United States Patent Office

3,682,634
Patented Aug. 8, 1972

3,682,634

METHOD FOR DEVELOPING PHOTOGRAPHIC MATERIALS

Jozef Frans Willems, Wilrijk, Belgium, assignor to Gevaert-Agfa N.V., Mortsel, Belgium

No Drawing. Filed Sept. 22, 1970, Ser. No. 74,492
Claims priority, application Great Britain, Oct. 27, 1969, 52,568/69
Int. Cl. G03c 5/54, 5/30, 1/06
U.S. Cl. 96—29 R 5 Claims

ABSTRACT OF THE DISCLOSURE

Photographic developing methods are described wherein an exposed silver halide emulsion layer of a photographic material is developed with an aqueous alkaline composition in the presence of a N,N-dialkylhydroxylamine developing agent and a quaternary ammonium compound having the formula

$$\overset{+}{Q}-(CH_2)_x-(OCH_2CH_2)_{n-1}-R]X^-$$

wherein

$\overset{+}{Q}$ stands for a quaternary ammonium group either cyclic or acyclic,

R stands for an alkyl group comprising from 7 to 20 C-atoms or for the group

$$\overset{+}{Q}]X^-$$

X^- is an anion,

n stands for an integer from 1 to 250, n being at least 2 when R stands for alkyl, and

x stands for 2 when n is different from 1 and for an integer from 2 to 16 when $n=1$.

The development is accelerated without adverse effects.

This invention relates to the development of photographic materials containing exposed silver halide, to new developing combinations and to photographic materials and solutions containing such combinations.

It is known that onium compounds such as quaternary ammonium, quaternary phosphonium and ternary sulphonium compounds are able to accelerate photographic development by agents which act as doubly or more highly charged negative ions for instance hydroquinone, hydroquinone derivatives, ascorbic acid, etc. whether as an additive to the developer or to the emulsion. It is further known (see for example T. H. James, Photographic Science and Technique, vol. 19B (1953) p. 36) that development by the singly ionized developer anions of hydroxylamine is markedly retarded by quaternary ammonium salts.

It has now been found that the development by N,N-dialkylhydroxylamine and derivatives thereof, contrary to what could be expected, can be effectively accelerated if the development is carried out in the presence of quaternary ammonium compounds corresponding to the following general formula:

$$\overset{+}{Q}-(CH_2)_x(OCH_2CH_2)_{n-1}-R]X^-$$

wherein

$\overset{+}{Q}$ stands for a quaternary ammonium group either cyclic or acyclic such as the group



wherein R_1, R_2 and R_3 are aliphatic radicals such as methyl, ethyl, hydroxyethyl, propyl, benzyl, or the group



wherein Z stands for the non-metallic atoms necessary to complete a heterocyclic nucleus such as pyridyl, α-picolyl, morpholinyl, piperidyl and quinolyl,

X^- is an anion or acid radical for example halide, p-toluene sulphonate, alkyl sulphate, or perchlorate,

R stands for alkyl comprising from 7 to 20 carbon atoms or for the group

$$-\overset{+}{Q}]X^-$$

n stands for an integer from 1 to 250, n being at least 2 when R stands for alkyl, and

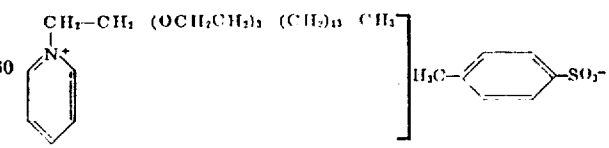
x stands for 2 when n is different from 1 or for an integer from 2 to 16 when $n=1$.

This is rather surprising since, as will be illustrated by the examples hereinafter, it was found on the one hand that alkylmonopyridinium salts comprising no polyoxyalkylene groups retard development by N,N-dialkylhydroxylamines and polyoxyalkylene compounds comprising no quaternary ammonium groups as well as polyoxyalkylene compounds comprising pyridinium groups but no long chain aliphatic groups have so to say no effect at all on development by N,N-dialkylhydroxylamines and on the other hand that the compounds of use according to the present invention inhibit development by hydroxylamine itself and by monoalkylhydroxylamines.

