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2-MERCAPTOOXAZOLINES AS DEVELOPER RETARDERS

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9 Claims. (Cl. 96—66)

This invention relates to the use of 2-mercaptooxazolines as developer retarders for improved sensitometric characteristics in photographic films and papers.

The use of developer retarders and inhibitors has been known for many years. Thus the employment of such compounds as 6-nitrobenzimidazole in an effort to slow down development, permit prolonged development without excessive fog, increase contrast, and minimize reciprocity law failure (R. L. F.) of sensitive photographic products is well known. Similarly, 5-mercapto-1-phenyltetrazole has been proposed as a developer retarder specifically for controlling development fog.

Unfortunately these and other compounds used as developer retarders do not operate to yield optimum results for the intended purpose. For example, the 6-nitrobenzimidazole must be used in relatively high concentrations and leaves much to be desired in minimizing R. L. F. On the other hand, the aforesaid tetrazole causes marked loss in speed and contrast.

It is the purpose and object of the present invention to provide improved development retarders which

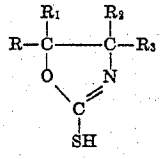
(1) Effectively control fog without loss of speed;

(2) Minimize low intensity R. L. F.;

(3) Achieve a high net maximum density on prolonged development without appreciably affecting the speed or contrast while reducing to a low level the tendency toward high fog resulting from prolonged development;

(4) Make it possible to obtain normal useful negative images from strongly overexposed photographic materials by processing said materials in a developer containing a relatively low concentration of the developer retarder.

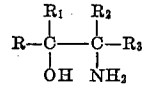
It has been discovered that these characteristics are portrayed by that group of compounds which may be characterized as 2-mercaptooxazolines depicted by the following formula:



wherein R, R_1, R_2, and R_3 are hydrogen, an aliphatic radical such as alkyl, i. e., methyl, ethyl, propyl, isopropyl, butyl, etc., carboxyalkyl, i. e., carboxymethyl, carboxyethyl, etc., hydroxyalkyl, i. e., hydroxymethyl, hydroxyethyl, etc., alkylsulfonic acid, i. e., ethylsulfonic acid, propylsulfonic acid, etc., a cycloaliphatic radical, i. e., bornyl, camphonyl, iononyl, etc., an aromatic radical, i. e., phenyl, chlorophenyl, nitrophenyl, tolyl, hydroxyphenyl, napthyl, hydroxynapthyl, etc., heterocyclic, i. e., pyridyl, quinolyl, benzothiazolyl, benzimidazolyl, thiazolyl, triazolyl, pyrimidyl, pyridyl, benzoxazolyl, oxazolyl, imidazolyl, thiodiazolyl, etc. In the above general formula R, R_1, R_2, and R_3 can be the same or different.

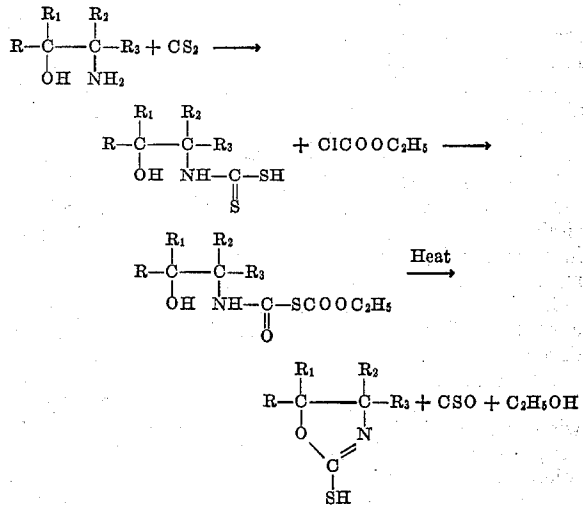
The method of preparation employed in the synthesis of the 2-mercaptooxazolines of this invention follows the

procedures of Sergeev and Ivanovna, J. Gen. Chem. U. S. S. R. 7, 1495 (1937). This procedure comprises treating an aminoalcohol of the following general formula:



wherein R, R_1, R_2, and R_3 have the values given above with carbon disulfide in alkaline solution to form a dithiocarbamic which is then esterified with ethyl chloroformate. The resulting unstable dithiocarbamic ester is heated to form the 2-mercaptooxazolines.

