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3,287,124

SULFONE-HYDROXYLAMINES AS PHOTOGRAPHIC DEVELOPERS

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11 Claims. (Cl. 96—29)

This invention relates to photography and more particularly to novel chemical compounds useful in the development of photosensitive silver halide elements.

It is one object of the present invention to provide novel chemical compounds which may be employed in the development of silver halide emulsions.

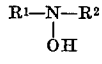
Another object of the present invention is to provide novel developer compositions and processes employing such novel developer compositions for the development of silver halide emulsions.

A further object of this invention is to provide novel developer compositions useful in diffusion transfer processes.

The invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others, and the compositions possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

Other objects of this invention will in part be obvious and will in part appear hereinafter.

The present invention relates to novel N-substituted hydroxylamines containing from one to two intralinear sulfone (—SO_2—) groups as part of an alkyl group or groups substituted on the nitrogen atom, and may be represented by the formula:

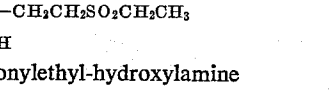


wherein at least one of R^1 and R^2 is an alkyl group containing an intralinear —SO_2— group, and the other of R^1 and R^2 is selected from the group consisting of alkyl groups and alkyl groups containing an intralinear —SO_2— group, and R^1 and R^2 when taken together may comprise the atoms necessary to complete a heterocyclic radical containing said —SO_2— group and said



group. R^1 and R^2 preferably contain from 1 to 4 carbons each, but may contain more carbons provided the resulting compound is soluble in 5% aqueous sodium hydroxide.

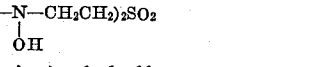
The preferred hydroxylamines of this invention include:

(1) 

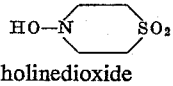
N-methyl-N-2-ethylsulfonylethyl-hydroxylamine

(2) $(CH_2CH_2SO_2CH_2CH_2)_2N—OH$

N,N-bis-(2-ethylsulfonylethyl)-hydroxylamine

(3) 

Bis-2-(methylhydroxylamino)-ethylsulfone

(4) 

N-hydroxythiomorpholinedioxide
[4-hydroxytetrahydro-1,4-thiazine-1,1-dioxide]

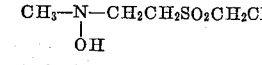
The use of hydroxylamines in developing silver halide

emulsions is disclosed, e.g., by Land et al., U.S. Patents Nos. 2,857,274, 2,857,275, and 2,857,276. A particularly useful hydroxylamine has been N,N-diethyl-hydroxylamine. The novel chemical compounds of the present invention exhibit many properties making them more desirable as silver halide developing agents than hydroxylamines previously used, as will be noted hereinafter.

The novel sulfone-containing hydroxylamines of this invention generally may be prepared by an additional reaction between a hydroxylamine, e.g., hydroxylamine or N-methyl-hydroxylamine and the activated double bond of the corresponding vinyl sulfone compound. In general, the reaction is exothermic, and use of cooling means, e.g., addition of ice, may be desirable to hold the temperature below the critical point. Isolation of the product preferably is accomplished by recrystallization from a suitable solvent, though in some cases extraction or other purification procedures may be used.

The following detailed examples are given only to illustrate the preparation of preferred compounds within the scope of this invention, and are not intended to be in any way limiting.

Example 1



N-methyl-N-2-ethylsulfonylethyl-hydroxylamine

A flask was charged with 16.7 g. (0.2 mole) of N-methyl-hydroxylamine hydrochloride in 100 ml. of water, to which 10.6 g. (0.1 mole) of sodium carbonate and 18 g. (0.15 mole) of ethylvinylsulfone were added dropwise with stirring. After 30 minutes a crystalline material was filtered off and recrystallized from benzene to provide 13 g. of the desired product as white needles soluble in alkali and melting at 105–106° C. The infrared spectrum of the product in chloroform showed major bands at 2.98 (OH); 7.6, 8.85 μ (SO_2). Analysis gave the following results:

Calculated for $C_5H_{13}NO_3S$: Percent C, 35.91; Percent H, 7.38; Percent N, 8.37. Found: Percent C, 36.50; Percent H, 8.31; Percent N, 8.30.