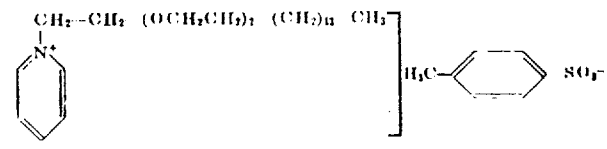
The compounds corresponding to the above general formula wherein $\overset{+}{Q}$ stands for pyridinium are especially advantageously employed.

The following are representative examples of quaternary ammonium compounds suitable for accelerating development by N,N-dialkyl hydroxylamine developing agents.

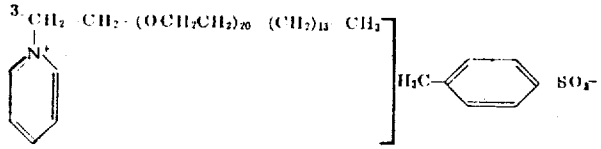
1.



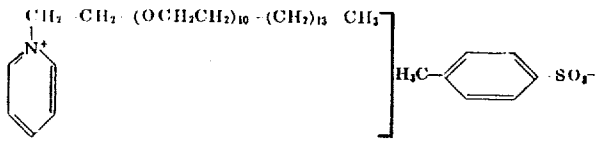
2.



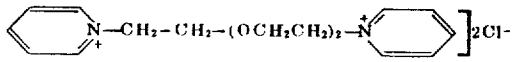
3.



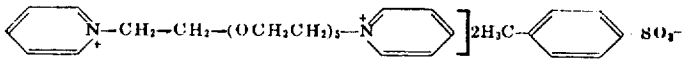
4.



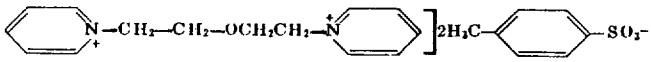
5.



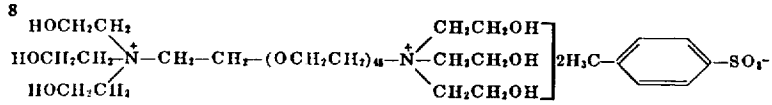
6.



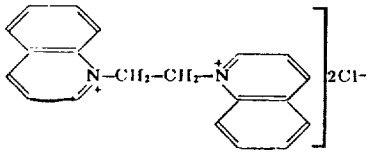
7.



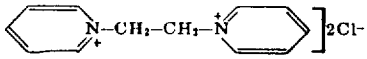
8



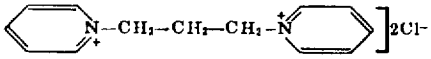
9.



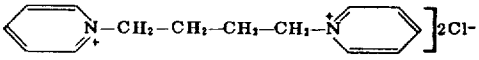
10.



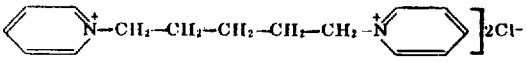
11.



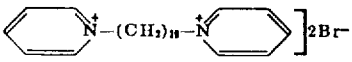
12.



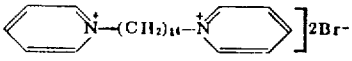
13.



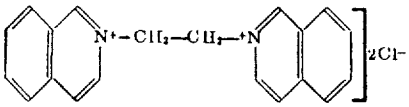
14.



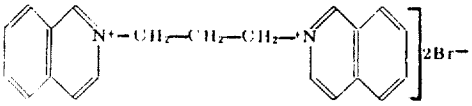
15.



16.



17.



The compounds of use according to the present invention can be prepared by methods known to those skilled in the art and as described in literature. For instance, the compounds wherein

$$R=\overset{+}{Q}$$

and n is different from 1 can be prepared according to the method described in U.S. Pat. 2,944,902 of Burt H. Carroll, John Sagal Jr. and Dorothy J. Beavers issued July 12, 1960, by reaction of polyalkylene oxides of varying molecular weight with alkylsulphonyl halides such as methane sulphonyl chloride, ethane sulphonyl chloride, p-toluenesulphonyl chloride followed by quaternization with

tertiary bases as pyridines, picolines and trialkylamines such as trimethylamine, dimethylbenzylamine, dimethyllaurylamine, etc.

