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3,740,221

DEVELOPMENT OF PHOTOGRAPHIC MATERIAL
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52,567/69

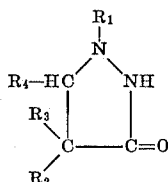
Int. Cl. G03c 5/54, 5/30

U.S. Cl. 96—29 R

6 Claims

ABSTRACT OF THE DISCLOSURE

A method of developing light-sensitive silver halide elements is described whereby the elements are treated after exposure with an aqueous alkaline composition in the presence of a hydroxylamine developing agent and a 1-aryl-3-pyrazolidinone compound of the formula:



wherein R₁ is aryl, R₂ and R₃ are hydrogen, alkyl, aralkyl or aryl, and R₄ is hydrogen, alkyl, alkoxy, aralkoxy or aryloxy. The 1-aryl-3-pyrazolidinone compound exhibits a superadditive effect on the hydroxylamine developing agent.

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 certain chemical compounds, which used alone are poor developers for photographic silver halide emulsions, become much more effective when used in conjunction with other developers, the effect being known as superadditivity. Thus, for example it is known that 1-aryl-3-pyrazolidinone compounds show the phenomenon of superadditivity when used in conjunction with developing agents the ionized forms of which in alkaline medium carry two or more negative charges such as hydroquinone, hydroquinone sulphonate, ascorbic acid, etc.

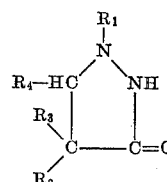
It has now been found that these 1-aryl-3-pyrazolidinone compounds also exhibit a superadditive character when used in conjunction with the at most singly ionized developer anions of hydroxylamine and derivatives thereof.

The use of hydroxylamine and derivatives thereof, 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 United States patent specification 2,857,276 of Edwin H. Land and Helen J. Tracy, issued Oct. 21, 1958. Hydroxylamine itself and the monoalkyl derivatives are less suitable because they can give rise to fog, but the N,N-dialkylhydroxylamines such as N,N-diethylhydroxylamine and the heterocyclic N-hydroxylamines such as N-hydroxymorpholine, N-hydroxypiperidine and N-hydroxypyrrolidine disclosed in the above United States patent specification are particularly suitable. Other hydroxylamine derivatives that have been proposed for use as silver halide develop-

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ing agents and of which the development activity is higher than that of the N,N-dialkyl hydroxylamines 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 United States 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 United States 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 intralinear sulphonyl (—SO₂—) group, examples of which can be found in United States patent specification 3,287,124 of Milton Green, Adnan A. Sayigh and Henri Ulrich, issued Nov. 22, 1966. Further N,N-dialkylhydroxylamines having in at least one of the N-alkyl groups a quaternary ammonium group either cyclic or acyclic which excel by their high development activity have been proposed for use as silver halide developing agents in the co-pending application filed on even date herewith for "Novel Photographic Developers" assigned U.S. Ser. No. 78,916.

The 1-aryl-3-pyrazolidinone compounds having a superadditive development effect with hydroxylamine developing agents can be represented by the following general formula:



wherein:

R₁ stands for aryl such as phenyl, α-naphthyl and β-naphthyl including substituted aryl e.g. substituted by alkyl such as methyl, aralkyl such as benzyl, alkoxy such as methoxy, amino, dialkylamino, halogen such as bromine and chlorine, acetamido, hydroxyalkyl, and hydroxy,

each of R₂ and R₃ (the same or different) stands for hydrogen, alkyl preferably comprising at most 4 C-atoms, aralkyl such as benzyl or aryl such as phenyl, and

R₄ stands for hydrogen, alkyl preferably comprising at most 4 C-atoms, alkoxy preferably comprising at most 4 C-atoms, aralkoxy or aryloxy.