The following equations illustrate the above series of chemical reactions:



The 2-mercaptooxazolines contemplated for use herein are not only recommended by their possession of the aforesaid characteristics, but in addition by virtue of the fact that they are relatively inexpensive and can be used in minimum amounts as compared to other developer retarders.

The 2-mercaptooxazolines may be employed effectively either in the photographic developer or in a pre-bath used subsequent to exposure but prior to development. It is apparent that where the developer retarder is used in a pre-bath, its effect is manifested in the developing step. The quantity of the compound employed will be dictated by the specific end desired as subsequently indicated but in general will range from 0.79 mg. to 100 mgs. per liter of developer.

While we are unaware of the precise mechanism regarding the action of these substances, we have found that the results obtained are a function of the concentration of the compound used, the particular compound employed, and the developer to which it is added. In high concentrations within the above range, the 2-mercaptooxazoline suppresses both reciprocity law failure and fog on prolonged development. At lower concentrations, development is slowed down but eventual maximum speed is not particularly impaired. At still lower concentrations, the development process is only slightly retarded while the rate of fog increase with development is preferentially retarded. This results in a favorable differential inhibition of fog versus useful photographic density.

The following examples will serve to illustrate the invention but it is to be understood that the invention is not limited thereto.

EXAMPLE I

2-mercaptooxazoline was tested for its developer retarder and fog inhibitor properties by adding it in various concentrations to a high-alkali hydroquinone-metol developer and developing in this solution a sensitometrically-exposed high speed negative film which is characterized by its high contrast and high maximum density coupled with a marked tendency to fog on prolonged development. Development in each case was carried out in a tank at 68° F. under conditions of moderate agitation. The film was processed in the usual fashion through short stop and fixer, and then washed. The sensitometric characteristics were determined from density reading taken on an "Ansco-Macbeth" densitometer. The gradient values were taken at maximum gradient of the sensitometric curve. The speed values were taken at net densities above fog, and are expressed in arbitrary units. The net maximum density values are derived from total maximum density which has been corrected for both fog density and base density.

The characteristics of the film when developed as above for various lengths of time up to 16 minutes without any retarder, are given in Table I.

The characteristics of the film when developed in the above developer, to which have been added 2-mercaptooxazoline in concentrations between 0.79 mg. per liter and 100 mgs. per liter are given in Table II.

The characteristics of the film, when developed in the same developer, to which have been added 6-nitrobenzimidazole, a known developer inhibitor and antifoggant, in concentrations between 7.9 mgs. per liter and 1000 mgs. per liter are given in Table III.

It will be seen that the use of 2-mercaptooxazoline at a concentration of 100 mgs. per liter enables one to develop the film to a given speed and contrast within a short time, 4 minutes, and to maintain these characteristics virtually constant during an additional 12 minutes without appreciable increase in development fog. This property is a unique advantage since it permits a wider tolerance of processing time.

The above 2-mercaptooxazoline was prepared as follows:

A solution of 10 gms. of ethanolamine, 11 gms. of potassium hydroxide in 100 cc. of water was treated dropwise with a solution of 13 gms. of carbon disulfide in 80 cc. of dioxane during a period of 5 minutes. To the orange colored homogeneous mixture which resulted, 17.8 gms. of ethyl chlorocarbonate were slowly added. The reaction mixture was heated on a steambath for 30 minutes. It was then evaporated to dryness by vacuum distillation on a hot water bath. The residue was extracted several times with boiling benzene. Concentration of the benzene extract gave 3.5 gms. of slightly impure 2-mercaptooxazoline which was recrystallized to give colorless needles, M. P. 94.5–96.5° C. This substance is quite soluble in water and is not precipitated on the addition of acids or bases.

EXAMPLE II

High speed negative film was exposed in a time scale sensitometer and then developed in a hydroquinone-metol metaborate developer for times ranging from 3 to 30 minutes. Similar films were developed in the same type developer containing 2-mercaptooxazoline in concentrations of 20 mgs. per liter and 60 mgs. per liter. Sensitometric characteristics observed are given in Table IV.

