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DEVELOPING COMPOSITION WITH PYRROLIDONE ANTI-SLUDGING AGENT

Henry John Schwalenstocker, Jr., Pittsford, N.Y., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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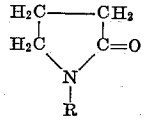
7 Claims. (Cl. 96—66)

This invention relates to new and improved photographic developer solutions and more particularly to concentrated aqueous developer solutions.

Concentrated liquid developer compositions are becoming increasingly important in photography because of such obvious advantages as smaller volume storage requirements and ease of shipment. However, a number of important chemical ingredients for such developer compositions are not only difficult to dissolve during the preparation of the compositions but tend to precipitate on standing, particularly at low temperature.

Accordingly, it is an object of the present invention to provide new photographic developer compositions, containing high concentrations of difficultly soluble ingredients. It is a further object to provide such concentrated developer solutions which have excellent stability and in which the dissolved materials have a reduced tendency to precipitate, even at relatively low temperatures. It is a still further object to provide new developing compositions in which exposed photographic material can be processed to yield increased image density. Further objects will be apparent from the following description of the invention.

These and other objects are accomplished by the new compositions obtained by adding an anti-sludging agent to a solution containing a photographic developing agent where the anti-sludging agent is added in amounts of about 10 to 110 grams per liter of the developing solution and said antisludging agent is a compound of the formula



where R is selected from the group consisting of hydrogen, lower alkyl radicals, hydroxy substituted lower alkyl radicals, hydroxy substituted lower alkyl radicals and amido substituted lower alkyl radicals. It is preferable that the lower alkyl is within the range of from 1 to 4 carbon atoms. As can be seen, this would allow up to a total of five carbon atoms when the amido substituent is used since this substituent is

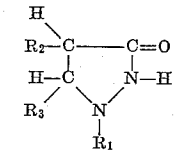


In a particularly preferred embodiment, the developing solution is a concentrated developer of the type used in processing a photographic paper element and the photographic developing agent has a low solubility in water at ordinary temperatures. N-methyl-2-pyrrolidone, has been found to be especially useful as an anti-sludging agent in preparing stable, concentrated developer solutions particularly where 1-phenyl-3-pyrazolidone is used as the primary developing agent. By a "concentrated" developer, is meant a solution designed for minimum volume storage but which is normally diluted with water prior to use.

Concentrated developer solutions contain a greater quantity of developer than is necessary for use in standard developing procedures which are well known in the art. Since some developing agents are sparingly soluble in their developing solutions and others are quite

soluble, the anti-sludging agents of this invention increase the solubility of developing agents relative to their original solubility. The concentrated developer solutions are more easily identified as being aqueous solutions of developing agents containing a quantity of the developing agents necessary to at least give a saturated solution of said agents at 40° F. Generally, the concentrated developer solutions contain amounts of developing agents in excess of that necessary for a saturated solution at 40° F. when the anti-sludging agents of this invention are employed in the solution. The 40° F. temperature limitation for measuring saturated solutions is quite arbitrary and was selected as a representative temperature at which concentrated developer solutions would be exposed in transmittal to purchasers.

Although 1-phenyl-3-pyrazolidone is a particularly preferred developing agent for use in the compositions of this invention, a number of other related pyrazolidone developing agents are also exceptionally useful with the anti-sludging agents. These developing agents are of the type that are difficult to keep in aqueous solutions. Most obvious of this type are the class of developing compounds disclosed in Kendall, U.S. 2,289,367, of which 1-phenyl-3-pyrazolidone is a member, viz., compounds of the formula



where R_1, R_2 and R_3 are the same or different and are hydrogen atoms or hydrocarbon groups, for instance, alkyl groups, e.g., methyl, ethyl, propyl, isopropyl, or higher alkyl groups, aryl groups, e.g., phenyl and naphthyl groups or aralkyl groups, aryl groups, e.g., benzyl groups. Such hydrocarbon groups may themselves be substituted; for example, aryl groups may be substituted with hydroxy, alkoxy, oxyalkyl, amino, substituted amino, nitro, sulfonic or carboxylic groups or halogen atoms.

Specific 3-pyrazolidones which may be employed are 3-pyrazolidone itself, 5-phenyl-3-pyrazolidone, 1-phenyl-3-pyrazolidone, 1-phenyl-5-methyl-3-pyrazolidone and 1-p-chlorophenyl-3-pyrazolidone. Compounds in which the group R_1 in the above formula is an aryl group, and the groups R_2 and R_3 are hydrogen atoms were disclosed in the Kendall patent as being particularly valuable developers.

Furthermore, according to the present invention, it has been found advantageous to employ the anti-sludging agents in solutions containing any conventional photographic developing agent. For example, useful developing solutions containing an anti-sludging agent have been prepared in which the developing agent was any one of the following: hydroquinone, 2,4-diaminophenol hydrochloride (Amidol), ascorbic acid, chlorohydroquinone, methyl-p-aminophenol sulfate (metol), and p-aminodiethylaniline. Developing solutions may also comprise two or more of these developing agents in combination with the anti-sludging agents.

The developing solutions of this invention may also comprise any of the usual additional components such as halides, buffers, antifoggants, toning and intensifying compounds, anti-plumming agents, alkalies, silver halide solvents (e.g., potassium thiocyanate, sodium thiosulfate, etc.), polyalkylene glycols of Stanton, U.S. 2,531,832, etc. A preferred developing solution, according to this invention contains a photographic developing agent such as 1-phenyl-3-pyrazolidone, a second developing agent (e.g., hydroquinone), sodium carbonate, sodium sulfite, an antifoggant such as benzotriazole or

5-nitrobenzimidazole, N-methyl-2-pyrrolidone and sufficient water to maintain all of the components in a stable solution.

The invention will be further illustrated but is not intended to be limited by the following examples. In the following examples the optical reflection densities of the exposed and processed papers were measured with a "Densichron" 1 densitometer manufactured by the Welch Scientific Company.

Example I

Developer concentrates of the following compositions were prepared:

	A	B
1-phenyl-3-pyrazolidone	3 gm	3 gm.
Hydroquinone	30 gm	30 gm.
Sodium carbonate (anhyd.)	100 gm	100 gm.
Sodium sulfite	100 gm	100 gm.
Benzotriazole	1.7 gm	1.7 gm.
N-methyl-2-pyrrolidone	None	20.54 gm.
Water to make	1 liter	1 liter.

Developer A (without N-methyl-2-pyrrolidone) exhibited marked crystal formation within 24 hours storage at 40° F. although it had been clear when prepared. Developer B remained clear after seven days storage at 40° F. Similarly prepared concentrates were diluted to working strength by adding two parts of water to one part of concentrate. These freshly prepared working solutions were then used to develop exposed samples of a silver bromide photographic paper for 10 sec. at 100° F. Although fog densities (with no exposure) are equal for the two developers, composition B containing N-methyl-2-pyrrolidone gives higher densities at useful exposure levels as shown in the table below.

Relative Exposure	Image Density	
	Developer A	Developer B
0	.00	.00
1	.00	.01
2	.04	.05
4	.09	.11
8	.18	.23
16	.32	.41
32	.45	.52

Example II

The following developer concentrate was prepared:

	Gm.
1-phenyl-3-pyrazolidone	6
Hydroquinone	30
Sodium carbonate (anhyd.)	100
Sodium sulfite	100
Benzotriazole	1.7
2-pyrrolidone	22.14
Water to make 1 liter.	

This developer remained clear with no crystallization after storage for 24 hours at 40° F.

Example III

The following developer concentrate was prepared:

	Gm.
1-phenyl-3-pyrazolidone	6
Hydroquinone	30
Sodium carbonate (anhyd.)	100
Sodium sulfite	100
Benzotriazole	1.7
N-methylol pyrrolidone	20
Water to make 1 liter.	

