Patented Feb. 13, 1951 2,541,889

UNITED STATES PATENT OFFICE

2,541,889

ALKYL ETHERS OF POLYHYDROXYARALKYLAMINES AS ACCELERATORS

Ivy V. Runyan, Binghamton, N. Y., assignor to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

No Drawing. Application November 16, 1949, Serial No. 127,780

12 Claims. (Cl. 95—88)

1

This invention relates to photographic developers and particularly to alkyl ethers of polyhydroxyaralkylamines.

It is well known that various amines, such as primary and secondary alkyl and alkylene amines containing from 3 to 7 carbon atoms may be added to photographic black and white and color developing solutions for the purpose of increasing the rate of development. In other words, these amines accelerate the development so as to cause the developing agent to form the image (silver or color image) more rapidly than is possible without the presence of such amines.

Although developing solutions containing such amines cut the developing time to 12–15 minutes, such period is still unsatisfactory where large scale operations are involved, as in commercial processing where time is of the essence.

It has been established that aralkylamines and phenoxyaralkylamines in which the aminoalkyl group contains from 2 to 3 carbon atoms accelerate developing rates and energize weak developers. While such compounds when present in developing solutions decrease the developing time, their full efficiency can not be utilized because of their limited solubility in alkaline developer solutions. Moreover, they are characterized by unpleasant odors, which tend to discourage their commercial use.

It is, therefore, an object of the present invention to provide a black and white and color developer having an increased rate of development so that the developing time is decreased by less than one-half of the normal time without loss of speed and contrast.

Another object of the present invention is to provide a delevoper which is not only less toxic than those heretofore used, but also characterized by a very pleasant odor.

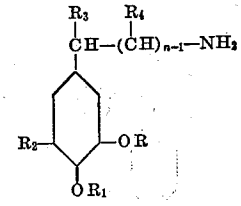
Other objects and advantages will appear hereinafter.

The foregoing objects are accomplished by adding an alkyl ether of a polyhydroxyaralkylamine, particularly a 3,4-dihydroxy or 3,4,5-trihydroxyaralkylamine, to the usual black and white developer and to a color forming developer in which a primary aromatic amine is used as the developing agent. It has been found that in developing color images in multicolor photographic layers containing color formers fast to diffusion, as disclosed in United States Patents 2,178,612, 2,179,228, 2,179,234, 2,179,238–9, 2,179,244, 2,186,719, 2,186,732–3–4, 2,186,849, 2,200,306, 2,280,722, 2,292,575, 2,303,928, and 2,307399, with a color developer containing an alkyl ether of a polyhydroxyaralkylamine, the developing time is cut from 20–30 minutes to 2–10 minutes. All of the layers are simultaneously developed and the dye images formed are of excellent quality.

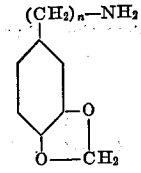
2

The developing time with black and white developers, for instance, solutions of hydroquinone and Metol (p-methylaminophenol sulfate) and the like, is also cut by more than half without causing fog when such solutions contain an alkyl ether of a polyhydroxyaralkylamine.

The alkyl ethers of polyhydroxyaralkylamines employed in accordance with the present invention are characterized by the following general formulae:

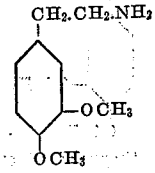


and



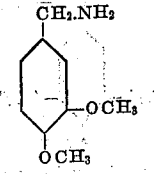
wherein R represents a methyl or ethyl group, R_1 represents hydrogen, a methyl or ethyl group, R_2 represents hydrogen or a methoxy or ethoxy group, R_3 and R_4 represent hydrogen or a methyl group, and n represents a positive integer of from 1 to 2, R_3 is only methyl when n is 1 and R_4 is only methyl when R_3 is hydrogen.

The following are illustrative examples of such alkyl ethers of polyhydroxyaralkylamines:



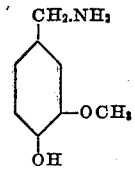
β-(3.4-dimethoxyphenyl)ethylamine

Ber. 42, 1986.



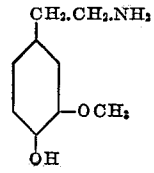
3,4-dimethoxybenzylamine

Ber. 41, 18.



