United States Patent Office 3,293,034 Patented Dec. 20, 1966

3,293,034

ALKOXY HYDROXYLAMINES AS PHOTOGRAPHIC DEVELOPERS

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No Drawing. Filed June 26, 1963, Ser. No. 290,619
21 Claims. (Cl. 96—29)

This invention relates to photography and more particularly to novel chemical componuds 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.

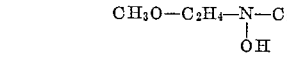
Other objects of this invention will in part be obvious and will in part appear hereinafter.

The present invention relates to novel N-substituted hydroxylamines corresponding to the formula:

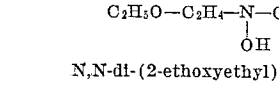


wherein at least one of R^1 and R^2 is an alkoxyalkyl or alkoxyalkoxyalkyl radical, and the other of R^1 and R^2 is selected from the group consisting of alkyl, alkoxyalkyl, alkoxyalkoxyalkyl, or alkenyl radical. The alkyl, alkoxy and alkenyl radicals preferably contain from 1 to 3 carbons, but may contain more carbons provided the resulting compound is soluble in 5% aqueous sodium hydroxide.

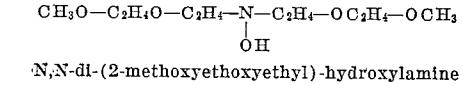
The preferred alkoxyalkyl hydroxylamines include:

(1) 

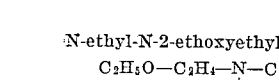
N,N-di-(2-methoxyethyl)-hydroxylamine

(2) 

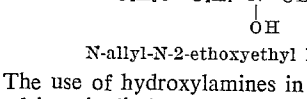
N,N-di-(2-ethoxyethyl)-hydroxylamine

(3) 

N,N-di-(2-methoxyethoxyethyl)-hydroxylamine

(4) 

N-ethyl-N-2-ethoxyethyl hydroxylamine

(5) 

N-allyl-N-2-ethoxyethyl hydroxylamine

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-diethylhydroxylamine. 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 hydroxylamines of this invention generally may be prepared by oxidizing the corresponding secondary amine, the reaction being carried out by slowly adding a suitable oxidizing agent, e.g., hydrogen peroxide. 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 vacuum factionating, though in some cases extraction on other purification procedures may be desirable before distillation.

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

$(CH_3OCH_2CH_2)_2NOH$

A flask was charged with 80 grams of di-(methoxyethyl)-amine which had been diluted with 69 ml. of water, and 59 grams of 35% hydrogen peroxide was added slowly over a period of approximately twenty minutes. A slow exothermic reaction took place causing the temperature to rise. After the temperature rose to 55° C., it was controlled by ice cooling. The water was evaporated under vacuum and the product vacuum fractionated. The fraction boiling at 63–68° C. at a pressure of 0.1 mm., amounted to a 22% yield, was soluble in alkali, and gave the following analysis:

	Found	Calculated for $C_6H_{15}NO_3$
Percent C	48.30	48.30
Percent H	10.12	10.13
Percent N	9.50	9.39

Example 2

$(CH_3CH_2OCH_2CH_2)_2NOH$

A flask was charged with 80.5 grams of di-(ethoxyethyl) amine which had been diluted with 80 ml. of water, and 55 grams of 30% hydrogen peroxide was added dropwise over a period of ten minutes. The reaction temperature rose from 31 to 41° C., and subsequently to 60° C. and was controlled at 50–60° C. by ice water. The exothermic reaction ceased after about one hour. The water was evaporated in vacuum and the product vacuum fractionated. The fraction boiling at 80–84° C. at a pressure of 0.2 mm., amounted to a 24% yield, was soluble in alkali, and gave the following analysis:

	Found	Calculated for $C_8H_{19}NO_3$
Percent C	54.61	54.21
Percent H	10.91	10.81
Percent N	7.95	7.90

Example 3

$(CH_3OCH_2CH_2OCH_2CH_2)_2NOH$

A 66.3 gram portion of di-(methoxyethoxyethyl) amine was diluted with 40 ml. of water, and 29 grams of 35% hydrogen peroxide was added at 55° C. There was no immediate evidence of an exothermic reaction, and the temperature dropped to room temperature; however, on standing an exothermic reaction was observed, and overnight the color of the reaction mixture turned to yellow. The reaction mixture was extracted with one 100 ml., and two 50 ml. portions of monochlorobenzene and the combined extracts were dried over sodium sulfate. After evaporation of the solvent the product was vacuum frac-

tionated. The product boiling between 140 and 152° C. at a pressure of 1.1 mm., amounted to a 12.5% yield, was soluble in alkali and gave the following analysis:

	Found	Calculated for $C_{10}H_{23}NO_5$
Percent C	50.84	50.61
Percent H	10.04	9.77
Percent N	5.89	5.90

