of:



and a hydroxylamine compound which has the structure of:



wherein n may be 0 or an integer from 1 to 10 and wherein R_1, R_2, R_3, and R_4 may be hydrogen and substituted or unsubstituted alkyl, aryl, alkaryl, and aralkyl groups, and wherein R_1, R_2, R_3, and R_4 may be the same or different, and wherein either or both the diamine compound and the hydroxylamine compound may be the acid addition compounds thereof.

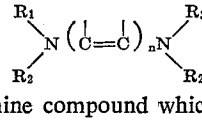
8. A photographic development composition as in claim 7 wherein the pH of the development composition is between about 3.0 and 7.0.

9. A photographic development composition as in claim 7 wherein the diamine compound is present in the amount of 0.001 to 1.0 mole of diamine compound per mole of hydroxylamine compound.

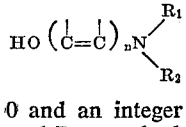
10. A photographic development composition as in claim 7 wherein the diamine compound is selected from the group consisting of p-phenylenediamine, N,N-dimethyl-p-phenylenediamine, N,N-diethyl-p-phenylenediamine, N-methyl-p-phenylenediamine, N-(p-methoxyphenyl)-p-phenylenediamine, 4'-diethylamino acetanilide, 1,2,4-benzenetriamine, 2,4-diamino diphenylamine, 2-(p-aminoanilino)-5-nitrobenzene sulfonic acid sodium salt, hydrazine, and the acid addition compounds thereof, and wherein the hydroxylamine compound is selected from the group consisting of hydroxylamine, p-amino-phenol, p-anilinophenol, p-methylaminophenol, p-benzylaminophenol, 4-amino-2,6-dibromophenol, 4-amino-3-methylphenol, and the acid addition compounds thereof.

11. A photographic development composition as in claim 7 wherein diamine compound is N,N-dimethyl-p-phenylenediamine sulfate and the hydroxylamine compound is p-methylaminophenol sulfate in an aqueous solution.

12. In a process of recording an image pattern of activating radiation by exposing a photosensitive copy medium to an image pattern of activating radiation and subsequently contacting the medium with (1) a solution of a readily reducible material which is at least as strong an oxidizing agent as cupric ion, and (2) a solution of a reducing agent for the metal ion, the improvement comprising utilizing for said reducing agent an acid to neutral solution of a diamine compound which has the structure of:



and a hydroxylamine compound which has the structure of:



wherein n may be 0 and an integer from 1 to 10 and wherein R_1, R_2, R_3, and R_4 may be hydrogen and substituted or unsubstituted alkyl, aryl, alkaryl, and aralkyl groups, and wherein R_1, R_2, R_3, and R_4 may be the same or different, and wherein either or both the diamine compound and the acid addition salts thereof may include the acid addition compounds thereof.

13. A process as in claim 12 wherein the diamine compound is present in the amount of 0.001 to 1.0 mole of diamine compound per mole of hydroxylamine compound.

14. A process as in claim 12 wherein the solution of readily reducible material which is at least as strong an oxidizing agent as cupric ion and the reducing agent for the metal ion form a unitary aqueous solution.

15. A process as in claim 12 wherein the solution of readily reducible material which is at least as strong an oxidizing agent as cupric ion and the reducing agent are in separate aqueous solutions.

16. A process as in claim 12 wherein the pH of the development system is between about 3.0 and 7.0.

17. A process as in claim 12 wherein the photosensitive copy medium comprises a metal containing compound and wherein the diamine compound is selected from the group consisting of p-phenylenediamine, N,N-dimethyl-p-phenylenediamine, N,N-diethyl-p-phenylenediamine, N-methyl-p-phenylenediamine, N' - (p-methoxyphenyl)-p-phenylenediamine, 4'-diethylamino acetanilide, 1,2,4-benzenetriamine, 2,4-diamino diphenylamine, 2-(p-aminoanilino)-5-nitrobenzene sulfonic acid sodium salt, hydrazine, and the acid addition compounds thereof, and wherein the hydroxylamine compound is selected from the group consisting of hydroxylamine, p-aminophenol, p-anilinophenol, p-methylaminophenol, p-benzylaminophenol, 4-amino-2,6-dibromophenol, 4-amino-3-methylphenol, and the acid addition compounds thereof.

18. A process as in claim 17 wherein the photosensitive copy medium comprises TiO_2 and a water permeable binder coated on a flexible substrate.

19. A process as in claim 18 wherein the diamine compound is N,N-dimethyl-p-phenylenediamine sulfate and the hydroxylamine compound is p-methylaminophenol sulfate and the readily reducible material comprises a metal ion at least one member of which is selected from the group consisting of silver, copper, mercury, gold and platinum ion.

20. A process as in claim 19 wherein the metal ion is silver ion and the substrate is paper.

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