The ethylvinylsulfone used in this example was synthesized as follows: 2 g. of phosphoric acid and 200 g. of 35% hydrogen peroxide were added to 106 g. of ethyl-2-hydroxyethylsulfide dropwise with stirring over a period of 1 hour. The exothermic reaction was controlled at 60 to 70° C. Then the reaction mixture was refluxed for two hours. Evaporation of the water in vacuo gave 136 g. of ethyl-2-hydroxyethylsulfone. 202 g. of thionyl-chloride were added to a stirred mixture of 117 g. of the thus prepared ethyl-2-hydroxyethylsulfone and 67 g. of dry pyridine, dropwise with stirring at 25 to 30° C. The stirring was continued for 30 minutes at room temperature, after which the reaction mixture was heated at 90–95° C. for 30 minutes. After cooling, the reaction mixture was poured onto ice, extracted with chloroform and rectified in vacuum to yield 75.5 g. of 2-chloroethylethylsulfone, boiling at 115–128° C. (with slight decomposition) at a pressure of 3.4 to 4.0 mm. 40 g. of triethylamine were added to 43.5 g. of the thus-prepared 2-chloroethylethyl-sulfone in 350 cc. of dry benzene with stirring and ice cooling. The stirring was continued for 30 minutes and 35.5 g. of the triethylaminehydrochloride were filtered off. Evaporation of the benzene and distillation of the residue yielded 28.9 g. of ethylvinylsulfone, boiling at 69–70° C. at a pressure of 0.7 mm.

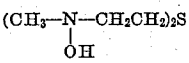
Example 2

$(CH_3CH_2SO_2CH_2CH_2)_2N—OH$

N,N-bis-(2-ethylsulfonylethyl)-hydroxylamine

A flask was charged with 13.9 g. (0.2 mole) of hydroxylamine hydrochloride in 50 cc. of water and 10.6 g. (1.0 mole) of sodium carbonate were added with ice cooling, followed by 14.4 g. (0.12 mole) of ethylvinylsulfone, prepared as in Example 1. Within several minutes crystals began to separate, and after stirring for 10 minutes the crystalline reaction product was collected. Recrystallization from methanol yielded the desired product as white needles, soluble in alkali, with a melting point of 134–135° C. Infrared analysis (KBr) showed major bands at 2.97 (OH); 7.85 (SO_2); 8.08, 8.78 (SO_2); 9.85; 13.75 μ. Nitrogen analysis as $C_8H_{19}NO_5S_2$ showed 4.70% as compared with the theoretical value of 5.11%.

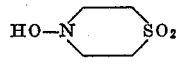
Example 3



Bis-(2-methylhydroxylaminoethyl)-sulfone

13 g. of sodium carbonate were added, with ice cooling, to 20 g. of N-methylhydroxylamine hydrochloride in 100 cc. of water. Then 11.8 g. of divinylsulfone were added dropwise and after stirring for about 20 minutes white crystals separated out. The mixture was allowed to stand overnight, the crystals filtered off and recrystallized from ethanol, to give 15.7 g. of the desired product, soluble in alkali, melting at 166–167° C. Nitrogen analysis as $C_6H_{16}N_2O_4S$ gave 12.93% as compared with the calculated value of 13.19%. The infrared spectrum (KBr) showed major bands where expected for OH and SO_2.

Example 4



N-hydroxythiomorpholinedioxide

A flask was charged with 6.9 g. of hydroxylamine hydrochloride in 200 cc. of water and 6 g. of sodium carbonate were added with ice cooling. 11.8 g. of divinylsulfone then were added slowly with vigorous stirring. After several minutes white solid material began to precipitate. The reaction product was filtered off and washed with water and methanol to yield 12.9 g. of the desired product which was soluble in warm 5% sodium hydroxide, dimethyl formamide and dimethylsulfoxide, and melted at 192–193° C. (with decomposition). The infrared spectrum (KBr) showed major bands where expected for OH and SO_2. Elemental analysis showed:

Calculated for $C_4H_9NO_3S$: percent C, 31.77; percent H, 5.99; percent N, 9.26. Found: percent C, 31.74; percent H, 6.19; percent N, 9.35.