The fog retarding and development inhibiting activity of 2-mercaptooxazoline are self evident.

EXAMPLE III

Table V shows the developer retarder and development fog inhibitor properties of 5-methyl-2-mercaptooxazoline. This table shows the sensitometric characteristics of the film used when developed as in Example I in the developer which contains 5-methyl-2-mercaptooxazoline in concentrations between 0.79 mg. per liter and 100 mgs. per liter.

The 5-methyl-2-mercaptooxazoline used in this example was prepared as follows:

A solution of 38 gms. of carbon disulfide and 11.2 gms. of sodium hydroxide in 200 cc. of water was cooled to 10° C. and 18.8 gms. of 1-amino-2-propanol was added with stirring. The mixture was heated on a steambath for two hours, cooled to room temperature and 27.1 gms. of ethyl chloroformate were added. The reaction mixture was then heated for thirty minutes on a steambath while the evolved carbon oxysulfide was vented. The cooled solution was neutralized, evaporated to one-third volume, and let stand in a refrigerator. The white crystalline precipitate so obtained, was recrystallized from water to give 12.3 gms. of 5-methyl-2-mercaptooxazoline, M. P. 72–73° C.

EXAMPLE IV

High speed negative film was developed in a developer as in Example II, which contained 5-methyl-2-mercaptooxazoline in concentrations from 3 mgs. per liter to 60 mgs. per liter. Sensitometric characteristics observed are given in Table VI.

The fog retarding and development inhibiting activity of 5-methyl-2-mercaptooxazoline are clearly evident.

EXAMPLE V

The sensitometric characteristics of another 2-mercaptooxazoline, namely 4-ethyl-2-mercaptooxazoline, are given in Table VII. It was tested with the photographic materials and developer of Example I in a range of concentrations between 0.79 mg. per liter and 100 mgs, per liter of the developer.

The 4-ethyl-2-mercaptooxazoline used in this experiment was prepared from 2-amino-1-butanol by the method described in Example III.

EXAMPLE VI

The compound 4-ethyl-2-mercaptooxazoline was tested as in Example II. Sensitometric characteristics observed, are given in Table VIII.

The fog retarding and development inhibiting activity of 4-ethyl-2-mercaptooxazoline are clearly evident from this table.

EXAMPLE VII

Reciprocity law failure activity of 2-mercaptooxazolines

The data for R. L. F. are given in Table IX. In this table concentration is expressed in mgs. of compound per liter of developer. Reciprocity law failure is the maximum variation in speed over a range of exposure times from 1 second to 40 hours. Speed and R. L. F. are measured at net density 0.4. The data in the table represent a simultaneous comparison of the results obtained with the mercaptooxazolines on one hand and 6-nitrobenzimidazole on the other.

TABLE I

Developing Time, In Minutes	Relative Net D=0.2	Speed at: Net D=1.0	Maximum Gradient	Maximum Density Above Fog	Net Fog
1	140	40	1.64	2.02	.04
2	205	63	2.34	3.07	.05
4	240	80	2.74	3.22	.08
6	320	99	2.70	3.26	.13
10	450	112	2.60	3.22	.38
16	900	108	2.22	2.73	1.02

TABLE II

Concentration (mgs./l.)	Developing Time, In Minutes	Relative Net D=0.2	Speed at: Net D=1.0	Maximum Gradient	Maximum Density Above Fog	Net Fog
100	1	95	11	.90	1.27	.03
100	2	122	34	1.72	2.18	.04
100	4	128	40	2.02	2.37	.04
100	6	141	45	2.25	2.57	.05
100	10	135	48	2.40	2.70	.07
100	16	135	46	2.28	2.74	.08
3	6	270	86	3.09	3.24	.18
3	10	285	95	2.84	3.18	.44
3	16	275	87	2.40	2.55	1.20
.79	6	325	100	2.64	3.24	.14
.79	10	475	114	2.48	3.10	.40
.79	16		102	1.90	2.59	1.02

TABLE III

Concentration (mgs./l.)	Developing Time, In Minutes	Relative Net D=0.2	Speed at: Net D=1.0	Maximum Gradient	Maximum Density Above Fog	Net Fog
1,000	1					0.00
1,000	2	14		.48	.56	0.00
1,000	4	53	16	2.08	2.22	0.00
1,000	6	86	29	2.50	2.74	.02
1,000	10	127	39	2.42	2.84	.02
1,000	16	140	45	2.46	2.93	.04
30	6	195	69	3.30	3.24	.10
30	10	230	78	3.10	3.30	.16
30	16	230	77	3.10	3.28	.24
7.9	6	285	90	2.80	3.21	.12
7.9	10	335	97	2.62	3.09	.34
7.9	16	385	100	2.28	2.74	.92

TABLE IV

Concentration (mgs./l.)	Developing Time, In Minutes	Relative Speed at: Net D. 0.20	Maximum Density Above Fog	Net Fog
0	3	47	1.02	0.03
0	6	112	1.68	0.05
0	10	159	1.96	0.09
0	20	182	2.18	0.20
0	30	269	2.19	0.29
60	3		0.10	0
60	6	2.1	0.38	0
60	10	7.6	0.76	0
60	20	22	1.31	0.01
60	30	32	1.63	0.02
20	3	8.3	0.66	0
20	6	40	1.24	0.02
20	10	71	1.66	0.03
20	20	85	2.04	0.04
20	30	103	2.18	0.05

TABLE V

Concentration (mgs./l.)	Developing Time, In Minutes	Relative Net D=0.2	Speed at: Net D=1.0	Maximum Gradient	Maximum Density Above Fog	Net Fog
100	1	31		.52	.70	0
100	2	49	10	1.14	1.41	0
100	4	49	14	1.64	1.77	0
100	6	57	17	2.04	1.97	0
100	10	58	20	2.00	1.96	0
100	16	64	24	2.12	2.16	0
3	6	265	84	2.95	3.27	.11
3	10	350	103	3.00	3.37	.18
3	16	620	136	2.50	3.17	.46
.79	6	255	86	3.04	3.14	.12
.79	10	310	106	2.86	3.17	.27
.79	16	610	125	2.44	2.80	.84

TABLE VI

Concentration (mgs./l.)	Developing Time, In Minutes	Relative Speed at: Net D. 0.20	Maximum Density Above Fog	Net Fog
60	3		0.03	0
60	6	1.0	0.20	0
60	10	3.3	0.57	0.01
60	20	19	1.40	0.02
60	30	30	1.70	0.02
20	3	1.7	0.34	0
20	6	13.5	0.91	0
20	10	47	1.47	0.01
20	20	103	1.98	0.03
3	3	30	0.95	0.04
3	6	74	1.61	0.04
3	10	110	1.91	0.06
3	20	151	2.20	0.10
3	30	186	2.28	0.13

TABLE VII

Concentration (mgs./l.)	Developing Time, In Minutes	Relative Net D=0.2	Speed at: Net D=1.0	Maximum Gradient	Maximum Density Above Fog	Net Fog
100	1	18		.52	.62	0
100	2	32	7	1.29	1.33	0
100	4	36	12	1.86	1.87	0
100	6	41	14	1.85	1.87	0
100	10	46	17	2.20	2.06	0
100	16	54	18	2.06	2.06	0
3	6	2.75	85	3.08	3.31	.10
3	10	2.80	99	2.96	3.48	.14
3	16	345	120	2.84	3.55	.20
.79	6	245	85	3.30	3.26	.12
.79	10	335	110	2.90	3.37	.22
.79	16	350	115	2.98	3.18	.48

TABLE VIII

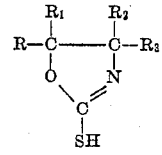
Concentration (mgs./l.)	Developing Time, In Minutes	Relative Speed at: Net D. 0.20	Maximum Density Above Fog	Net Fog
60	3		0	0
60	6		0.02	0
60	10		0.06	0
60	20		0.18	0
60	30	1.3	0.39	0
20	3	1.1	0.26	0
20	6	6.5	0.81	0
20	10	24	1.48	0.01
20	20	65	2.00	0.02
20	30	69	2.15	0.04
3	3	13	0.89	0.02
3	6	53	1.48	0.03
3	10	79	1.76	0.05
3	20	112	2.10	0.05
3	30	129	2.19	0.05

TABLE IX

Compound	Concentration (mgs./l.)	Gross Fog	R. L. F., Percent	Relative Maximum Speed
None		.46	350	100
6-nitrobenzimidazole	1100	.08	170	28
5-methyl-2-mercaptooxazoline	90	.16	85	38
4-ethyl-2-mercaptooxazoline	70	.18	85	38
2-mercaptooxazoline	130	.18	100	36

We claim:

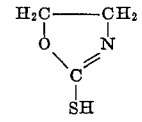
1. A photographic developer for silver-halide comprising a silver-halide developer and as a developer retarder a 2-mercaptooxazoline of the following general formula:



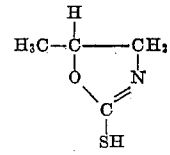
wherein R, R_1, R_2, and R_3, are selected from the class

consisting of hydrogen, aliphatic, aromatic and heterocyclic radicals.

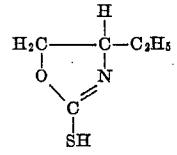
2. An alkaline photographic developer for silver-halide comprising a silver-halide developer and a 2-mercaptooxazoline of the following formula:



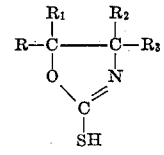
3. An alkaline photographic developer for silver-halide comprising a silver-halide developer and a 2-mercaptooxazoline of the following formula:



4. An alkaline photographic developer for silver-halide comprising a silver-halide developer and a 2-mercaptooxazoline of the following formula:

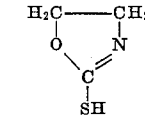


5. In the development of an exposed silver-halide emulsion the improvement which comprises effecting such development in an alkaline developer containing a developing agent for said silver-halide emulsion and in the presence of a 2-mercaptooxazoline developer retarder corresponding to the following general formula:

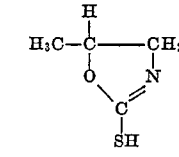


wherein R, R_1, R_2, and R_3, are selected from the class consisting of hydrogen, aliphatic, aromatic, and heterocyclic radicals.

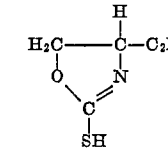
6. In the development of a photographic negative the step comprising the development of an exposed silver-halide emulsion in an alkaline developer containing a developing agent for said emulsion and as a developer retarder a 2-mercaptooxazoline corresponding to the following formula:



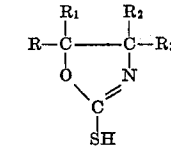
7. In the development of a photographic negative the step comprising the development of an exposed silver-halide emulsion in an alkaline developer containing a developing agent for said emulsion and as a developer retarder a 2-mercaptooxazoline corresponding to the following formula:



8. In the development of a photographic negative the step comprising the development of an exposed silver-halide emulsion in an alkaline developer containing a developing agent for said emulsion and as a developer retarder a 2-mercaptooxazoline corresponding to the following formula:



9. In the development of an exposed silver-halide emulsion the step comprising treating an exposed silver-halide emulsion with a pre-bath containing a developer retarder of the following general formula:



wherein R, R_1, R_2, and R_3, are selected from the class consisting of hydrogen, aliphatic, aromatic, and heterocyclic radicals and then developing said silver-halide emulsion in an alkaline developer containing a developing agent for said emulsion.

References Cited in the file of this patent

UNITED STATES PATENTS

2,614,925 Carroll et al. ---------- Oct. 21, 1952

UNITED STATES PATENT OFFICE

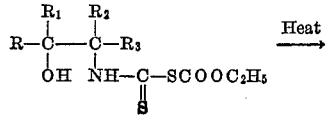
Certificate of Correction

Patent No. 2,855,301 October 7, 1958

Ernest T. Larson, Jr., et al.

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

Column 2, lines 28 to 31 should appear as shown below instead of as in the patent—



column 6, TABLE VII, under the heading "Relative Net D=0.2", for "2.75" read *275*; and for "2.80" read *280*.

Signed and sealed this 13th day of January 1959.

[SEAL]

Attest:
KARL H. AXLINE,
Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.