The compounds wherein R=alkyl comprising from 7 to 20 C-atoms, $x=2$ and n is at least 2, can also be prepared according to the method described in U.S. Pat 2,944,902 as mentioned above by reaction of the appropriate polyalkylene oxide monoethers with formula

$$HO—CH_2CH_2—(OCH_2CH_2)_{n-2}—OCH_2CH_2$$

(R being alkyl having from 7 to 20 C-atoms) with the above-mentioned sulphonyl halides followed by quaternization as described just above.

The bisquaternary ammonium compounds wherein

$$R=\overset{+}{Q} \text{ and } n=1$$

can be prepared according to the methods described in U.S. Patent 2,288,226 of Burt H. Carroll and Charles F. H. Allen issued June 30, 1942.

The use of N,N-dialkyl hydroxylamines, such as N,N-diethyl hydroxylamine, of which the oxidation products have the favourable property of leaving no residual stain in the silver image obtained, has been disclosed amongst others in U.S. Patent 2,857,276 of Edwin H. Land and Helen J. Tracy issued Oct. 21, 1958. Other N,N-dialkyl hydroxylamines that have been proposed for use as silver halide developing agents and of which the development activity is higher than of N,N-diethyl hydroxylamine include for example aminoalkyl hydroxylamines, more especially N,N-dialkylhydroxylamines having in at least one of the N-alkyl group an intralinear amino nitrogen atom, either cyclic or acyclic, examples of which can be found in U.S. Patent 3,287,125 of Milton Green, Adnan A. Sayigh and Henri Ulrich issued Nov. 22, 1966, alkoxyalkyl hydroxylamines, 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 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 intralinear sulphonyl (—SO_2—) group, examples of which can be found in U.S. Patent 3,287,124 of Milton Green, Adnan A. Sayigh and Henri Ulrich issued Nov. 22, 1966.

Thus, in accordance with the present invention there is provided a process for making photographic records which comprises treating a photographic material having layers containing developable silver salts with an aqueous alkaline solution in the presence of an N,N-dialkyl hydroxylamine developing agent and a quaternary ammonium compound as described above. The invention also includes developer compositions comprising in addition to an N,N-dialkylhydroxylamine developing agent, a quaternary ammonium compound as described. By N,N-dialkylhydroxylamine developing agent it is intended to embrace unsubstituted N,N-dialkyl hydroxylamines as well as derivatives thereof as described above.

The quaternary salts of use according to the present invention may be added to the developer or to the emulsion or to both simultaneously, the developing bath being preferred however.

The developing composition may comprise in addition to the N,N-dialkylhydroxylamine developing agents any of the common ingredients employed in developing compositions e.g. alkalies such as sodium hydroxide, potassium hydroxide, sodium carbonate, sodium hydroxide, potassium hydroxide, sodium carbonate, trisodium phosphate, etc., silver halide solvents such as sodium thiosulphate, sodium thiocyanate or cyclic imides such as barbiturates and uracils, 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-nitro-benzotriazole and 6-nitrobenzimidazole and wetting agents as well as other compounds known in the photographic development technique.

The amount of quaternary ammonium compound used according to the present invention 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 amount of onium compound incorporated into the developing bath can vary between very wide limits and depends on the particular N,N-dialkylhydroxylamine used. The optimum concentration for any onium compound of use according to the invention can best be determined by employing a series of concentrations in several batches of the same developer and determining the speed obtained before and after incorporation of the said compound in the usual manner which is of course well known to those skilled in the art. Generally the quaternary ammonium compound is used in amounts ranging between 0.01 and 20 millimoles per litre.