The following are representative examples of 1-aryl-3-pyrazolidinone compounds suitable for use as superadditive developing agents in conjunction with hydroxylamine developers:

- (1) 1-phenyl-3-pyrazolidinone
- (2) 1-phenyl-4-methyl-3-pyrazolidinone
- (3) 1-phenyl-5-methyl-3-pyrazolidinone
- (4) 1-phenyl-4-dihydroxymethyl-3-pyrazolidinone
- (5) 1-phenyl-4,4-dimethyl-5-methoxy-3-pyrazolidinone
- (6) 1-phenyl-4,4-dimethyl-5-ethoxy-3-pyrazolidinone
- (7) 1-phenyl-4,4-dimethyl-5-n-propoxy-3-pyrazolidinone
- (8) 1-phenyl-4,4-dimethyl-5-isopropoxy-3-pyrazolidinone
- (9) 1-phenyl-4,4-dimethyl-5-benzyloxy-3-pyrazolidinone
- (10) 1-phenyl-4,4-dimethyl-5-phenoxy-3-pyrazolidinone

- (11) 1-(p-tolyl)-4,4-dimethyl-5-methoxy-3-pyrazolidinone
- (12) 1-(p-tolyl)-4,4-dimethyl-5-ethoxy-3-pyrazolidinone
- (13) 1-(p-tolyl)-4,4-dimethyl-5-n-propoxy-3-pyrazolidinone
- (14) 1-(p-tolyl)-4,4-dimethyl-5-isopropoxy-3-pyrazolidinone
- (15) 1-(p-tolyl)-4,4-dimethyl-5-n-butoxy-3-pyrazolidinone
- (16) 1-(p-tolyl)-4,4-dimethyl-5-benzyloxy-3-pyrazolidinone
- (17) 1-phenyl-4,4-dimethyl-3-pyrazolidinone
- (18) 1-p-chlorophenyl-4-methyl-4-ethyl-3-pyrazolidinone
- (19) 1-p-acetamidophenyl-4,4-diethyl-3-pyrazolidinone
- (20) 1-p- β -hydroxyethylphenyl-4,4-dimethyl-3-pyrazolidinone
- (21) 1-p-hydroxyphenyl-4,4-dimethyl-3-pyrazolidinone
- (22) 1-p-methoxyphenyl-4,4-diethyl-3-pyrazolidinone
- (23) 1-p-tolyl-4,4-dimethyl-3-pyrazolidinone

The 1-aryl-3-pyrazolidinone compounds of use according to the present invention can be prepared as known in the art, e.g. as described in United States patent specifications 3,330,839 of Jozef Frans Willems, Albert Lucien Poot and Raymond Albert Roosen, issued July 11, 1967 and 2,772,282 of Charles F. H. Allen and John R. Byers, issued Nov. 27, 1956.

In accordance with the present invention there is provided a process of making photographic records which comprises treating a photographic material having layers containing developable silver salts with an aqueous alkaline solution in the presence of a hydroxylamine developing agent and an 1-aryl-3-pyrazolidinone compound as described above. The invention also includes developer compositions comprising in addition to a hydroxylamine developing agent, an 1-aryl-3-pyrazolidinone compound as described. By hydroxylamine developing agent it is intended to embrace hydroxylamine itself as well as derivatives thereof as described above.

The 1-aryl-3-pyrazolidinones of use according to the present invention may be added to the developing bath or to the emulsion or to both simultaneously.

Developer compositions that comprise the superadditive developing agents according to the present invention may comprise in addition thereto 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 thiosulphate, 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.

The ratio of hydroxylamine developing agent to 1-aryl-3-pyrazolidinone compound used in the present invention can be chosen in such a way that the combination is suited for the development of all kinds of materials including materials having silver chloride emulsion layers of low sensitivity as well as materials having highly sensitive silver bromo-iodide emulsion layers. This ratio may vary within wide limits and also depends on the particular hydroxylamine developing agent used. In most cases the ratio is chosen in such a way that the amount of the hydroxylamine developing agent strongly outweighs the 1-aryl-3-pyrazolidinone compound.

A strong superadditive effect is obtained by using an amount of 0.05 millimole to 10 millimole, preferably from 0.3 millimole to 6 millimole, of 1-aryl-3-pyrazolidinone to an amount of 10 to 100 millimole of hydroxylamine developing agent, per litre of developing composition. Of course larger amounts of said 1-aryl-3-pyrazolidinone compounds can be used, although the superadditive

effect obtained with higher concentrations is not more considerable.

The novel combination of developing agents 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, 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 stabilisation 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 colourless light-insensitive compounds that need not be removed by washing.

The developing agents 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. When the developing agents are incorporated into the materials to be processed it is possible to limit the processing liquid to a simple aqueous alkaline solution. It is also possible, of course, to incorporate only the 1-aryl-3-pyrazolidinone developing agents into the materials to be processed and to employ the hydroxylamine developing agent in the processing liquid or vice versa.

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 only hydroxylamine hydrochloride and having the following composition:

Sodium sulphite	g--	100
Sodium hydroxide	g--	10
5-nitro-benzotriazole	mg--	80
Potassium bromide	g--	1
Hydroxylamine hydrochloride	mole--	0.06
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 amount given.

The densities obtained are listed in the following table.

Developing bath	Densities obtained after a developing time of—				
	0 sec.	20 sec.	1 min.	3 min.	5 min.
Bath A.....	0.04	0.05	0.34	0.95	1.43
Bath A plus 50 mg. (0.31 mmole) of Compound 1.....	0.04	0.07	0.84	1.73	2.57
Bath A plus 1 g. (4.27 mmole) of Compound 6.....	0.04	0.15	0.83	2.10	>3

EXAMPLE 2

This example is analogous to Example 1, with the only difference that now a developing bath B is used

according to the co-pending application filed on even date herewith for "Novel Photographic Developers."

The following results are attained.

Developing bath	Densities obtained after a developing time of—				
	0 sec.	20 sec.	1 min.	3 min.	5 min.
Bath D.....	0.04	0.04	0.20	1.29	2.08
Bath D plus 50 mg. (0.31 mmole) of Compound 1.....	0.04	0.13	0.93	2.32	>3
Bath D plus 1 g. (4.27 mmole) of Compound 6.....	0.04	0.58	1.27	2.56	>3

which only differs from a bath A in that the hydroxylamine hydrochloride has been replaced by 0.06 mole of N-methylhydroxylamine hydrochloride.

The following results are attained.

EXAMPLE 5

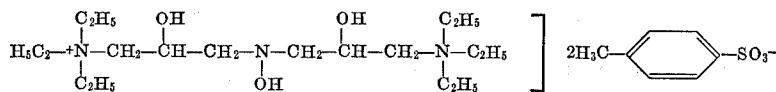
This example is analogous to Example 1, with the difference that now a developing bath E is used which

Developing bath	Densities obtained after a developing time of—				
	0 sec.	20 sec.	1 min.	3 min.	5 min.
Bath B.....	0.05	0.05	0.07	0.60	1.09
Bath B plus 50 mg. (0.31 mmole) of Compound 1.....	0.05	0.05	0.37	1.61	2.29
Bath B plus 1 g. (4.27 mmole) of Compound 6.....	0.04	0.29	1.17	2.19	>3

EXAMPLE 3

This example is analogous to Example 1, with the only difference that now a developing bath C is used which

only differs from bath A in that the hydroxylamine hydrochloride has been replaced by 0.06 mole of the hydroxylamine derivative with the formula:



only differs from bath A in that the hydroxylamine hydrochloride has been replaced by 0.06 mole of N,N-diethylhydroxylamine oxalate.

according to the co-pending application filed on even date herewith for "Novel Photographic Developers."

The following results are attained.

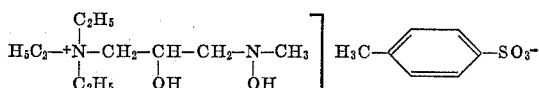
Developing bath	Densities obtained after a developing time of—				
	0 sec.	20 sec.	1 min.	3 min.	5 min.
Bath E.....	0.04	0.50	1.13	2.19	>3
Bath E plus 50 mg. (0.31 mmole) of Compound 1.....	0.04	0.83	1.40	2.55	>3
Bath E plus 1 g. (4.27 mmole) of Compound 6.....	0.04	0.89	1.65	>3	>3

The following results are attained.