This developer remained clear with no crystallization after storage for 24 hours at 40° F. The same results were obtained when 100 gm. of anti-sludging agent were used.

Example IV

The following developer concentrate was prepared:

	Gm.
1-phenyl-3-pyrazolidone	6
Hydroquinone	30
Sodium carbonate (anhyd.)	100
Sodium sulfite	100
Benzotriazole	1.7
Pyrrolidonyl-4-butyramide	15
Water to make 1 liter.	

This developer remained clear with no crystallization after storage for 24 hours at 40° F. The same results were obtained when 30 gm. of anti-sludging agent were used.

Example V

The following developer concentrate was prepared:

1-phenyl-3-pyrazolidone, gm.	6
N-methyl-2-pyrrolidone, gm.	51.35
Sodium sulfite, gm.	75
2,4-diaminophenol hydrochloride (Amidol), gm.	12
Triethanolamine, ml.	60
Potassium bromide, gm.	9
Water to make 1 liter.	

This developer concentrate shows no tendency to crystallize on prolonged storage at room temperature. If N-methyl-2-pyrrolidone is omitted from the composition, the maximum concentration of 1-phenyl-2-pyrazolidone is reduced to 2.5 gm. per liter and the concentrate develops crystals and sludge on storage at room temperature.

Example VI

Developers of the following composition were prepared:

	Developer A	Developer B	Developer C	Developer D
1-phenyl-3-pyrazolidone.	2.5 gm	2.5 gm	2.5 gm	2.5 gm.
Ascorbic acid	25 gm	25 gm	25 gm	25 gm.
Potassium Carbonate (anhyd).	100 gm	100 gm	100 gm	100 gm.
Ammonium bromide.	10 gm	10 gm	10 gm	10 gm.
Benzotriazole	8 gm	8 gm	8 gm	8 gm.
N-metnyl-2-pyrrolidone.	None	20.54 gm	51.35 gm	102.7 gm.
Water to make	1 liter	1 liter	1 liter	1 liter.

These solutions were used without dilution to develop exposed samples of a silver bromide photographic paper. It was found that developed image density at equal exposure was increased without fog as the concentration of N-methyl-2-pyrrolidone is increased. Image densities are recorded below:

Relative Exposure	Image Density, Developer			
	A	B	C	D
0	.00	.00	.00	.00
1	.01	.02	.03	.08
2	.07	.11	.17	.28
4	.27	.29	.42	.50
8	.50	.55	.64	.83
16	.69	.86	.84	.93
32	.84	.90	.96	1.00

Example VII

Developers of the following composition were prepared:

	Developer A	Developer B
1-phenyl-3-pyrazolidone	6 gm	6 gm.
Hydroquinone	15 gm	15 gm.
Ascorbic acid	25 gm	25 gm.
Potassium carbonate (anhyd.)	100 gm	100 gm.
Sodium sulfite	30 gm	30 gm.
Ammonium bromide	10 gm	10 gm.
Benzotriazole	8 gm	8 gm.
N-methyl-2-pyrrolidone	None	51.35 gm.
Water to make	1 liter	1 liter.

Upon storage at 40° F. for 24 hours, developer A exhibited a large number of crystals. Developer B remained clear.

When these solutions were used without dilution to develop exposed samples of silver bromide photographic paper it was found that developed image density produced by developer B with N-methyl-2-pyrrolidone was higher than that produced by developer A as shown in the following table.

Relative Exposure	Image Density	
	Developer A	Developer B
1	.03	.08
2	.14	.29
4	.32	.57
8	.61	.84
16	.82	.93
32	.89	.98

Example VIII

Developers of the following composition were prepared:

	Developer A	Developer B
1-phenyl-3-pyrazolidone	6 gm	6 gm.
Hydroquinone	5 gm	5 gm.
Chloro-hydroquinone	25 gm	25 gm.
Sodium hydroxide	5 gm	5 gm.
Potassium carbonate (anhyd.)	100 gm	100 gm.
Sodium sulfite	30 gm	30 gm.
Ammonium bromide	10 gm	10 gm.
Benzotriazole	8 gm	8 gm.
N-methyl-2-pyrrolidone	None	102.7 gm.
Water to make	1 liter	1 liter.

Upon storage at 40° F. for 24 hours, developer A showed many crystals and sludge while developer B remained in clear solution.

Image densities obtained when these freshly prepared developers were used without dilution to process an exposed silver bromide photographic paper are shown below.

Relative Exposure	Image Density	
	Developer A	Developer B
1	.01	.10
2	.03	.19
4	.21	.39
8	.49	.69
16	.65	.81
32	.74	.93

Example IX

Developer solutions of the following composition were prepared:

	Developer A	Developer B	Developer C
Metol	1 gm	1 gm	1 gm.
Sodium sulfite (anhyd.)	15 gm	15 gm	15 gm.
Hydroquinone	4 gm	4 gm	4 gm.
Sodium carbonate (anhyd.)	22 gm	22 gm	22 gm.
Potassium bromide	0.6 gm	0.6 gm	0.6 gm.
N-methyl-2-pyrrolidone.	0	20.54 gm	102.7 gm.
Water to make	1 liter	1 liter	1 liter.

These solutions were used without dilution to develop exposed samples of a silver iodo-bromide, variable contrast, projection photographic paper of approximately 3.5% silver iodide and 96.5% silver bromide, of the type described in Potter et al., U.S. 2,280,300. Reflection density readings are listed below:

Relative Exposure	Image Density		
	Developer A	Developer B	Developer C
0	0	0	0
1	.01	.01	.03
2	.03	.05	.11
4	.19	.24	.34
8	.46	.53	.64
16	.83	.91	.95
32	1.22	1.26	1.25

Example X

The effect of N-methyl-2-pyrrolidone in preventing crystallization and sedimentation of a standard photographic developing agent is illustrated below. A developer solution of the following composition was prepared:

	Gram
Metol	6
Sodium sulfite (anhyd.)	90
Hydroquinone	24
N-methyl-2-pyrrolidone	None
Sodium carbonate (anhyd.)	130
Potassium bromide	3.8

Water to make 1 liter.

When this solution was allowed to stand overnight at 40° F., a large volume of precipitate was formed; however, an identical solution to which was added 20.54 gm. of N-methyl-2-pyrrolidone did not form a precipitate under the same conditions.

Example XI

N-methyl-2-pyrrolidone was found to effect improved solubility of color photographic developing agents as well as black-and-white developing agents. The following solution was prepared:

Water	ml	750
Sodium sulfite (anhydrous)	gm	6
Potassium bromide	gm	1
Borax	gm	15
Sodium carbonate	gm	15
Potassium iodide (0.1% by wt., aqueous solution)	gm	15
Polyethylene glycol of molecular weight 4000	gm	3
Sodium thiocyanate	gm	1.5

Dilute with water to 800 ml.

The above solution was divided into two 400 ml. portions:

	Solution A	Solution B
Volume of Solution	400 ml.	400 ml.
Added 3N NaOH	15 ml.	15 ml.
Water	85 ml.	35 ml.
N-methyl-2-pyrrolidone	0	51.35 gm.
p-Aminodiethylaniline hydrochloride	7.5 gm.	7.5 gm.
Water to	500 ml.	500 ml.

One hundred ml. portions were taken from Solutions A and B and labeled A–1, A–2 . . . B–1, B–2, etc. Additional quantities of the color developing agent (p-aminodiethylaniline hydrochloride) were added in the amounts shown below, the pH adjusted to 11.5 with NaOH, and the solutions stirred at room temperature with an electric motor.

Solution:	Additional color developing agent Gram
A–1	0.5
A–2	1.0
A–3	1.5
A–4	2.0
B–1	0.5
B–2	1.0
B–3	1.5
B–4	2.0

It was found that the additional color developing agent dissolved easily in all of the "B" solutions (where N-methyl-2-pyrrolidone was present) after a few minutes stirring and no precipitation was observed after the solution stood at room temperature (72° F.) for 48 hours. However, in none of the "A" solutions was it possible to dissolve the additional developing agent at room temperature.

As shown in the above examples, the concentration of the anti-sludging agent has been varied between 10.27 to 110 grams per liter of developer concentrate and the useful concentration range should extend even beyond these limits.

The concentrated aqueous developers of this invention are advantageously used in processing a wide variety of photographic papers and photographic films. Many products, particularly X-ray films and oscillographic recording papers, are quite commonly processed in a developer solution supplied as a concentrate (to save on shipping weight and storage volume) which is diluted before use. The same advantages apply to solutions used for processing other black and white products (e.g., cine films, graphic arts films, etc.) as well as color papers and films, i.e., positive, negative and reversal color products.

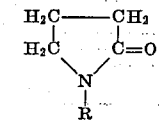
Although the anti-sludging agents have been described as being particularly useful in improving the water solubility of developing agents, it is likely that other difficulty soluble organic compounds can in the same manner, be made to dissolve more readily and to exhibit a reduced tendency to precipitate out of solution.

For convenience in handling and use, it is desirable to prepare concentrated photographic developer solutions to be diluted when needed. It is also desirable, particularly in the case of high speed oscillographic paper processing, to use concentrated developer solutions directly without dilution in order to obtain high activity and short development times.

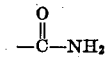
Although the primary advantage of the use of the anti-sludging agents according to this invention is in the preparation of stable developer solution of higher concentrations than could otherwise be prepared, it is obvious from the examples that there are sometimes sensitometric benefits as well, e.g., in improved image density resulting from the use of N-methyl pyrrolidone. No harmful photographic effects on developability are noted from these anti-sludging agents.

What is claimed is:

1. A photographic developing composition comprising an aqueous solution of a silver halide developing agent and about 10 to 110 grams per liter of said solution of an anti-sludging compound having the formula

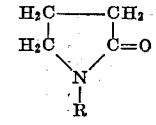


where R is selected from the group consisting of hydrogen, lower alkyl radicals, hydroxy substituted lower alkyl radicals and

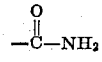


substituted lower alkyl radicals.

2. A photographic developing composition comprising an aqueous solution containing at least a quantity of a silver halide developing agent to give a saturated solution of said developer at 40° F. and about 10 to 110 grams per liter of said solution of an anti-sludging compound having the formula



where R is selected from the group consisting of hydrogen, lower alkyl radicals, hydroxy substituted lower alkyl radicals and



substituted lower alkyl radicals.

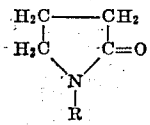
3. A photographic developing composition comprising an aqueous solution containing at least a quantity of a silver halide developing agent to give a saturated solution of said deveolper at 40° F. and about 10 to 110 grams per liter of said solution of the anti-sludging compound N-methyl-2-pyrrolidone.

4. A composition as described in claim **3** where said anti-sludging compound is 2-pyrrolidone.

5. A composition as described in claim **3** where said anti-sludging compound is N-methylol pyrrolidone.

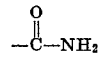
6. A composition as described in claim **3** where said anti-sludging compound is pyrrolidonyl-4-butyramide.

7. A photographic developing composition comprising an aqueous solution of a pyrazolidone developing agent and about 10 to 110 grams per liter of said solution of an anti-sludging compound having the formula



where R is selected from the group consisting of hydro-

gen, lower alkyl radicals, hydroxy substituted lower alkyl radicals and



substituted lower alkyl radicals.

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J. TRAVIS BROWN, *Acting Primary Examiner.*

C. DAVIS. *Assistant Examiner.*