The development acceleration obtained with the products according to the present invention can be combined with a chemical sensitization by means of chemical sensitizing agents such as sulphur-containing compounds e.g. allyl isothiocyanate, allyl thiourea, or sodium thiosulphate, reducing agents such as the tin compounds described in the Belgian Patents 493,464 filed Jan. 24, 1950 and 568,687 filed June 18, 1958 both by Gevaert Photo-Producten N.V., the iminoaminomethane sulphinic acid compounds described in the British Patent 789,823 filed Apr. 29, 1955 by Gevaert Photo-Producten N.V. or precious metal compounds such as gold, platinum, palladium, iridium, ruthenium and rhodium compounds.

The products influencing development by N,N-dialkyl hydroxylamines according to the invention can also be used in combination with stabilizing agents for silver halide emulsions, such as mercury compounds and the compounds described in Belgian Patents 571,916 and 571,917 both filed Oct. 10, 1958 by Gevaert Photo-Producten N.V. and in combination with sensitizing and stabilizing cadmium salts in the light-sensitive material as well as in the developer.

The novel developing combination of the invention may be used 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 carboxymethyl 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 emul-

sion into colourless light-insensitive compounds that need not be removed by washing.

As noted above the development accelerators of use according to 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 they 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.

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 a separate developing bath. One of them is developed in a bath A containing as developing agent N,N-diethylhydroxylamine oxalate and having the following composition:

sodium sulphite—100 g.
sodium hydroxide—10 g.
5-nitrobenzotriazole—80 mg.
potassium bromide—1 g.
N,N-diethylhydroxylamine oxalate—8 g.
water to make—1 litre

The other strips are developed in baths having the same composition as bath A but containing moreover one of the compounds listed in the table below in the amounts given.

The densities obtained are listed in the following table.

groups but no long-chain aliphatic groups have either no effect on or inhibit this development.

EXAMPLE 2

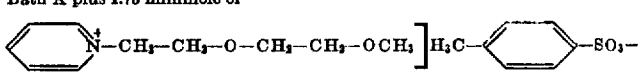
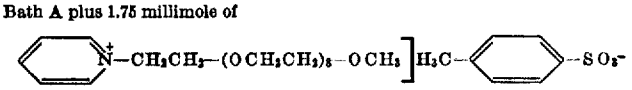
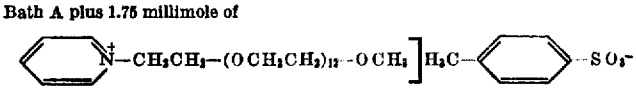
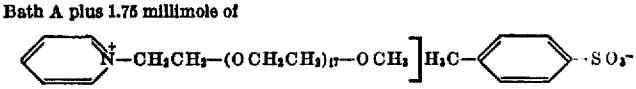
A photosensitive element was prepared comprising on a paper support a silver bromoiodide emulsion layer containing per kg. an amount of silver halide corresponding to 60 g. of silver nitrate.

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. Pat. 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—100 ml.
sodium carboxymethyl cellulose—5 g.
sodium hydroxide—15 g.
uracil—11.25 g.
30% ammonium hydroxide—3.5 ml.
N,N-diethylhydroxylamine oxalate—8 g.
1-phenyl-2-tetrazoline-5-thione—0.2 g.
compound 3—2.35 g. (1.75 millimole)

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 using a same developing composition but comprising no compound 3 the density of the positive print obtained was markedly lower. Moreover, in the presence of compound 3 better quality transfer images are obtained at lower illumination levels than is the case when using N,N-diethylhydroxylamine alone.

Developing bath	Densities obtained after a development time of—				
	0 sec.	10 sec.	1 min.	3 min.	5 min.
Bath A	0.04	0.04	0.04	0.09	0.3[illegible]6
Bath A plus 1.75 millimole of dodecylpyridinium chloride	0.04	0.04	0.04	0.07	0.1
Bath A plus 0.31 millimole of dodecylpyridinium chloride	0.04	0.04	0.04	0.04	0.0
Bath A plus 0.05 millimole of dodecylpyridinium chloride	0.04	0.04	0.04	0.05	0.08
Bath A plus 0.5 g. of polyethylene glycol having an average molecular weight of 1,000	0.04	0.04	0.04	0.08	0.30
Bath A plus 0.5 g. of polyethylene glycol having an average molecular weight of 6,000	0.04	0.04	0.04	0.08	0.16
Bath A plus 0.5 g. of $CH_3-(CH_2)_{15}-O-(CH_2CH_2O)_{20}-H$	0.04	0.04	0.04	0.08	0.27
Bath A plus 1.75 millimole of 	0.04	0.04	0.04	0.08	0.32
Bath A plus 1.75 millimole of 	0.04	0.04	0.04	0.07	0.21
Bath A plus 1.75 millimole of 	0.04	0.04	0.04	0.06	0.18
Bath A plus 1.75 millimole of 	0.04	0.04	0.04	0.06	0.15
Bath A plus 1.75 millimole of compound 2	0.04	0.04	0.04	0.18	1.32
Bath A plus 1.75 millimole of compound 4	0.04	0.04	0.04	0.11	0.85
Bath A plus 1.75 millimole of compound 3	0.04	0.04	0.05	0.28	1.50
Bath A plus 1.75 millimole of compound 6	0.04	0.04	0.04	0.12	0.97
Bath A plus 1.75 millimole of compound 12	0.04	0.04	0.05	0.43	1.77
Bath A plus 0.31 millimole of compound 12	0.04	0.04	0.04	0.22	1.44

From the foregoing results it clearly appears that the compounds of use according to the present invention have a favourable accelerating effect on development by N,N-diethylhydroxylamine whereas alkylmonopyridinium salts without polyoxyalkylene units retard this development, and the polyoxyalkylene compounds comprising no quaternary ammonium groups or comprising pyridinium

The same favourable results are attained when replacing compound 3 by 0.5 g. (1.75 millimole) of compound 12.

We claim:

1. Photographic developing method which comprises developing an exposed silver halide emulsion layer of a photographic material with an aqueous alkaline compo-

sition in the presence of a N,N-dialkylhydroxylamine developing agent and a quaternary ammonium compound corresponding to the general formula:

$$\overset{+}{Q}-(CH_2)_x-(OCH_2CH_2)_{n-1}-R\Big]X^-$$

wherein

$\overset{+}{Q}$ stands for a quaternary ammonium group either cyclic or acyclic

R stands for an alkyl group comprising from 7 to 20 C-atoms or for the group

$$\overset{+}{Q}\Big]X^-$$

X^- is an anion

n stands for an integer from 1 to 250, *n* being at least 2 when R stands for alkyl, and

x stands for 2 when *n* is different from 1 and for an integer from 2 to 16 when $n=1$.

2. Photographic developing method according to claim **1**, wherein the said quaternary ammonium compound is present in the said aqueous composition in an amount comprised between 0.01 and 20 millimoles per litre.

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

4. Photographic developing composition for developing an exposed silver halide emulsion layer of a photographic material comprising in aqueous alkaline solution in addition to an N,N-dialkylhydroxylamine developing agent, a quaternary ammonium compound corresponding to the general formula:

$$\overset{+}{Q}-(CH_2)_x-(OCH_2CH_3)_{n-1}-R\Big]X^-$$

wherein:

$\overset{+}{Q}$ stands for a quaternary ammonium group either cyclic or acyclic

R stands for an alkyl group comprising from 7 to 20 C-atoms or for the group

$$\overset{+}{Q}\Big]X^-$$

X^- is an anion

n stands for an integer from 1 to 250, *n* being at least 2 when R stands for alkyl, and

x stands for 2 when *n* is different from 1 and for an integer from 2 to 16 when $n=1$.

5. Phtotographic developing composition according to claim **4** containing per litre from 0.01 millimole to 20 mmoles of the said quaternary ammonium compound.

References Cited

UNITED STATES PATENTS

2,288,226	6/1942	Carroll et al.	96—107
2,944,900	7/1960	Carroll et al.	96—107
2,944,902	7/1960	Carroll et al.	96—107

OTHER REFERENCES

Photographic Science and Technique, vol. 193, pp. 36–39, February 1953.

NORMAN G. TORCHIN, Primary Examiner

M. F. KELLEY, Assistant Examiner

U.S. Cl. X.R.

96—66 R, 66.3, 95