Example 4

$$CH_3CH_2OCH_2CH_2—N(OH)—CH_2CH_3$$

Ethylbromide (109 g.) was added dropwise with stirring to 178 g. of 2-ethoxyethylamine over a period of ninety minutes. A slight exothermic reaction was observed and the temperature rose to 55° C. With stirring the reaction mixture was allowed to come to room temperature. The reaction mixture was extracted with ether, the solvent evaporated off and the product distilled in vacuo. To 58.5 grams of crude ethyl-2-ethoxyethylamine thus prepared in 50 ml. of water, a 50 gram portion of 35% hydrogen peroxide was added dropwise with stirring over a period of twenty minutes. The reaction temperature rose to 50° C. and was maintained at 50° C. with occasional cooling. After allowing the reaction mixture to stand overnight it was extracted with chloroform. After the solvent had been removed, the dried extract was subjected to several rectifications in vacuum to yield 6.8 g. (10.5% yield) of the desired alkali soluble product boiling at 73 to 74° C. at a pressure of 3.5 mm.

Example 5

$$CH_2CH_2OCH_2—N(OH)—CH_2CH=CH_2$$

Allyl-2-ethoxyethyl amine was prepared in a manner similar to that set forth in Example 4, using 38.25 g. of allyl chloride and 89 g. of 2-ethoxyethylamine. At the end of the addition of the allyl chloride the reaction mixture temperature rose to 80° C. The reaction mixture was cooled to room temperature and treated with ether. Colorless hygroscopic leaflets of 2-ethoxyethyl amine hydrochloride were precipitated. The ether extract was dried, and after evaporation was subjected to distillation to obtain a crude product boiling at 111–149° C., which product was rectified and further fractionated to yield a crude product boiling at 126–164° C. To a 20.8 gram portion of the crude allyl 2-ethoxyethylamine in 30 ml. of water was added 17.6 grams of 30% hydrogen peroxide slowly over a period of five minutes. A slow exothermic reaction occurred causing the temperature to rise to 41° C. over a period of one hour. The reaction mixture was allowed to stand and cool after which it was extracted with methylene chloride. The dried extract, after evaporation, was vacuum fractionated to yield 1.0 gram of product having the desired I.R. spectrum, soluble in alkali, and boiling at 100–101° C. at a pressure of 22 mm.

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 6

A silver iodobromide emulsion sold by E. I. du Pont de Nemours & Co., Wilmington, Delaware, was exposed and processed with 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
N,N-di-(2-ethoxyethyl)-hydroxylamine	cc.. 41.6
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 the positive print.

Example 7

The procedure described in Example 6 was repeated using approximately 75 cc. of N,N,-di-(2-methoxyethyl)-hydroxylamine as the developing agent.

Example 8

The procedure described in Example 6 was repeated using a mixture of approximately 40 cc. of N,N-di-(2-ethoxyethyl)-hydroxylamine and approximately 6 cc. of N,N,-di-(2-methoxymethyl)-hydroxylamine.

The silver transfer images obtained in the above examples were characterized by substantially longer range and more neutral tones than were obtained using N,N-diethyl-hydroxylamine under similar conditions. The latter compound 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.

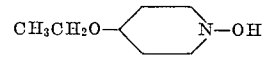
The induction periods of the novel developing agents of this invention were tested by applying an approximately 1 molar solution of the hydroxylamine in 5% sodium hydroxide to a fogged silver iodobromide emulsion and noting the elapsed time before strong developing starts. The compounds prepared in Examples 1–5 all showed induction periods of from 1 to 2 seconds as compared with 2.5 to 3 seconds for N,N-diethyl-hydroxyl-

amine and 8 seconds for N,N-dimethyl-hydroxylamine. The developed area also reached its blackest color (or full development) in less or no longer times than the last-mentioned compounds.

It also has been discovered that the addition of 1,1-dimethylhydrazine unexpectedly prevented aerial oxidation of N,N-di-(2-ethoxyethyl)-hydroxylamine in 5% sodium hydroxide.

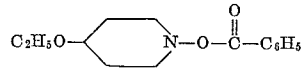
It will be understood that R^1 and R^2 taken together may comprise the atoms necessary to complete a heterocyclic ring including the nitrogen atom, a carbon atom of said heterocyclic ring being substituted by an alkoxy group. An example of such a compound is N-hydroxy-4-ethoxypiperidine, the synthesis of which is set forth in the following example.

Example 9



N-hydroxy-4-ethoxypiperidine

A flask was charged with 11.5 grams of benzoylperoxide in 100 ml. of anhydrous ether, and 12.3 grams of 4-ethoxypiperidine was added dropwise at reflux temperature. The mixture was then refluxed for 2 hours, at which point all of the benzoyl peroxide had been consumed. The reaction mixture was extracted with water and sodium carbonate. Evaporation of the ether gave 10.3 g. of the red-brown O-benzoylhydroxylamine derivative



as an oil which did not crystallize on standing in the icebox. This product was stirred overnight with 5.6 grams of potassium carbonate in 50 ml. of water, but a substantial amount of the product remained unchanged. Addition of methanol gave a homogeneous solution which was refluxed for 5 hours. Most of the methanol was removed and, after a minute amount of water was added and the aqueous phase was saturated with sodium carbonate, it was extracted with chloroform. Distillation of the dried chloroform extract in vacuo gave 1.1 g. (17% yield) of the desired product as a colorless liquid soluble in alkali, boiling at 80–81° C. at a pressure of 0.7 mm. Analysis showed:

	Found	Calculated for $C_7H_{15}NO_2$
Percent C	59.23	57.90
Percent H	10.58	10.41
Percent N	9.01	9.65

This compound gave good results when used as a silver halide developing agent in the manner described above, giving a development induction period of 4 seconds, slightly longer than that of N,N-diethylhydroxylamine.

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.

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, antifoggants, 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 selected from the group consisting of alkoxyalkyl and alkoxyalkoxyalkyl radicals, and the other of said R^1 and R^2 is selected from the group consisting of alkyl, alkoxyalkyl, alkoxyalkoxyalkyl, and alkenyl radicals, and R^1 and R^2 when taken together with said



is an alkoxy-substituted heterocyclic group.

2. A developer composition as defined in claim **1**, wherein said silver halide developing agent is N,N-di-(2-methoxyethyl)-hydroxylamine.

3. A developer composition as defined in claim **1**, wherein said silver halide developing agent is N,N-di-(2-ethoxyethyl)-hydroxylamine.

4. A developer composition as defined in claim **1**, wherein said silver halide developing agent is N,N-di-(2-methoxyethoxyethyl)-hydroxylamine.

5. A developer composition as defined in claim **1**, wherein said silver halide developing agent is N-ethyl-N-2-ethoxyethyl-hydroxylamine.

6. A developer composition as defined in claim **1**, wherein said silver halide developing agent is N-allyl-N-2-ethoxyethyl-hydroxylamine.

7. A developer composition as defined in claim **1**, wherein said silver halide developing agent is N-hydroxy-4-ethoxypiperidine.

8. 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 selected from the group consisting of alkoxyalkyl and alkoxyalkoxyalkyl radicals, and the other of said R^1 and R^2 is selected from the group consisting of alkyl, alkoxyalkyl, alkoxyalkoxyalkyl, and alkenyl radicals, and R^1 and R^2 when taken together with said



is an alkoxy-substituted heterocyclic group.

9. 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-di-(2-methoxyethyl)-hydroxylamine for a sufficient time to develop said exposed silver halide emulsion.

10. 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-di-(2-ethoxyethyl)-hydroxylamine for a sufficient time to develop said exposed silver halide emulsion.

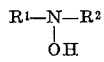
11. A method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion with an aqueous solution comprising an alkaline material and N,N-di-(2-methoxyethoxyethyl)-hydroxylamine for a sufficient time to develop said exposed silver halide emulsion.

12. 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-ethyl-N-2-ethoxyethyl-hydroxylamine for a sufficient time to develop said exposed silver halide emulsion.

13. 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-allyl-N-2-ethoxyethyl-hydroxylamine for a sufficient time to develop said exposed silver halide emulsion.

14. 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-hydroxy-4-ethoxypiperidine for a sufficient time to develop said exposed silver halide emulsion.

15. 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 developing agent being selected from the group consisting of compounds represented by the formula:



wherein at least one of R^1 and R^2 is selected from the group consisting of alkoxyalkyl and alkoxyalkoxyalkyl radicals, and the other of said R^1 and R^2 is selected from the group consisting of alkyl, alkoxyalkyl, alkoxyalkoxyalkyl, and alkenyl radicals, and R^1 and R^2 when taken together with said



is an alkoxy-substituted heterocyclic group, to form a positive silver print on said image-receiving material.

16. A process as defined in claim 9, wherein said developing agent is N,N-di-(2-methoxyethyl)-hydroxylamine.

17. A process as defined in claim 15, wherein said developing agent is N,N-di-(2-ethoxyethyl)-hydroxylamine.

18. A process as defined in claim 15, wherein said developing agent is N,N-di-(2-methoxyethoxyethyl)-hydroxylamine.

19. A process as defined in claim 15, wherein said developing agent is N-ethyl-N-2-ethoxyethyl-hydroxylamine.

20. A process as defined in claim 15, wherein said developing agent is N-allyl-N-2-ethoxyethyl-hydroxylamine.

21. A process as defined in claim 15, wherein said developing agent is N-hydroxy-4-ethoxypiperidine.

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