

Dec. 26, 1972

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3,707,379

PROCESS FOR THE FORMATION OF PHOTOGRAPHIC IMAGES

Filed May 16, 1969

FIG. 1

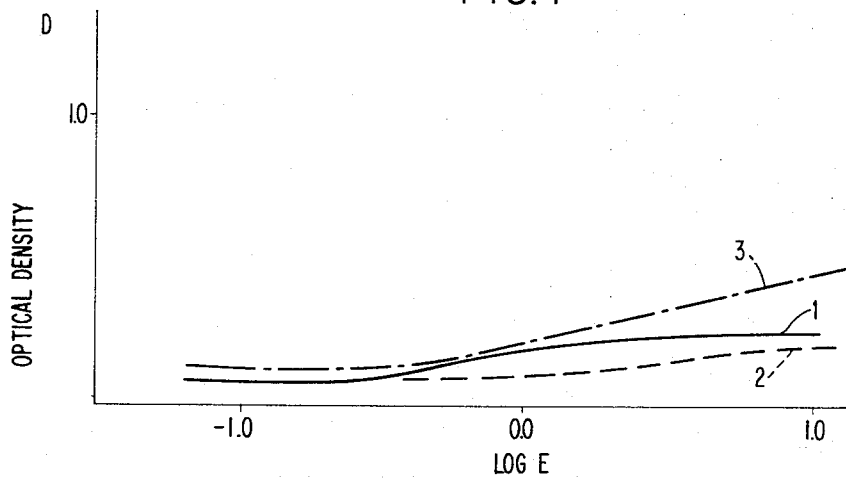
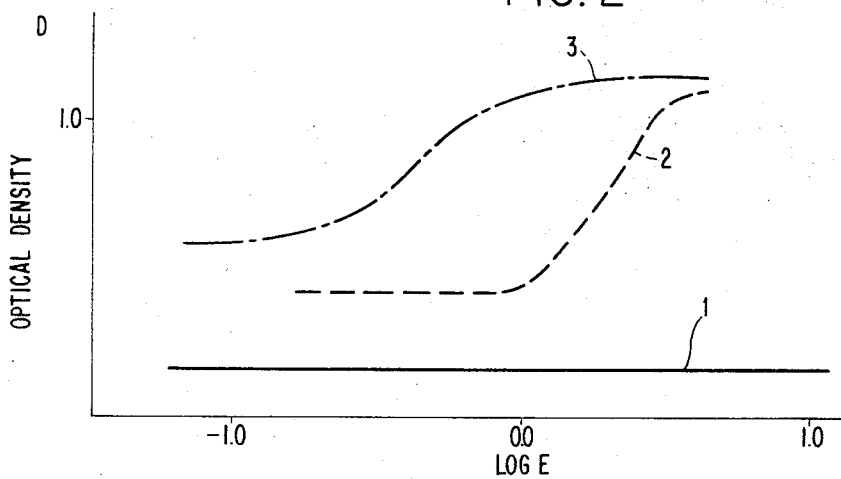


FIG. 2



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PROCESS FOR THE FORMATION OF PHOTOGRAPHIC IMAGES

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Filed May 16, 1969, Ser. No. 825,347

Claims priority, application Japan, May 16, 1968, 43/33,031

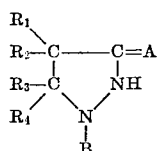
U.S. Cl. 96—115

Int. Cl. G03c 1/68

36 Claims

ABSTRACT OF THE DISCLOSURE

A polymer image is formed on a photographic film on those areas which have been exposed and developed, the image proportional to the amount of exposure. The polymer image may then be dyed. The image is developed from a latent image in a photographic emulsion by developing the emulsion, in the presence of a vinyl or vinylidene monomer, with a reducing agent capable of developing the silver halide emulsion layer and at the same time initiating polymerization, said agent selected from resorcinols, m-aminophenols, naphthols, pyrazoline-5-ones and phenols, and a reducing agent of the general formula



wherein A represents an oxygen atom or an imino group, B represents a phenyl group, R_1 , R_2 and R_3 each represents a hydrogen atom or an alkyl group having 1-6 carbon atoms, and R_4 represents a hydrogen atom, an alkyl group having 1-6 carbon atoms, an aryl group, or a carboxyl group. By the use of the compound of the general formula in combination with the reducing agent capable of initiating polymerization, the developing speed is increased and the sensitivity of the photographic emulsion is also increased.

The present invention relates to a process for the formation of photographic images and more particularly to a process for forming a polymeric image on a photographic film, the polymeric image corresponding to the latent image formed by exposure of the photographic emulsion layer.

It is known that by developing a photographic silver halide emulsion layer having a latent image with a specific reducing agent in the presence of a vinyl compound or a vinylidene compound, the formation of a silver image and the polymerization of the above-mentioned vinyl or vinylidene compound occur simultaneously.

By utilizing the aforesaid polymerization reaction, it is possible to obtain a colored image by forming an image corresponding to the developed silver image of a high molecular weight compound having charges and then dyeing the image.

As specific reducing agents capable of initiating polymerization, there are illustrated resorcinol, m-aminophenols, derivatives thereof, naphthol derivatives, 2-pyrazoline-5-ones, 3-pyrazoline-5-ones, and phenols. However, since these reducing agents generally have a weaker reducing power than developing agents commonly employed in photographic processings, it takes a considerably longer

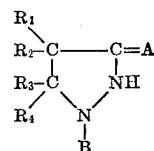
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period of time to finish the development. Consequently, photographic sensitivity is lowered.

On the other hand, usual developing agents such as p-methylaminophenol and hydroquinone do not initiate the polymerization of a vinyl compound or a vinylidene compound. On the contrary, these developing agents or the oxidation product thereof frequently act as a radical polymerization inhibitor.

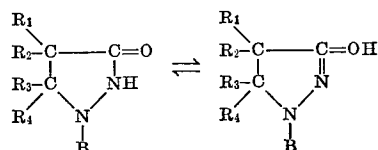
An object of the present invention is to provide an improved process for forming a polymer image corresponding to a latent image by developing a silver halide photographic emulsion layer having the latent image with a reducing agent such as, a resorcinol, a m-aminophenol, a naphthol, a pyrazoline-5-one, and a phenol, capable of initiating the polymerization of a vinyl or vinylidene compound and reducing at the same time the silver halide in the photographic emulsion layer, in the presence of a vinyl compound or a vinylidene compound, wherein the developing speed is increased and the sensitivity of the photographic emulsion is also increased.

The object of the present invention can be attained by incorporating into the developing solution for a silver halide emulsion layer containing therein a reducing agent capable of initiating the polymerization of a vinyl or vinylidene compound in the presence of the vinyl or vinylidene compound, a 3-oxopyrazolidine or a 3-iminopyrazoline represented by the general Formula I

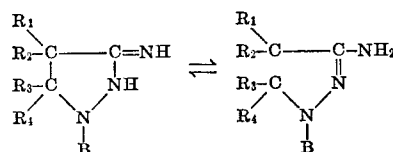


wherein A represents an oxygen atom or an imino group; B represents a phenyl group or a substituted phenyl group; R_1 , R_2 and R_3 each represents a hydrogen atom or an alkyl group having 1-6 carbon atoms; and R_4 represents a hydrogen atom, an alkyl group having 1-6 carbon atoms, an aryl group, or a carboxyl group. The compound of Formula I may also be incorporated into the processing solution for the silver halide photographic emulsion layer, thereafter developing the emulsion layer with the above-mentioned reducing agent in the presence of the vinyl or vinylidene compound.

The compound represented by the above-mentioned general formula may be the tautomer as shown below



or



As reducing agents capable of reducing silver halide in a silver halide emulsion and at the same time initiating the polymerization of a vinyl compound or a vinylidene compound, there may be employed in the present invention the aforesaid resorcinols, m-aminophenols, naphthols,

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2-pyrazoline-5-ones, 3-pyrazoline-5-ones, and phenols. The typical examples of these compounds are resorcinol, m-aminophenol, 1-amino-8-naphthol-3,6-disulfonic acid, 3,4-dimethyl-5-pyrazolone, o-xylene, and the like.

The 3-oxypyrazolidines used in the present invention, represented by general Formula I, are compounds usually effective as photographic developing agents and are disclosed in various publications. For example, see A. J. Axford and J. D. Kendall; "Journal of Photographic Science," 2, 21-27 ('54); G. E. Ficken and B. G. Sander-
son; *ibid.* 11, 157-164 ('63); A. J. Axford and J. D. Kendall; "Wissenschaftliche Photographie (Ergebnisse der Intern. Konf. für Wissenschaftliche Photographie, Köln, 1956)"; and W. Eichler, H. Frieser and O. Heilwich ed.; "Verlag Dr. O. Helwich," 400-404 ('58), published by Darmstadt.

Typical examples of these compounds are

1-phenyl-3-oxypyrazolidine,
1-phenyl-4-methyl-3-oxypyrazolidine,
1-phenyl-3-oxypyrazolidine-5-carboxylic acid,
1-p-tolyl-3-oxypyrazolidine,
1-p-methoxyphenyl-3-oxypyrazolidine,
1-phenyl-4-ethyl-3-oxypyrazolidine,
1-phenyl-4-isopropyl-3-oxypyrazolidine,
1-phenyl-4,4-dimethyl-3-oxypyrazolidine,
1-phenyl-5-methyl-3-oxypyrazolidine,
1-phenyl-5,5-dimethyl-3-oxypyrazolidine,
1-phenyl-4,5-dimethyl-3-oxypyrazolidine,
1,5-diphenyl-3-oxypyrazolidine and

the like.

The 3-iminopyrazolidines represented by general Formula I are also effectively used as usual photographic developing agents and are disclosed in British Pat. No. 757,840 and German Pat. No. 870,418. Typical examples of the 3-iminopyrazolidines are 1-phenyl-3-iminopyrazolidine, 1,5-diphenyl-3-iminopyrazolidine, 1-p-hydroxyphenyl-3-iminopyrazolidine, 1-p-methoxyphenyl-3-iminopyrazolidine, and the like.

It is well known that when the aforesaid 3-oxypyrazolidine is used together with p-aminophenol or hydroquinone, a synergistic action is obtained, that is, the developing speed is faster than the value that would be expected calculating the results using each component. For this synergistic property, various mechanisms have been proposed. However, it shall be noticed that the combination in the present invention is different from the conventional combination in the kind of reducing agent as well as purposes. In other words, in the conventional combination, the purpose of employing both reducing agents (developing agents) is to reduce silver halide into silver and the synergistic property is obtained in the speed of the formation of the silver. On the other hand, in the combination of this invention, the reducing agent serves the dual function of reducing a silver halide to silver and at the same time initiating the radical polymerization of a vinyl compound or a vinylidene compound, while the pyrazolidine derivative represented by general Formula I reduces a silver halide to silver but does not initiate polymerization. As shown in the examples, 1-phenyl-3-oxypyrazolidine exhibits a strong developing action but has no function of initiating the polymerization of the monomer. Thus, the advantage of the present invention lies in the fact that by using the reducing agent having a strong developing power together with the reducing agent capable of initiating the polymerization of the monomer but having a weak reducing power, the initiation of the polymerization by the latter reducing agent can be conducted rapidly, while also obtaining a high sensitivity for the photographic silver halide emulsion layer.

The developing mechanism, particularly the initial mechanism by the silver halide photographic emulsion in the process of this invention has not been sufficiently clarified. It is not clear how the combination in this invention

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acts effectively but the following two mechanisms are considered:

In the first mechanism, since the developed silver acts self catalytically in the course of development on each silver halide particle, the developing agent of the structure of Formula I having a high developing activity, acts first on the developing nuclei to increase the size thereof, whereby the developing action of the reducing agent having a function of initiating polymerization and a weak developing activity is facilitated. In the second mechanism, the polymerization reaction is started by oxidizing the reducing agent having a function of initiating polymerization with the oxidation product of the developing agent having the structure (I).

The fact that weakly developing with the developing agent having the structure (I) and then developing with the developing agent having the function of initiating polymerization, promotes the initiation of polymerization is considered to back up the first mechanism.

On the other hand, since the oxidation reduction potential of the developing agent having the structure (I) shown above is lower (stronger in reducing property) than that of the reducing agent having the function of initiating polymerization by 200-300 m.v., if the concentration ratio of the latter to the former is not sufficiently high, neither the reduction of silver halide nor the reduction of the oxidation product of the former becomes possible. This is the reason why the amount of the developer having the structure (I) must be less than the amount of the reducing agent having the function of initiating polymerization.

In the case of using the reducing agent having the function of initiating polymerization and the developer having the structure (I), although the optimum ratio of the latter to the former is varied according to the kinds of the compounds, the ratio is preferably less than $\frac{1}{10}$ in mole ratio preferably $\frac{1}{20}$ to $\frac{1}{20,000}$ in mole ratio.

Also in the case of developing with the reducing agent having the structure (I) before the development with the reducing agent having the function of initiating polymerization, there is no particular limitation about the concentration of the latter, but it is desirable that a washing step be added between both developing procedures so that an excessive amount of the latter is not carried in the polymerization system.

Also, the inventors have previously reported that the same effect as in the present invention can be obtained by employing p-amino-phenol, pyrocatechin, amidol or the like together with the reducing agent having the function of initiating polymerization.

However, since p-aminophenol, pyrocatechin, amidol and the like tend to inhibit the radical polymerization in general, the amount of them is extremely restricted. Since the pyrazolidines of the instant invention have almost no or completely no tendency to inhibit the radical polymerization, they can be employed in greater amounts compared with the aforesaid compounds.

The photographic emulsion, light source, etc. used in the present invention, are those generally employed in conventional developing procedures.

Furthermore, as the vinyl compound or the vinylidene compound used in the present invention, there are illustrated acrylamide, acrylonitrile, N-hydroxymethyl acrylamide, methacrylic acid, acrylic acid, calcium acrylate, sodium acrylate, methacrylamide, methyl methacrylate, methyl acrylate, ethyl acrylate, vinylpyrrolidone, vinyl methyl ether, vinyl butyl ether, vinyl isopropyl ether, vinyl isobutyl ether, vinyl butyrate, 2-vinyl-pyridine, 4-vinyl-pyridine, 2-methyl-N-vinylimidazole, potassium vinylbenzene sulfonate, vinylcarbazole, N,N'-methylenebis acrylamide, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, divinyl ether, divinyl benzene and the like.

It is particularly preferable that sulfite ions are present in the system when the polymerization of the above mono-

mer is conducted according to the process of this invention. Moreover, by dyeing the polymer image formed by the process of this invention, a color image can be prepared.

In the following examples, polymer images formed by using methacrylic acid as the monomer were dyed with basic dyes. The invention is not to be limited by these cases.

EXAMPLE 1

A photographic light-sensitive film having a photographic gelatino silver halide emulsion was light-exposed and then developed with 8-amino-1-naphthol-3,6-disulfonic acid and 1-phenyl-3-oxopyrazolidine to conduct the polymerization of methacrylic acid.

The photographic light-sensitive film was prepared as follows: After applying under coatings to both surfaces of a polyethylene terephthalate film, an antihalation layer was formed on the one surface thereof and the other surface thereof was coated with a fine particle-type gelatino silver halide emulsion containing about 0.7 mole of chlorine, about 0.3 mole of bromine, about 0.001 mole of iodine and about 100 g. of gelatin per mole of silver, said silver halide emulsion having further been mixed with a merocyanine dye having a sensitivity maximum at 550 m μ , as a sensitizing dye, mucochloric acid in an amount of about 1.5 g. per 100 g. of gelatin as a hardening agent, and a suitable stabilizer and a surface active agent so that 50 mg. of silver per 100 cm.² of the emulsion layer was contained in the silver halide emulsion layer. Thereafter a protective layer consisting of gelatin was applied to the emulsion layer in a thickness of about 0.8 micron. The photographic light-sensitive film thus prepared was a type usually employed for making line and half-tone images for graphic arts.

From the photographic film thus prepared, three sample films were cut off and each of the samples was exposed for one second at 50 luxes through a sensitometric optical wedge with a density increment of 0.15 per step and then developed in a developer having the following composition.

Sodium methacrylate	75 g.
8-amino-1-naphthol-3,6-disulfonic acid	See table, below.
1-phenyl-3-oxopyrazolidine	Do.
Potassium metabisulfite	3 g.
2 N NaOH	Amount necessary for adjusting the pH to 9.0.

Water to make 150 ml.

TABLE

Sample Number	1	2	3
8-amino-1-naphthol-3,6-disulfonic acid	14.4 g.	14.4 g.	14.4 g.
1-phenyl-3-oxopyrazolidine	8.5 mg.	8.5 mg.	8.5 mg.

After developing for 10 minutes at 30° C., the sample film was washed for 30 seconds with 1.5% acetic acid and then fixed in the following fixing solution:

Sodium thiosulfate (anhydrous)	g--	150
Potassium metabisulfite	g--	15
Water to make	ml--	1000

After fixing, each sample film was washed with water and cut into two parts. One of the parts was immersed in an aqueous 0.1% solution of a red basic dye, Rhodamine 6 G.C.P. (C.I. Basic Red 1) for five minutes, washed for five minutes with an aqueous 5% acetic acid solution, washed with water, processed in a Farmer's reducer to remove completely the silver image, washed with water and dried.

Thus, one part of each sample was not subjected to dyeing while the other part, subjected to the dyeing and bleaching procedure, formed a dyed polymer image. Each image

was measured for optical density through a green filter, the results of which are shown in FIG. 1 and FIG. 2.

FIG. 1 shows a characteristic curve obtained from the silver image. FIG. 2 shows a characteristic curve obtained from the dyed image and corresponds to the amount of the polymer formed. In these figures, No. 1 stands for sample number 1, No. 2 for sample number 2, and No. 3 for sample number 3.

As is clear from FIG. 1, for the undyed polymer image, sample 3 containing 1-amino-8-naphthol-3,6-disulfonic acid and 1-phenyl-3-oxopyrazolidine has a density equal almost to the sum of the density of sample 1 and sample 2.

On the other hand, from sample 1 of FIG. 2, it was confirmed that when exposed emulsion layer was developed with 1-phenyl-3-oxopyrazolidine, no dye image was obtained, that is, the formation of polymer corresponding to the amount of light-exposure was not observed. However, when 1-amino-8-naphthol-3,6-disulfonic acid was used together with 1-phenyl-3-oxopyrazolidine (sample 3), a dye image was formed quickly and the image of polymer was observed even in the areas where the amount of exposure was slight. In other words, it is clear that 1-phenyl-5-oxopyrazolidine alone has no function of forming polymer image but promotes the formation of polymer image by 1-amino-8-naphthol-3,6-disulfonic acid.

In comparing the results at the point where log $E=0$ (E is the amount of exposure), the density was increased by only 0.03 due to the formation of fog in sample 2, while the density was increased by about 0.4 due to the formation of fog in sample 3, and when both results are compared at the exposure amount necessary to give a density of 0.1 higher than background fog, the exposure amount in sample 3 may be about 0.6 (as logarithm of the exposure amount) lower than the exposure amount in sample 2, which shows the effective sensitivity of sample 3 was increased to about four times that of sample 2.

EXAMPLE 2

The same kind of the photographic light sensitive film as in Example 1 was exposed as in that example and then developed in a solution having the following composition:

Sodium methacrylate	G.
Reducing agent having a function of initiating polymerization	75
Pyrazolidine derivative	*
Potassium metabisulfite	*
2 N sodium hydroxide—amount necessary for adjusting the pH to.*	3.0
Water to make 150 ml.	

*Shown in Table 1.

After developing as above for a period of time as shown in Column A of Table I, the sample was subjected to fixing, washing, bleaching, and drying. The step number of least exposure susceptible to dyeing at which the dye image was observed was measured visually, the results of which are shown in Column B of Table I. Also, at a specific step, the density of dye image of each sample was measured, and the results compared. In Table I, the step number used in the above measurement is shown in Column C, the density of dye image at the step is shown in Column D, the density of the background fog is shown in Column E, and the true density of dye image (i.e., D-E) is shown in Column F. Thus, the value in Column F corresponds to the amount of the polymer formed caused by the specific amount of exposure given to the emulsion layer. In the experiments, it was observed that by addition of the pyrazolidine derivatives, the step number by which the formation of dye image was observed was increased and at the same time the F value was increased. This shows that the formation rate of polymer was increased and the effective sensitivity was also increased.

TABLE I

Number	Reducing agent having a function of initiating polymerization	Amount g.	Pyrazoline derivative	Amount, mg.	pH	A	B	C	D	E	F
4a	Resorcinol	4.95	1-phenyl-3-oxopyrazolidine	8.6	11.5	7	10	10	0.18	0.14	0.04
4b	do.	4.95	1-phenyl-3-oxopyrazolidine	8.6	11.5	5	13	10	0.33	0.16	0.17
5a	N,N-dimethylmethanimophenol	8.22	1-phenyl-3-oxopyrazolidine	8.6	11.1	10	10	10	0.47	0.45	0.02
5b	do.	8.22	1-phenyl-3-oxopyrazolidine	8.6	11.1	10	12	10	0.60	0.33	0.27
6a	3,4-dimethyl-5-pyrozolone	2.80	1-phenyl-3-oxopyrazolidine	8.6	10.0	20	0	5	0.16	0.16	0
7a	O-xlenol	2.80	1-phenyl-3-oxopyrazolidine	8.6	10.0	20	11	5	1.06	0.22	0.84
7b	do.	3.15	1-phenyl-3-oxopyrazolidine	8.6	10.0	40	12	5	1.32	0.43	0.89
8a	Resorcinol	4.95	1-phenyl-4-methyl-3-oxopyrazolidine	10	11.0	15	4	5	0.19	0.19	0
9a	do.	4.95	1-phenyl-5-methyl-3-oxopyrazolidine	10	11.0	15	10	5	1.37	0.23	1.14
9b	do.	4.95	1-phenyl-5-methyl-3-oxopyrazolidine	10	11.0	15	11	5	1.34	1.21	1.13
10a	do.	4.95	1-hydroxyphenyl-3-iminopyrazolidine	10	11.0	10	0	10	0.17	0.17	0
10b	do.	4.95	1-p-methoxyphenyl-3-iminopyrazolidine	10	11.0	10	13	10	0.98	0.10	0.79
10c	do.	4.95	1-phenyl-5-carboxy-3-oxopyrazolidine	10.3	11.0	20	8	5	0.39	0.20	0.19
10d	do.	4.95	do.	10.3	11.0	20	12	5	0.94	0.17	0.77
10e	do.	4.95	do.	10.3	11.0	10	12	5	1.00	0.16	0.84

NOTE.—A=Developing time; B=Step Number of maximum density; C=Step Number of comparison; D=Density of dye image; E=Density of fog; F=True density of dye image.

Furthermore, when the pyrazolidine derivative was used alone, the density corresponding to the value shown in Column F of FIG. 1 was not obtained under the same conditions as shown in Table I. Accordingly, it is clear that the increase in density and sensitivity in this case is not caused by only the sum of the actions of the both reducing agents but by a synergistic addition property thereof.

EXAMPLE 3

The photographic light-sensitive film as in Example 1 was exposed, pre-treated in an aqueous alkaline solution of 1-phenyl-3-oxopyrazolidine, and then developed by using resorcinol to conduct polymerization.

After exposing the sample for 10 seconds at 50 luxes as in Example 1, the sample was pretreated in an aqueous solution containing 0.1 g./liter of 1-phenyl-3-oxopyrazolidine, the pH of which had been adjusted to 10.5 by adding sodium carbonate, at 30° C. for a period of time shown in Table II, washed thrice for 15 seconds each with distilled water, and then immersed in a solution having the following composition for 30 minutes at 30° C. to conduct development and polymerization:

Sodium methacrylate	54
Resorcinol	4.95
Potassium metabisulfite	1.5
2 N sodium hydroxide—amount necessary for adjusting the pH to 10.5.	
Water to make 150 ml.	

The sample thus developed was processed as in Example 2 and the same measurements as in Example 2 were conducted, the results of which are shown in Table II. In Table II, A stands for the period of time required for the pretreatment, B for the step number of at least exposure susceptible to dyeing at which a dye image was observed, C for the step number used in the measurement of density, D for the density of the fog portion of dye image and F the true density of the dye image (D-E).

TABLE II

A	B	C	D	E	F
0 (control)	6	5	0.32	0.13	0.19
20 seconds	10	5	0.34	0.12	0.22
1 minute	15	5	1.07	0.21	0.86
4 minutes	20	5	2.67	0.56	2.11

In this case, the oxopyrazolidine processing solution contained no methacrylic acid monomer and hence by the treatment by the oxopyrazolidine processing solution, no polymer was formed and hence a dye image was of course not obtained. Therefore, it is clear that the pretreatment by oxopyrazolidine promoted the development and polymerization by the resorcinol-methacrylate system.

In addition, even though the development and polymerization by the resorcinol-methacrylate system was stopped after 15 minutes, a dye image, i.e., a polymer image was observed but when the pretreatment was con-

ducted using 0.1 g./liter of a pyrocatechin under the same conditions as above, no polymer image was formed after processing for 15 minutes but a polymer image was obtained after processing for 30 minutes. This is considered to be caused in the latter case by a polymerization inhibiting action, while in the case of employing pyrazolidines, almost no such inhibiting action exists.

EXAMPLE 4

The same procedure as in Example 3 was repeated using a silver iodobromide emulsion.

After applying under coatings to both surfaces of the cellulose triacetate support, and applying an antihalation layer to one coated surface thereof, the other surface was coated with a fine particle-type gelatino silver halide emulsion containing 0.012 mole of iodine, 0.988 mole of bromine, and about 204 g. of gelatin per 1 mole of silver, which had been sensitized by a rhodan complex salt of mono-valent gold and mixed with 0.3 g. of 6-methyl-4-hydroxy-1,3,32,7-tetraazaindene per mole of silver as a stabilizer, about 0.7 g. of mucochloric acid per 100 g. of gelatin as a hardening agent, and also a suitable surface active agent so that 60 mg. of silver was contained in the emulsion layer of 100 cm.². Further, a protective gelatin layer of about 0.8 micron in thickness was formed on the emulsion layer. Such a type of photographic light sensitive film is usually used for making line images by photoengraving process and continuous positive images of soft tone.

After exposing the film sample thus prepared for 1 second at 50 luxes as in Example 1, the sample was pretreated in an aqueous solution of 1-phenyl-3-oxopyrazolidine as in Example 3, washed with water thrice each for 15 seconds with distilled water, and then immersed for 15 minutes at 30° C. in a solution having the following composition to conduct the development and polymerization simultaneously:

Sodium methacrylate	54
1-amino-8-naphthol-3,6-disulfonic acid	10
Potassium metabisulfite	1.5
2 N NaOH—Amount necessary for adjusting the pH to 10.5.	

The thus developed film was further processed as in Example 3 and the measurements as in Example 3 were conducted, the results of which are shown in Table III. A-F in Table III are the same as those in Table II.

TABLE III

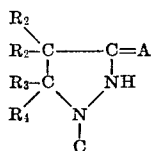
A	B	C	D	E	F
0 (control)	3	5	0.06	0.06	0
30 seconds	5	5	0.12	0.06	0.06
1 minute	14	5	0.66	0.10	0.56
2 minutes	18	5	2.16	0.20	1.96

From the above results, the effect of the pyrazolidine derivative was clearly confirmed. Also, these pyrazolidine derivatives showed the same effects as metol, amidol, etc.,

and hence they may be used together with these compounds and by using a suitable amount of them, better results can be obtained.

What is claimed is:

1. In a process for forming an image of a vinyl polymer or a vinylidene polymer on a photographic film in conformity with a photographic latent image by developing an image-wise exposed photographic silver halide emulsion layer bearing the photographic latent image in the presence of a vinyl compound or a vinylidene compound and an organic reducing agent capable of simultaneously initiating the polymerization of said vinyl or vinylidene compound, the improvement which comprises treating said exposed emulsion layer at a point no later than said development with a pyrazolidine compound or a tautomer thereof, incapable of initiating polymerization of said vinyl or vinylidene compound, but capable of reducing said silver halide to silver, said pyrazolidine compound being represented by the general formula:



wherein A represents an oxygen atom or an imino group; B represents a phenyl group or a substituted phenyl group; R_1 , R_2 and R_3 each represents a hydrogen atom, or an alkyl group having 1-6 carbon atoms; and R_4 represents a hydrogen atom, an alkyl group having 1-6 carbon atoms, an aryl group or a carboxyl group.

2. The process of claim 1, wherein said reducing agent is a member selected from the group consisting of a resorcinol, a m-aminophenol, a naphthol, a pyrazoline-5-one, and a phenol.

3. The process of claim 1, wherein said reducing agent is a member selected from the group consisting of resorcinol, N,N-dimethylmethaminophenol, 3,4 - dimethyl-5-pyrazolone, and o-xyleneol.

4. The process of claim 1, wherein said reducing agent is 1-amino-8-naphthol-3,6-disulfonic acid.

5. The process of claim 1, wherein the ratio of said pyrazolidine or a tautomer thereof to said reducing agent is less than 1:10 in mole ratio.

6. The process of claim 1, wherein the ratio of said pyrazolidine or a tautomer thereof to said reducing agent ranges from 1:20 to 1:20,000 in mole ratio.

7. The process of claim 1, wherein said developer contains sulfite ions.

8. The process of claim 7, wherein the precursor for said sulfite ions is potassium metabisulfite.

9. The process of claim 1, wherein said vinyl or vinylidene compound is a member selected from the group consisting of acrylamide, acrylonitrile, N-hydroxymethylacrylamide, methacrylic acid, acrylic acid, calcium acrylate, sodium acrylate, methacrylamide, methylmethacrylate, methylacrylate, ethylacrylate, vinylpyrrolidone, vinylmethyl ether, vinyl butyl ether, vinyl isopropyl ether, vinyl isobutyl ether, vinyl butyrate, 2-vinyl-pyridine, 4-vinylpyridine, 2-methyl-N-vinylimidazole, potassium vinyl benzene sulfonate, vinylcarbazole, N,N'-methylene-bis acrylamide, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, divinyl ether, and divinyl benzene.

10. The process of claim 1, wherein said pyrazolidine compound is a member selected from the group consisting of 1-phenol-3-oxopyrazolidine, 1-phenol-4-methyl-3-oxopyrazolidine, 1-phenol-3-oxopyrazolidine-5-carboxylic

acid, 1 - p-tolyl-3-oxopyrazolidine, 1-p-methoxyphenol-3-oxopyrazolidine, 1 - phenol-4-ethyl-3-oxopyrazolidine, 1-phenol - 4-isopropyl-3-oxopyrazolidine, 1-phenol-4,4-dimethyl - 3-oxopyrazolidine, 1-phenol-5-methyl-3-oxopyrazolidine, 1 - phenol - 5,5-dimethyl-3-oxopyrazolidine, 1-phenol-4,5-dimethyl-3-oxopyrazolidine, and 1,5-diphenol-3-oxopyrazolidine.

11. The process of claim 1, wherein the silver image formed during the polymerization procedure is removed by fixation and washing with an oxidizing agent.

12. The process of claim 1, wherein said polymer image is a colored image obtained by dyeing said polymer image which contains a member selected from the group consisting of an acidic and a basic group with a dye having an acidity or basicity opposite to that of said polymer.

13. In a process for forming an image of a vinyl polymer or a vinylidene polymer on a photographic film in conformity with a photographic latent image by developing an image-wise exposed photographic silver halide emulsion layer bearing the photographic latent image in the presence of a member selected from the group consisting of a vinyl compound and a vinylidene compound with an organic reducing agent capable of simultaneously initiating polymerization of said vinyl or vinylidene compound and reducing said silver halide to silver, the improvement which comprises processing said photographic silver halide emulsion layer, before development, in a bath containing a member selected from the group consisting of a pyrazolidine compound and a tautomer thereof, said pyrazolidine compound being a member selected from the group consisting of an m-aminophenol, a naphthol, a pyrazoline-5-one, and a phenol, said pyrazoline compound being capable of reducing said silver halide to silver but not capable of initiating polymerization of said vinyl or vinylidene compound.

14. The polymer image formed by the process of claim 1.

15. The polymer image formed by the process of claim 21.

16. The polymer image formed by the process of claim 12.

17. The polymer image formed by the process of claim 30.

18. The process of claim 1 wherein said treating comprises contacting the exposed emulsion layer with said pyrazolidine compound or a tautomer thereof and said reducing agent in the same solution, wherein said pyrazolidine or tautomer is present in a molar amount less than said reducing agent.

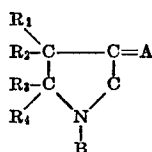
19. The process of claim 1 wherein said treating comprises firstly contacting said exposed emulsion layer with a solution of said pyrazolidine or tautomer thereof and thereafter secondly contacting said exposed emulsion with a solution of said reducing agent and said vinyl compound or vinylidene compound.

20. The process of claim 13, wherein said treating is development.

21. In a process for forming an image of vinyl polymer or a vinylidene polymer on a photographic film in conformity with a photographic latent image by developing an image-wise exposed photographic silver halide emulsion layer bearing the photographic latent image in the presence of a member selected from the group consisting of a vinyl compound and a vinylidene compound with an organic reducing agent capable of simultaneously initiating polymerization of said vinyl or vinylidene compound and reducing said silver halide to silver, the improvement which comprises processing said photographic silver halide emulsion layer, before development, in a bath containing a member incapable of initiating polymerization of said vinyl or vinylidene compound, but capable of reducing said silver halide to silver, selected from the group consisting of a pyrazolidine compound and a tautomer there-

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of, said pyrazolidine compound represented by the general formula:



wherein A represents an oxygen atom or an imino group; B represents a phenyl group or a substituted phenyl group; R₁, R₂ and R₃ each represents a hydrogen atom or an alkyl group having 1-6 carbon atoms; and R₄ represents a hydrogen atom, an alkyl group having 1-6 carbon atoms, an aryl group, or a carboxyl group.

22. The process of claim 21, wherein said reducing agent is a member selected from the group consisting of resorcinol, a m-amino-phenol, a naphthol, a pyrazoline-5-one, and a phenol.

23. The process of claim 21, wherein said reducing agent is a member selected from the group consisting of resorcinol, N,N-dimethylmethaminophenol, 3,4-dimethyl-5-pyrazolone, and o-xlenol.

24. The process of claim 21, wherein said photographic silver halide emulsion layer is washed in water after processing in said bath and before subjecting to development.

25. The process of claim 21, wherein said developer contains sulfite ions.

26. The process of claim 25, wherein the precursor for said sulfite ions is potassium metabisulfite.

27. The process of claim 21, wherein said reducing agent is 1-amino-8-naphthol-3,6-disulfonic acid.

28. The process of claim 21, wherein said pyrazolidine compound is a member selected from the group consisting of 1-phenol-3-oxopyrazolidine, 1-phenol-4-methyl-3-oxopyrazolidine, 1-phenol-3-oxopyrazolidine-5-carboxylic acid, 1-p-tolyl-3-oxopyrazolidine, 1-p-methoxyphenol-3-oxopyrazolidine, 1-phenol-4-ethyl-3-oxopyrazolidine, 1-phenol-4-ethyl-3-oxopyrazolidine, 1-phenol-4-isopropyl-3-oxopyrazolidine, 1-phenol-4,4-dimethyl-3-oxopyrazolidine, 1-phenol-5-methyl-3-oxopyrazolidine, 1-phenol-5,5-dimethyl-3-oxopyrazolidine, 1-phenol-4,5-dimethyl-3-oxopyrazolidine, and 1,5-diphenol-3-oxopyrazolidine.

29. The process of claim 21, wherein said vinyl or vinylidene compound is a member selected from the group

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consisting of acrylamide, acrylonitrile, N-hydroxymethylacrylamide, methacrylic acid, acrylic acid, calcium acrylate, sodium acrylate, methacrylamide, methylmethacrylate, methylacrylate, ethylacrylate, vinylpyrrolidone, vinylmethylether, vinylbutylether, vinylisopropylether, vinyl isobutyl ether, vinyl butyrate, 2-vinyl-pyridine, 4-vinylpyridine, 2-methyl-N-vinylimidazole, potassium vinyl benzene sulfonate, vinyl carbazole, N,N'-methylene bis acrylamide, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, divinyl ether, and divinyl benzene.

30. The process of claim 21, wherein said polymer image is a colored image obtained by dyeing said polymer image having a member selected from the group consisting of an acidic or a basic group with a dye having an acidity or basicity opposite to that of said polymer.

31. The process of claim 21, wherein said silver image formed during polymerization is removed by fixation and washing with an oxidizing agent.

32. The process of claim 13, where said pyrazolidine or tautomer thereof has an oxidation reduction potential at least 200 m.v. lower than said reducing agent.

33. The process of claim 32 where said oxidation reduction potential is 200 to 300 m.v. lower.

34. The process of claim 14 where said pyrazolidine or tautomer thereof has an oxidation reduction potential at least 200 m.v. lower than said reducing agent.

35. The process of claim 18 where said oxidation reduction potential is 200 to 300 m.v. lower.

36. The process of claim 14 where between said first and said secondly contacting said exposed emulsion layer is washed.

References Cited

UNITED STATES PATENTS

3,019,104	1/1962	Oster	96—290
3,178,441	4/1965	Ficken	96—48

NORMAN G. TORCHIN, Primary Examiner

E. C. KIMLIN, Assistant Examiner

U.S. Cl. X.R.

96—35.1, 48