As previously mentioned, the novel silver halide developing agents of this invention are useful in conventional or wet development of silver halide emulsions, diffusion transfer processes, both dye and silver, and are especially useful in such photographic processes 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. Examples of such processes are disclosed in U.S. Patent No. 2,647,056 to Edwin H. Land.

In diffusion transfer processes of this type, 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. The liquid processing composition develops exposed silver halide to silver and reacts with unexposed silver halide to form 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 includes a silver halide solvent, such as sodium thiosulfate, and may also contain a film-forming material for increasing the viscosity of the composition. As used herein, the term "silver halide solvent" refers to reagents which will form a soluble complex with silver halide, as is well known in the art of forming silver images by transfer.

The following examples are intended to illustrate the use of the novel developing agents of this invention in diffusion transfer processes, and are intended to be illustrative only.

Example 5

A silver iodobromide emulsion sold by E. I. du Pont de Nemours & Co., Wilmington, Delaware, was exposed and processed with a composition prepared by adding 0.4 g. of N,N-bis-(2-ethylsulfonylethyl)-hydroxylamine to 10 cc. of a composition comprising:

Sodium carboxymethyl cellulose	g. 38.1
Sodium hydroxide	g. 34.2
6-nitrobenzimidazole nitrate	g. 60
Sodium sulfite	g. 53.6
Sodium thiosulfate	g. 20.0
Water	cc. 850

The image-receiving element comprised a silver-receptive stratum containing silver-precipitating nuclei dispersed in a matrix of colloidal silica coated on a water-impervious base according to the practice described in U.S. Patent No. 2,823,122, issued February 11, 1958. The exposed emulsion and the image-receiving element were advanced, in superposed relationship, between a pair of pressure-applying rollers to spread the processing solution between them in a thin layer. After an imbibition period of approximately sixty seconds, the emulsion, together with the layer of solution, was stripped from the image-receiving element to uncover a good quality positive print.

Example 6

The procedure described in Example 5 was repeated using, in turn, 0.4 g. of N-methyl-N-2-ethylsulfonylethyl-hydroxylamine, 0.4 cc. of bis-2-methylhydroxylaminosulfone, and 0.4 g. of N-hydroxylthiomorpholine dioxide added to 10 cc. of the base developing composition. Good quality positive transfer images were obtained in each case.

N,N-diethyl-hydroxylamine is characterized by substantial volatility at room temperatures. While this is a desirable property for many purposes, there results a strong "fishy" or amine odor which is objectionable in many applications, e.g., where a number of prints are to be made in a short time in the same room. In contrast, the novel developing agents of this invention do not exhibit strong odors at room temperature because their vapor pressures are appreciably lower than that of N,N-diethyl-hydroxylamine. The novel developing agents of this invention also are characterized by having colorless or substantially colorless oxidation products.

The induction periods of the novel developing agents of this invention were tested by applying an approximately 1 molar solution of the hydroxylamine in 5% sodium hydroxide to a fogged silver iodobromide emulsion and noting the elapsed time before strong developing starts. The compounds prepared in Examples 1–3 all showed induction periods of from 2 to 3 seconds as compared with 2.5 to 3 seconds for N,N-diethylhydroxylamine and 8 seconds for N,N-dimethyl-hydroxylamine. The compound of Example 4, N-hydroxythiomorpholine dioxide is less soluble in alkali than the other compounds, and gave a development induction period of approximately 10 seconds when tested in warm 5% NaOH.

The novel developing agents may be employed in solution or they may be initially incorporated in a layer of the photosensitive or image-receiving elements; in the latter case they are preferably employed as acid salts, e.g., as the hydrochloride or hydrobromide. They also may be employed in combination with other developing agents.