Developing bath	Densities obtained after a developing time of—				
	0 sec.	20 sec.	1 min.	3 min.	5 min.
Bath C.....	0.04	0.04	0.04	0.07	0.37
Bath C plus 50 mg. (0.31 mmole) of Compound 1.....	0.04	0.04	0.13	1.22	2.05
Bath C plus 72 mg. (0.31 mmole) of Compound 6.....	0.04	0.04	0.04	1.27	2.30
Bath C plus 1 g. (4.27 mmole) of Compound 6.....	0.04	0.15	0.70	1.93	>3
Bath C plus 1.061 g. (4.27 mmole) of Compound 8.....	0.04	0.32	1.00	2.56	>3
Bath C plus 1.264 g. (4.27 mmole) of Compound 9.....	0.04	0.30	1.00	2.41	>3
Bath C plus 1.118 g. (4.27 mmole) of Compound 13.....	0.04	0.30	0.95	2.39	>3
Bath C plus 1.323 g. (4.27 mmole) of Compound 16.....	0.04	0.28	0.88	2.28	>3

EXAMPLE 4

This example is analogous to Example 1, with the only difference that now a developing bath D is used which only differs from bath A in that the hydroxylamine hydrochloride has been replaced by 0.06 mole of the hydroxylamine derivative with formula:



EXAMPLE 6

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 United

States 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:

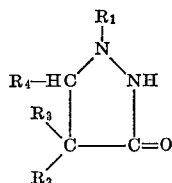
Water	ml.	100
Sodium carboxymethylcellulose	g.	5
Sodium hydroxide	g.	15
Sodium thiosulphate	g.	6
Ammonium hydroxide (30%)	ml.	3.5
N,N-diethylhydroxylamine oxalate	mole.	0.06
1-phenyl-2-tetrazoline-5-thione	g.	0.2
Compound 6	g.	1

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 6 the density of the positive print obtained was markedly lower. Moreover, in the presence of Compound 6 better quality transfer images are obtained at lower illumination levels than is the case when using N,N-diethylhydroxylamine alone.

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 a hydroxylamine developing agent and a 1-aryl-3-pyrazolidinone compound corresponding to the formula:



wherein:

R₁ stands for an aryl group,

each of R₂ and R₃ (the same or different) stands for hydrogen, alkyl, aralkyl or aryl, and

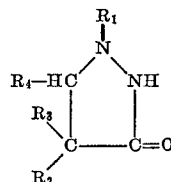
R₄ stands for hydrogen, alkyl, alkoxy, aralkoxy or aryloxy.

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

3. Photographic developing method according to claim 1, wherein said hydroxylamine developing agent and said

1-aryl-3-pyrazolidinone compound are both present in the said aqueous composition.

4. Photographic developing composition for developing an exposed silver halide emulsion layer of a photographic material comprising in aqueous alkaline solution in addition to a hydroxylamine developing agent, a 1-aryl-3-pyrazolidinone compound, corresponding to the formula:



wherein:

R₁ stands for an aryl group,

each of R₂ and R₃ (the same or different) stands for hydrogen, alkyl, aralkyl or aryl, and

R₄ stands for hydrogen, alkyl, alkoxy, aralkoxy or aryloxy.

5. The photographic developing method of claim 1 wherein R₁ is phenyl, each of R₂ and R₃ are hydrogen or alkyl of from 1 to 4 carbon atoms, and R₄ is hydrogen or alkyl of from 1 to 4 carbon atoms.

6. The photographic developing composition of claim 4 wherein R₁ is phenyl, each of R₂ and R₃ are hydrogen or alkyl of from 1 to 4 carbon atoms, and R₄ is hydrogen or alkyl of from 1 to 4 carbon atoms.

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U.S. Cl. X.R.

96—66 R, 66 HD, 66.3