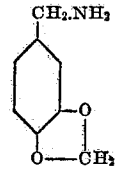
4-hydroxy-3-methoxybenzylamine

J. A. C. S. 41, 1118.



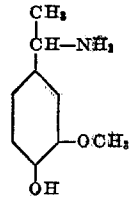
β-(4-hydroxy-3-methoxyphenyl)ethylamine

Beilstein, 1st Supplement XIII, 324.



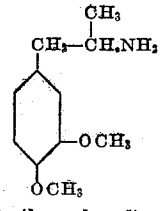
3,4-methylenedioxybenzylamine

Ber. 45, 318.



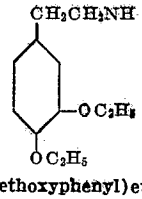
α-(4-hydroxy-3-methoxyphenyl)ethylamine

J. C. S. 99, 417.



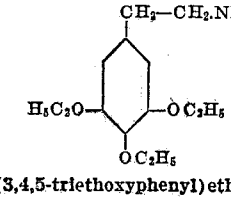
β-(3,4-dimethoxyphenyl)propylamine

Ber. 43, 193.



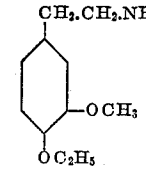
β-(3,4-diethoxyphenyl)ethylamine

Arch. Pharm. 272, 60 (C. A. 28, 3412).



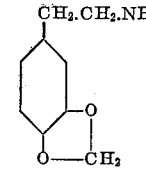
β-(3,4,5-triethoxyphenyl)ethylamine

J. Prakt. Chem. 137, 339.



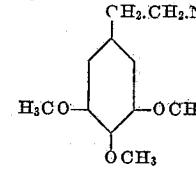
β-(3-methoxy-4-ethoxyphenyl)ethylamine

C. A. 23, 2951.



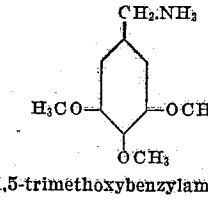
β-(3,4-methylenedioxyphenyl)ethylamine

Beilstein, 1st Supple. XIX, 766. Ber. 43, 3414.



β-(3.4,5-trimethoxyphenyl)ethylamine

Monatshefte 40, 145.



3,4,5-trimethoxybenzylamine

Zer. 38, 3639.

These alkyl ethers of polyhydroxyaralkylamines are soluble in water and in alkaline developers and may be used in specified amounts. Their solubility in water and in alkaline developers can be made appreciable by converting the base into a salt, such as, for example, the sulfate, hydrochloride, carbonate, or carbamate. The sulfate and hydrochloride salts are readily prepared by the addition of a stoichiometrical quantity of dilute sulfuric acid and hydrochloric acid, respectively, and the carbonate or carbamate is prepared by bubbling CO_2 into an alcohol, ether or benzene solution of the base.

The most useful concentrations in black and white developers range from about 1 gram to about 10 grams per liter of developer. In color developers the most useful concentrations range from about 2 grams to 8 grams per liter.

In developing color images in multicolor photographic layers containing color formers fast to diffusion with a color developer containing an alkyl ether of a polyhydroxyaralkylamine, the developing time is cut from 20–30 minutes to 2–12 minutes. All of the layers are simultaneously developed, and the dye images formed are of excellent quality.

The developing time with black and white developers, for instance, solutions of hydroquinone and monomethylaminephenol sulfate and the like, is also cut to one-half without causing fog when such solutions contain an alkyl ether of a polyhydroxyaralkylamine.

As illustrative of developing solutions containing such alkyl ethers of polyhydroxyaralkylamines, the following are given:

Example I

Sodium hexametaphosphate	grams	1.0
p-Methylaminophenol sulfate	do	3.0
Sodium sulfite (anhydrous)	do	50.0
Hydroquinone	do	6.0
Sodium carbonate (monohydrate)	do	40.0
Potassium bromide	do	2.0
Sodium thiocyanate	do	2.0
Potassium iodide	do	0.0035
4-hydroxy-3-methoxybenzylamine	do	4.0
Water to make	liters	1

The foregoing developer on five minutes' development at 20° C. of the usual black and white roll film gives a negative of good density and gradation after fixing and washing. The time required to develop an identical film in a similar solution but containing no 4-hydroxy-3-methoxybenzylamine ranges from 15 to 20 minutes.