It will be apparent that the relative proportions of the novel developing agents of the developer compositions set forth above may be varied to suit the requirements of the operator. Thus, it is within the scope of this invention to modify the above developer compositions by the substitution of preservatives, alkalies, silver halide solvents, anti-foggants, etc., other than those specifically mentioned. Where desirable, it is also contemplated to include in the developer composition common components such as restrainers, accelerators, etc.

Since certain changes may be made in the above compositions and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. As a new developer composition, an aqueous solution comprising an alkaline material, a silver halide solvent, and a silver halide developing agent selected from the group consisting of compounds within the formula:



wherein at least one of R^1 and R^2 is an alkyl group containing an intralinear $—SO_2—$ group, and the other of said R^1 and R^2 is selected from the group consisting of alkyl groups and alkyl groups containing an intralinear $—SO_2—$ group, R^1 and R^2 when taken together comprise the atoms necessary to complete a heterocyclic radical containing said $—SO_2—$ and said



groups.

2. A method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion with an aqueous solution comprising an alkaline material and a silver halide developing agent selected from the group consisting of compounds represented by the formula:



wherein at least one of R^1 and R^2 is an alkyl group containing an intralinear $—SO_2—$ group, and the other of said R^1 and R^2 is selected from the group consisting of alkyl groups and alkyl groups containing an intralinear $—SO_2—$ group, R^1 and R^2 when taken together comprise the atoms necessary to complete a heterocyclic radical containing said $—SO_2—$ and said



groups.

3. A method of developing a silver halide emulsion which comprises treating an exposed halide emulsion with an aqueous solution comprising an alkaline material and N - methyl-N-2-ethylsulfonylethyl-hydroxylamine for a sufficent time to develop said exposed silver halide emulsion,

4. A method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion with an aqueous solution comprising an alkaline material and N,N-bis(2-ethylsulfonylethyl)-hydroxylamine for a sufficient time to develop said exposed silver halide emulsion.

5. A method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion with an aqueous solution comprising an alkaline material and bis-2-methylhydroxylaminoethylsulfone for a sufficient time to develop said exposed silver halide emulsion.

6. A method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion with an aqueous solution comprising an alkaline material and N-hydroxythiomorpholine dioxide for a sufficient time to develop said exposed silver halide emulsion.

7. A photographic process comprising the steps of developing an exposed silver halide emulsion with an aqueous alkaline solution comprising a silver halide developing agent and a silver halide solvent in the presence of an image-receiving material superposed on said silver halide emulsion, said deevloping agent being selected from the group consisting of compounds represented by the formula:



wherein at least one of R^1 and R^2 is an alkyl group containing an intralinear $—SO_2—$ group, and the other of said R^1 and R^2 is selected from the group consisting of alkyl groups and alkyl groups containing an intralinear $—SO_2—$ group, R^1 and R^2 when taken together comprise the atoms necessary to complete a heterocyclic radical containing said $—SO_2—$ and said



groups to form a positive silver print on said image-receiving material.

8. A process as defined in claim 7, wherein said developing agent is N-methyl-N-2-ethylsulfonylethyl-hydroxylamine.

9. A process as defined in claim 7, wherein said developing agent is N,N-bis(2-ethylsulfonylethyl)hydroxylamine.

10. A process as defined in claim 7, wherein said developing agent is bis-2-methylhydroxylaminoethylsulfone.

11. A process as defined in claim 7, wherein said developing agent is N-hydroxythiomorpholine dioxide.

References Cited by the Examiner

UNITED STATES PATENTS

2,750,357	7/1956	Bredereck	260—607
2,857,276	10/1958	Land et al.	96—29

NORMAN G. TORCHIN, *Primary Examiner.*

DONALD LEVY, *Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,287,124 November 22, 1966

Milton Green et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 9, for "additional" read -- addition --; column 3, line 11, for "8.78" read -- 8.75 --; column 4, line 18, for "60 g." read -- 6.0 g. --; column 5, line 59, for "sufficent" read -- sufficient --; column 6, line 23, for "deevloping" read -- developing --.

Signed and sealed this 7th day of November 1967.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents