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3,806,345

HYDROXYLAMINE PHOTOGRAPHIC DEVELOPER

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U.S. Cl. 96—66 R 10 Claims

ABSTRACT OF THE DISCLOSURE

N,N-dialkylhydroxylamine derivatives having the formula

$$R_1-N(OH)-R_2$$

wherein at least one of R_1 and R_2 is an alkyl group comprising a quaternary ammonium group either cyclic or acyclic and the other of R_1 and R_2 is an alkyl group or an alkyl group comprising a quaternary ammonium group either cyclic or acyclic, and their use in developer compositions for the development of silver halide emulsions are described. The developers have high development activity and low fog.

This invention relates to novel chemical compounds, more particularly to novel hydroxylamine derivatives which are valuable for use as photographic developers in the development of photosensitive silver halide material.

The use as developers for silver halide material of hydroxylamine and derivatives thereof, of which the oxidation products have the favorable property of leaving no residual stain in the silver image obtained, has been disclosed amongst others in U.S. patent specification 2,857,276 of Edwin H. Land and Helen J. Tracy, issued Oct. 21, 1958. Hydroxylamine itself and N-monoalkylhydroxylamines, though they are developers at high pH-values, are less suitable because they give rise to heavy fog. N,N-dialkylhydroxylamines on the contrary such as N,N-diethylhydroxylamine give markedly less fog but have the disadvantage of being less active.

It has therefore been tried to increase the development activity of N,N-dialkylhydroxylamines by introduction in the alkyl chain of special groups or atoms. These N,N-dialkylhydroxylamine derivatives include for example aminoalkyl hydroxylamines, more especially N,N-dialkylhydroxylamines having in at least one of the N-alkyl groups an intralinear amino nitrogen atom, either cyclic or acyclic, examples of which can be found in U.S. patent specification 3,287,125 of Milton Green, Adnan A. Sayigh and Henri Ulrich, issued Nov. 22, 1966, alkoxyhydroxylamines, more especially N,N-dialkylhydroxylamines of which at least one of the N-alkyl groups is substituted by alkoxy or alkoxyalkoxy, examples of which can be found in U.S. patent specification 3,293,034 of Milton Green, Adnan A. Sayigh and Henri Ulrich, issued Dec. 20, 1966, and sulphone hydroxylamines, more especially N,N-dialkylhydroxylamines having in at least one of the N-alkyl groups an interlinear sulphonyl (—SO_2—) group, examples of which can be found in U.S. patent specification 3,287,124 of Milton Green, Adnan A. Sayigh and Henri Ulrich, issued Nov. 22, 1966.

In accordance with the present invention novel N,N-dialkylhydroxylamine derivatives are provided which excel by their high development activity as compared with the known N,N-dialkylhydroxylamines.

The present invention further provides novel developer compositions and processes employing such novel developer compositions for the development of silver halide emulsions.

It also provides novel developer compositions useful in diffusion transfer processes.

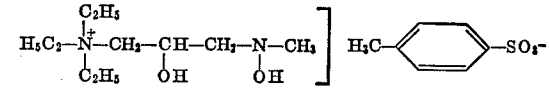
The novel N,N-dialkylhydroxylamine derivatives according to the present invention can be represented by the following general formula:

$$R_1-N(OH)-R_2$$

wherein at least one of R_1 and R_2 is an alkyl group comprising a quaternary ammonium group either cyclic or acyclic and the other of R_1 and R_2 is an alkyl group or an alkyl group comprising a quaternary ammonium group either cyclic or acyclic.

The novel N,N-dialkylhydroxylamine derivatives according to the present invention may be prepared by quaternization of the above N,N-dialkylhydroxylamines having in at least one of the N-alkyl groups an intralinear amino nitrogen atom, either cyclic or acyclic or as is illustrated by the following preparations, by reaction of hydroxylamine itself or a monoalkylhydroxylamine with quaternary salts of glycidylamines for which there can be referred to J. Org. Chem., 1963, 2283.

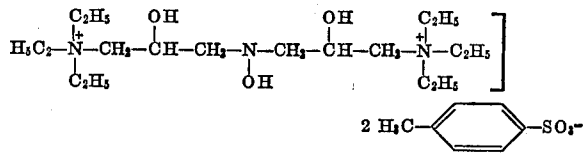
Preparation 1.—The compound having the following formula:



was prepared as follows:

To a solution of 15 g. (0.18 mole) of N-methylhydroxylamine hydrochloride in 400 ml. of ethanol 9.5 g. (0.09 mole) of sodium carbonate are added. Then a solution of 59 g. (0.18 mole) of 3-triethylammonium-1,2-epoxypropane-p-toluenesulphonate in 300 ml. of methanol are added with stirring and boiling. After having been boiled for 4 hours the mixture is concentrated by evaporation under reduced pressure and the residue is treated with acetone. The acetone filtrate is evaporated yielding 62 g. of the above compound.

Preparation 2.—The compound having the following formula:



was prepared as follows:

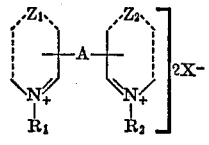
To a solution of 7 g. (0.1 mole) of hydroxylamine hydrochloride in 250 ml. of methanol, 5.3 g. (0.05 mole) of sodium carbonate are added. With stirring and boiling, a solution of 66 g. (0.2 mole) of 3-triethylammonium-1,2-epoxypropane p-toluenesulphonate in 300 ml. of methanol is added. After having been boiled for 5 hours the mixture is concentrated by evaporation under reduced pressure whereupon the residue is treated with acetone. The acetone filtrate is evaporated yielding 62 g. of the above compound.

The developing bath may comprise in addition to the novel developing agents any of the common ingredients employed in developing compositions e.g. alkalies such as sodium hydroxide, potassium hydroxide, sodium carbonate, trisodium phosphate, etc., silver halide solvents such as sodium hydroxide, potassium hydroxide, sodium carbonate, trisodium phosphate, etc., silver halide solvents such as sodium thiosulphate, sodium thiocyanate and cyclic imides, preservatives such as sulphites, bisulphites, metabisulphites and acids such as boric acid and citric

acid. Further the developer composition may comprise potassium bromide and water-softening agents such as polyphosphates and derivatives of ethylene diamine tetraacetic acid, antifoggants such as benzotriazole, 5-nitrobenzotriazole and 6-nitrobenzimidazole and wetting agents as well as other compounds known in the photographic development technique such as development restrainers and development accelerators for example onium compounds.

The novel developing agents according to the present invention can be used in conjunction with other developing compounds which may produce superadditivity. These compounds include the photographic developer substances known per se to give a super-additive development effect when used in conjunction with anionic developing agents such as hydroquinone. Among these superadditive developing agents there may be mentioned: 1-aryl-3-pyrazolidinone compounds such as 1-phenyl-3-pyrazolidinone, 1-phenyl-5-methyl-3-pyrazolidinone, the 1-aryl-4,4-dialkyl-3-pyrazolidinones described in U.S. patent specification 2,772,282 of Charles F. H. Allen and John R. Byers, issued Nov. 27, 1956 and the 1-aryl-4,4-dialkyl-5-alkoxy (or aryloxy)-3-pyrazolidinones described in U.S. patent specification 3,330,839 of Jozef Frans Willems, Albert Lucien Poot and Raymond Albert Roosen, issued July 11, 1967, bis[pyridone]azines as described in United Kingdom patent specification 1,154,385 filed Nov. 4, 1966 by Gevaert-Agfa N.V., p-aminophenol derivatives such as those described in U.S. patent specification 3,265,499 of Jozef Frans Willems, George Frans Van Veelen and Louis Maria De Haes, issued Aug. 9, 1966 and in United Kingdom patent specifications 858,432 filed Mar. 5, 1958 by Imperial Chemical Industry, and 928,671 filed Feb. 19, 1960 by Ilford Ltd. p-phenylene diamine derivatives such as those described in Belgian patent specification 715,500 filed May 22, 1968 by Gevaert-Agfa N.V. and in U.S. patent specification 3,264,502 of Jozef Frans Willems and George Frans Van Veelen, issued July 8, 1966, as well as the diquarternary cyclic ammonium compounds which by the uptake of 1 electron form stable Weitz-radicals described in the application S.N. 78,937 filed on Oct. 7, 1970, now U.S. Pat. No. 3,712,827, for "Process for the Development of Photographic Material" (=United Kingdom patent application No. 52,569/69).

These compounds have the formula:



wherein:

each of Z_1 and Z_2 (the same or different) stands for the atoms necessary to complete a pyridinium, thiazolium or imidazolium nucleus which may be substituted and carry fused-on-aryl nuclei,

A stands for a chemical bond linking the 2-position of Z_1=pyridinium, thiazolium or imidazolium to the 2-position of Z_2=pyridinium, thiazolium or imidazolium or to the 4-position of Z_2=pyridinium or for a chemical bond linking the 4-positions of Z_1=Z_2=pyridinium,

each of R_1 and R_2 stands for an alkyl group or R_1 together with R_2 may stand for an ethylene group when A is a chemical bond linking the 2-position of Z_1 to the 2-position of Z_2, and

X^- stands for an anion or acid radical.

The amount of novel hydroxylamine derivative to be used may vary within wide limits and depends on the very compound, on the nature of the colloid binder of the silver halide grains and on the amount and type of silver halide in the emulsion. The optimum concentration for any given hydroxylamine derivative can best be determined by employing a series of concentrations in several batches of the same developer and determining the speed obtained in the usual manner which is of course well known to those skilled in the art.

The novel silver halide developing agents of the invention are useful in conventional or wet development of silver halide emulsions, in diffusion transfer processes, both dye and silver, in such photographic processes known as stabilization processing wherein it is desired to eliminate or minimize the need for washing or stabilizing operations in liquid baths subsequent to the formation of the silver print, etc.

In diffusion transfer processes, as is well known in the art, an exposed silver halide emulsion is treated with a liquid processing composition while in superposed relationship with an image-receiving material. By this treatment the exposed silver halide is developed to silver and the unexposed silver halide is converted into a complex silver salt which is transferred to the image-receiving material and there reduced to silver to form a positive print. The processing composition normally includes a silver halide solvent, such as sodium thiosulphate, sodium thiocyanate, cyclic imides such as barbiturates or uracils which forms with silver halide a soluble complex as is well known in the art of forming silver images by transfer, and may also include a film-forming material such as sodium carboxylmethyl cellulose or hydroxyethyl cellulose, starch or gum for increasing the viscosity of the composition as for instance, in the case of in-camera silver complex diffusion transfer processing.

In stabilization processing the time-consuming fixing and washing operations are eliminated in order to produce the photographic record in the least possible time, by converting after development with the aid of stabilizing agents such as ammonium thiocyanate, the unexposed and undeveloped silver halide of the photographic emulsion into colorless light-insensitive compounds that need not be removed by washing.

The novel hydroxylamine derivatives of the invention may be employed in solution or they may be initially incorporated in a layer of the photosensitive material e.g. a silver halide emulsion layer or other colloid layer in water-permeable relationship therewith. In silver complex diffusion transfer processes the hydroxylamine derivatives according to the invention may also be incorporated in a layer of the image-receiving material, which, during processing, is in superposed relationship with the photosensitive silver halide material. When the developing agents are incorporated into the materials to be processed the processing liquid can be limited to a simple aqueous alkaline solution.

The following examples illustrate the present invention.

EXAMPLE 1

Strips of a photographic material comprising a light-sensitive silver halide emulsion layer coated on a cellulose triacetate support, are exposed through a grey filter with a light-quantity (E) which corresponds to the shoulder part of the density/log E curve.

Each of the exposed strips is developed at 20° C. in separate developing baths which differ from each other in that each time a different hydroxylamine developing agent is used. The developing baths used have the following basic composition:

Sodium sulphite	g	100
Sodium hydroxide	g	10
5-nitro-benzothiazole	mg	80
Potassium bromide	g	1
Hydroxylamine developing agent as listed in the table	mole	0.06

Water to make 1 liter.

The densities obtained are listed in the following table.

Developing agent	Densities obtained after a development time of— 0 sec.	20 sec.	1 min.	3 min.	5 min.
Hydroxylamine hydrochloride	0.04	0.05	0.34	0.95	[1] 1.43
N-methyl hydroxylamine hydrochloride	0.05	0.05	0.07	0.60	[1] 1.09
N,N-diethyl hydroxylamine oxalate	0.04	0.04	0.04	0.07	0.37
N-methyl-N-(2-hydroxy-3-diethylaminopropyl) hydroxylamine	0.04	0.04	0.04	0.11	0.56
Compound of—					
Preparation 1	0.04	0.04	0.20	1.29	2.08
Preparation 2	0.04	0.50	1.13	2.19	>3

[1] Heavy fog.

From the results appears that the compounds according to the present invention have a high development activity which surpasses markedly that of the known hydroxylamine developing agents.

EXAMPLE 2

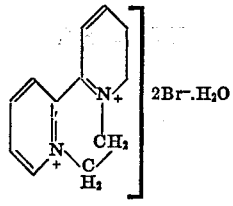
Example 1 is repeated with the difference that the developing bath now also includes 0.5 g. of 1,1'-tetramethylene-bis(pyridinium chloride) as development accelerating onium compound.

The results attained are listed in the following table.

Developing agent used	Densities after a development time of— 0 sec.	20 sec.	1 min.	3 min.	5 min.
N,N-diethylhydroxylamine oxalate	0.04	0.04	0.05	0.43	1.77
Compound of—					
Preparation 1	0.04	0.15	0.69	1.85	2.54
Preparation 2	0.04	0.88	1.53	2.62	>3

EXAMPLE 3

Example 1 is repeated with the difference that the developing bath now also includes as superadditive developer 0.5 g. of the compound having the formula:



according to our application filed for "Process for The Development of Photographic Material" referred to above.

The results attained are listed in the following table.

Developing agent used	Densities after a development time of— 0 sec.	20 sec.	1 min.	3 min.	5 min.
Compound of—					
Preparation 1	0.04	0.05	0.80	2.27	>3
Preparation 2	0.04	0.33	1.38	2.41	>3

EXAMPLE 4

A photosensitive element was prepared comprising on a paper support a silver bromoiodide emulsion layer containing per kg. an amount of silver halide corresponding to 60 g. of silver nitrate.

After exposure, the photosensitive element and an image-receiving element, which comprises a silver receptive layer containing development nuclei dispersed in a matrix of colloidal silica coated on a water-impervious support according to the practice described in U.S. patent specification 2,823,122 of Edwin H. Land, issued Feb. 11, 1958 were advanced in superposed relationship between

a pair of pressure-applying rollers to spread between them in a thin layer the following processing composition:

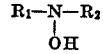
Water	ml	100
Sodium carboxymethyl cellulose	g	5
Sodium hydroxide	g	15
Uracil	g	11.5
30% ammonium hydroxide	ml	3.5
Diethylhydroxylamine oxalate	g	8
1-phenyl-2-tetrazoline-5-thione	g	0.2

After a contact period of 36 seconds, the emulsion together with the layer of processing liquid was stripped from the image-receiving element to uncover the positive print.

When repeating the procedure of this example using in the developing composition instead of N,N-diethylhydroxylamine equivalent amounts of the compounds of preparations 1 and 2 respectively the diffusion transfer images obtained showed better density. Moreover, better quality transfer images are obtained at lower illumination levels than is necessary in the case of N,N-diethylhydroxylamine.

We claim:

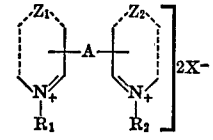
1. Photographic developing method which comprises developing an exposed silver halide emulsion layer of a photographic material with an aqueous alkaline composition in the presence of an N,N-dialkylhydroxylamine derivative corresponding to the formula:



wherein at least one of R_1 and R_2 is an alkyl group comprising a quaternary ammonium group having lower alkyl groups as the substituents on the nitrogen atom of said quaternary ammonium groups and the other of R_1 and R_2 is an alkyl group or an alkyl group comprising a quaternary ammonium group having lower alkyl groups as the substituents on the nitrogen atom of said quaternary ammonium groups.

2. Photographic developing method according to claim 1, wherein said N,N-dialkylhydroxylamine derivative is present in the said aqueous alkaline composition.

3. Photographic developing method according to claim 1, wherein said aqueous alkaline composition comprises a diquaternary cyclic ammonium salt which by the uptake of 1 electron forms stable Weitz-radicals having the formula



wherein:

each of Z_1 and Z_2 (the same or different) stands for the atoms necessary to complete a pyridinium, thiazolium or imidazolium nucleus which may be substituted and carry fused-on aryl nuclei,

A stands for a chemical bond linking the 2-position of Z_1=pyridinium, thiazolium or imidazolium to the 2-position of Z_2=pyridinium, thiazolium or imidazolium or to the 4-position of Z_2=pyridinium or for a chemical bond linking the 4-positions of Z_1=Z_2=pyridinium,

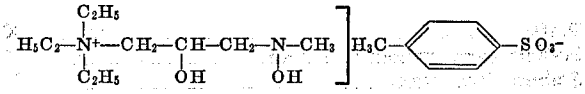
each of R_1 and R_2 stands for an alkyl group or R_1 together with R_2 may stand for an ethylene group when A is a chemical bond linking the 2-position of Z_1 to the 2-position of Z_2, and

X^- stands for an anion or acid radical.

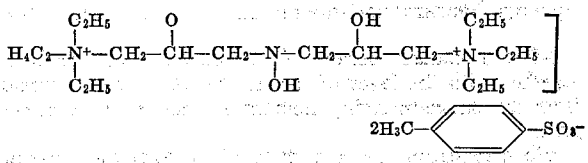
4. Photographic developing method according to claim 1, wherein said method is used for making images according to the silver complex diffusion transfer process.

5. Photographic developing method according to claim

1 wherein he N,N-dialkylhydroxylamine derivative has the formula:



6. Photographic developing method according to claim 1 wherein the N,N-dialkylhydroxylamine derivative has the formula:

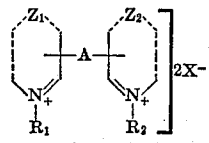


7. Photographic development composition for developing an exposed silver halide emulsion layer of a photographic material comprising in aqueous alkaline solution a N,N-dialkylhydroxylamine derivative corresponding to the formula:



wherein at least one of R_1 and R_2 is an alkyl group comprising a quaternary ammonium group having lower alkyl groups as the substituents on the nitrogen atom of said quaternary ammonium groups and the other of R_1 and R_2 is an alkyl group or an alkyl group comprising a quaternary ammonium group having lower alkyl groups as the substituents on the nitrogen atom of said quaternary ammonium groups.

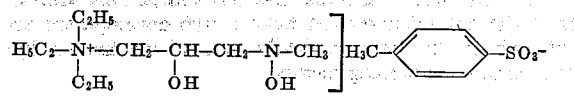
8. Photographic developing composition according to claim 7 and comprising also a diquaternary cyclic ammonium salt which by the uptake of 1 electron forms stable Weitz-radicals having the formula:



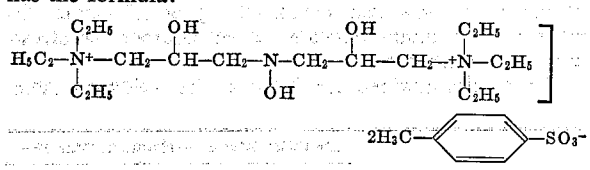
wherein:
each of Z_1 and Z_2 (the same or different) stands for the

atoms necessary to complete a pyridinium, thiazolium or imidazolium nucleus which may be substituted and carry fused-on aryl nuclei,
A stands for a chemical bond linking the 2-position of Z_1=pyridinium, thiazolium or imidazolium to the 2-position of Z_2=pyridinium, thiazolium or imidazolium or to the 4-position of Z_2=pyridinium or for a chemical bond linking the 4-positions of Z_1=Z_2=pyridinium,
each of R_1 and R_2 stands for an alkyl group or R_1 together with R_2 may stand for an ethylene group when A is a chemical bond linking the 2-position of Z_1 to the 2-position of Z_2, and
X^- stands for an anion or acid radical.

9. The photographic developing composition according to claim 6 wherein the N,N-dialkylhydroxylamine derivative has the formula:



10. Photographic developing composition according to claim 6 wherein the N,N-dialkylhydroxylamine derivative has the formula:



References Cited

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