The foregoing developing solutions containing the 4-hydroxy-3-methoxybenzylamine develops up to 1½–2 stops more speed in about 14 minutes as compared to the same developing solution containing no 4-hydroxy-3-methoxybenzylamine.

Example II

The following developer requires 30 minutes at 20° C. to give a satisfactory degree of color development for color paper:

Sodium hexametaphosphate	grams	1.0
Sodium sulfite (anhydrous)	do	2.5
p-Amino-di(β-hydroxyethyl)aniline sulfate	do	8.0
Sodium carbonate (monohydrate)	do	100.0
Hydroxylamine hydrochloride	do	1.0
Potassium bromide	do	1.0
Water to make	liters	1

By the addition of 4 grams of β-(3,4-dimethoxyphenyl) ethylamine to the foregoing solution, a color paper of excellent color rendition is developed in about 12 minutes with a higher shoulder density and improved contrast. Without the presence of said amine at least 30 minutes is required to give an acceptable print. Increasing the concentration of the amine further reduces the time of development.

The color photographic multilayer element utilized in the foregoing example consists of an integral tri-pack emulsion coated on either the usual paper base, or a clear cellulose acetate or nitrate film base, or in some cases an opaque white film base. Each of the emulsion layers is sensitized to one of the primary colors of light, namely, blue, green, and red. The top layer is blue sensitive. A filter layer, yellow in color and blue absorbing, lies under the top layer. Below this filter layer lies a green sensitive emulsion layer, and below this a red sensitive emulsion layer. Each of the three silver halide emulsion layers contains dye forming compounds which unite during the development of a silver image in an aromatic amine developing agent to form a dye with the oxidation product of the developing agent. As silver is also formed during development, it must be removed after color development by treatment in a bleach, followed by a bath of sodium thiosulfate, as is well known in the art. A yellow dye is formed in the blue sensitive emulsion; a magenta dye is formed in the green sensitive emulsion; and a cyan dye is formed in the red sensitive emulsion. The combination of the dye images from these three printing primaries yields the color picture. Suitable methods for the preparation of multicolor emulsion layers have been described in the literature relating to color photography, and are, therefore, not described here.

Example III

Example II was repeated with the exception that 8 grams of the p-amino-di(β-hydroxyethyl)-aniline sulfate were replaced by 6.9 grams of p-aminoethyl(β-hydroxyethyl) aniline sulfate. The development of the same color paper was reduced from 25–30 minutes at 70° F. to 8 minutes at the same temperature.

Example IV

Sodium hexametaphosphate	grams	1.0
Sodium sulfite	do	4.0
4-amino-ethyl(β-hydroxyethyl)aniline sulfate	do	5.0
Sodium carbonate (monohydrate)	do	50.0
Potassium bromide	do	1.0
Water to make	liters	1

The addition of 4 grams of 3,4-methylenedioxybenzylamine to the foregoing developing solution reduces the developing time of a multicolor film of the reversal type containing color formers fast to diffusion by 50% and in addition gave an increased shoulder density and improved contrast.

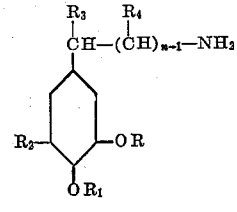
Example V

Example I was repeated with the exception that 4 grams of 4-hydroxy-3-methoxybenzylamine were replaced by 5 grams of 3,4,5-trimethoxy-β-phenylethylamine. The results were identical with those obtained in Example I.

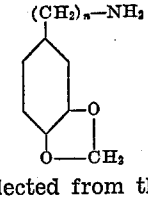
The above examples are to be regarded as merely illustrative of the invention and not in any sense restrictive. It will be obvious to those skilled in the art that many modifications, such as substituting equivalent materials and varying the proportions of the materials used, are within the spirit and scope of the invention. The scope, therefore, of the invention is to be limited solely by the following claims.

I claim:

1. An alkaline photographic developer for silver halide emulsions comprising an aromatic silver halide developing agent and an alkyl ether of a polyhydroxyaralkylamine selected from the class consisting of those of the following formulae:



and



wherein R is selected from the class consisting of methyl and ethyl, R_1 is selected from the class consisting of hydrogen, methyl and ethyl, R_2 is selected from the class consisting of hydrogen, methoxy and ethoxy, R_3 and R_4 are selected from the class consisting of hydrogen and methyl, and

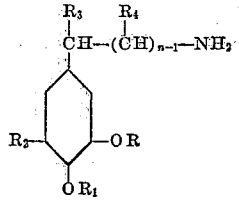
n is a positive integer of from 1 to 2, R_3 is only methyl when n is 1, and R_4 is only methyl when R_3 is hydrogen, and the salts of said amines.

2. An alkaline photographic developer for silver halide emulsions comprising an aromatic silver halide developing agent and 4-hydroxy-3-methoxybenzylamine.

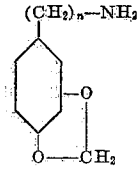
3. An alkaline photographic developer for silver halide emulsions comprising an aromatic silver halide developing agent and β-(3,4-dimethoxyphenyl) ethylamine.

4. An alkaline photographic developer for silver halide emulsions comprising an aromatic silver halide developing agent and 3,4-methylenedioxybenzylamine.

5. In the processing of photographic material, the improvement which comprises developing an exposed silver halide emulsion in an alkaline developer containing an aromatic silver halide developing agent and a developing accelerator consisting of an alkyl ether of a polyhydroxyaralkylamine selected from the class consisting of those of the following formulae:



and



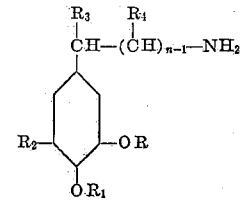
wherein R is selected from the class consisting of methyl and ethyl, R_1 is selected from the class consisting of hydrogen, methyl and ethyl, R_2 is selected from the class consisting of hydrogen, methoxy and ethoxy, R_3 and R_4 are selected from the class consisting of hydrogen and methyl, and n is a positive integer of from 1 to 2, R_3 is only methyl when n is 1, and R_4 is only methyl when R_3 is hydrogen, and the salts of said amines.

6. In the processing of photographic material, the improvement which comprises developing an exposed silver halide emulsion in an alkaline developer containing an aromatic silver halide developing agent and a developing accelerator consisting of 4-hydroxy-3-methoxybenzylamine.

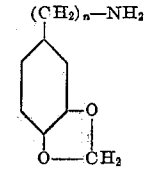
7. In the processing of photographic material, the improvement which comprises developing an exposed silver halide emulsion in an alkaline developer containing an aromatic silver halide developing agent and a developing accelerator consisting of β - (3,4 - dimethoxyphenyl) ethylamine.

8. In the processing of photographic material, the improvement which comprises developing an exposed silver halide emulsion in an alkaline developer containing an aromatic silver halide developing agent and a developing accelerator consisting of 3,4-methylenedioxybenzylamine.

9. A color forming photographic developer comprising a primary aromatic amino developing agent and an alkyl ether of a polyhydroxyaralkylamine selected from the class consisting of those of the following formulae:



and



wherein R is selected from the class consisting of methyl and ethyl, R_1 is selected from the class consisting of hydrogen, methyl, and ethyl, R_2 is selected from the class consisting of hydrogen, methoxy and ethoxy, R_3 and R_4 are selected from the class consisting of hydrogen and methyl, and n is a positive integer of from 1 to 2, R_3 is only methyl when n is 1, and R_4 is only methyl when R_3 is hydrogen, and the salts of said amines.

10. A color forming photographic developer comprising a primary aromatic amino developing agent and 4-hydroxy-3-methoxy benzylamine.

11. A color forming photographic developer comprising a primary aromatic amino developing agent and β-(3,4-dimethoxyphenyl) ethylamine.

12. A color forming photographic developer comprising a primary aromatic amino developing agent and 3,4-methylenedioxy-benzylamine.

IVY V. RUNYAN.

No references cited.