

## UNITED STATES PATENT OFFICE

2,691,589

PHOTOGRAPHIC DEVELOPER  
COMPOSITIONS

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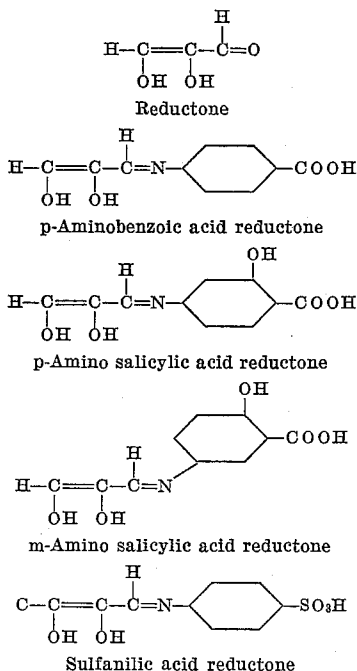
10 Claims. (Cl. 95—88)

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This invention relates to photographic developers and particularly to methods for accelerating the development rate of photographic developing agents.

A class of silver halide developing agents has come under consideration which in themselves are very weak developing agents for silver halide emulsions even under the most favorable conditions for development.

These developing agents are the ene-diol compounds known as the reductones such as the following:



Reference may be made to Chem. Zeit. 75, 21 (1951), for reductone and its derivatives.

We have discovered that the developing rate of developing solutions containing the reductones can be markedly accelerated by the addition to the reductone silver halide developing solutions of 3-pyrazolidone compounds which in themselves are only moderately active developing agents for silver halide. The activity of the resulting developer solution containing both the reductone and the pyrazolidone developing agents is very much greater than would be expected from summing up the separate activities. An added feature of the reductone-pyrazolidone developer compositions resides in the stability of the de-

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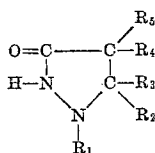
veloping solution. That is, 3-pyrazolidone compounds such as 1-phenyl-3-pyrazolidone are highly unstable in alkaline developer compositions free of a preservative and tend to darken and lose development activity quickly particularly through aerial oxidation. On the other hand, when development is carried out with the 3-pyrazolidone compounds in the presence of the ene-diol compounds, the latter function as preservatives and the developer is highly resistant to discoloration and loss of activity. Another advantageous characteristic of the ene-diol-pyrazolidone developer compositions is that the developers show little tendency for the formation of silver sludge or for the formation of dichroic stain on silver images. A further advantage is that since the ene-diol compounds are very effective preservatives for the pyrazolidone developing agents and are highly soluble in water, it is possible to prepare concentrated developer compositions more readily than in the case where a less soluble preservative such as sodium sulfite is used. A further characteristic of the ene-diol-pyrazolidone developer compositions of the invention resides in the fact that the compositions behave as strong surface latent image developers as opposed to internal latent image developers, as long as they are free of silver halide solvents such as sodium sulfite. That is, developer compositions containing 3-pyrazolidone compounds have been described in the literature but invariably they have been compounded so as to contain a silver halide solvent such as sodium sulfite as a preservative. In order to convert such a developer composition to a surface latent image developer, we have found it to be necessary to dispense with the silver halide solvent in the developer composition. However, as mentioned, the 3-pyrazolidone developers free of preservative are very unstable. When, according to our invention, the ene-diol compounds are incorporated into the 3-pyrazolidone developer compositions, the ene-diol compounds supply the required preservative effect and the surface latent image developer characteristics are maintained. Therefore, the fortuitous choice of 3-pyrazolidone compounds to accelerate the development rate of the ene-diol compounds has resulted in the latter compounds exerting a complementary preservative effect as well as providing a stable 3-pyrazolidone developer system which has surface latent image development characteristics and shows no tendency for physical development. For these reasons, the developers of the invention are very useful in color development processes where a black and white negative

developer is required. As a result of such use in color processes, clean highlights are obtained and the color developed images have increased saturation because of decreased physical development in the negative developer.

An additional unexpected feature of the developers containing the 3-pyrazolidone and ene-diol compounds resides in the fact that similar developer compositions can be prepared in which the pyrazolidone is replaced by a conventional developing agent, for example, containing a mixture of N-methyl-p-aminophenol and reductone, which compositions do not exhibit the mentioned development acceleration effect to any great extent.

The 3-pyrazolidone developer compositions of the invention containing the above ene-diol compounds can be readily converted to internal latent image developer compositions by merely adding a silver halide solvent such as sodium thiosulfate thereto. The resultant internal latent image developer composition, by virtue of the presence of one of the mentioned ene-diol compounds, likewise possesses excellent keeping properties even in the absence of the usual sulfite preservative.

The 3-pyrazolidone silver halide developing agents employed in the developer compositions together with the reductions, have the general structure



in which the R groups each represent various substituents such as hydrogen, alkyl or aryl groups, for example, R<sub>1</sub> can be hydrogen or a group such as alkyl preferably containing from 1 to 4 carbon atoms, or an aryl group of the benzene or naphthalene series substituted or not, and R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> can be hydrogen atoms or alkyl preferably of 1 to 4 carbon atoms or aryl such as phenyl.

The following compounds are representative of 3-pyrazolidone silver halide developing agents which are useful in the developer compositions of the invention:

1. 1-phenyl-3-pyrazolidone
2. 1-p-tolyl-3-pyrazolidone
3. 5-phenyl-3-pyrazolidone
4. 5-methyl-3-pyrazolidone
5. 1-p-chlorophenyl-3-pyrazolidone
6. 1-phenyl-5-phenyl-3-pyrazolidone
7. 1-m-tolyl-3-pyrazolidone
8. 1-phenyl-5-methyl-3-pyrazolidone
9. 1-p-tolyl-5-phenyl-3-pyrazolidone
10. 1-m-tolyl-3-pyrazolidone
11. 1-p-methoxyphenyl-3-pyrazolidone
12. 1-acetamidophenyl-3-pyrazolidone
13. 1-phenyl-2-acetyl-4,4-dimethyl-3-pyrazolidone
14. 1-phenyl-4,4-dimethyl-3-pyrazolidone
15. 1-m-aminophenyl-4-methyl-4-propyl-3-pyrazolidone
16. 1-o-chlorophenyl-4-methyl-4-ethyl-3-pyrazolidone
17. 1-m-acetamidophenyl-4,4-diethyl-3-pyrazolidone
18. 1-(p-β-hydroxyethylphenyl)-4,4-dimethyl-3-pyrazolidone
19. 1-p-hydroxyphenyl-4,4-dimethyl-3-pyrazolidone

20. 1-p-methoxyphenyl-4,4-diethyl-3-pyrazolidone
21. 1-p-tolyl-4,4-dimethyl-3-pyrazolidone
22. 1-(7-hydroxy-2-naphthyl)-4-methyl-4-n-propyl-3-pyrazolidone
23. 1-p-diphenyl-4,4-dimethyl-3-pyrazolidone
24. 1-(p-β-hydroxyethylphenyl)-3-pyrazolidone
25. 1-o-tolyl-3-pyrazolidone
26. 1-o-tolyl-4,4-dimethyl-3-pyrazolidone

The 4,4-dialkyl-3-pyrazolidone compounds 13 to 23 and 26 above are particularly efficacious for use in the developer compositions of our invention inasmuch as they are more active developing agents than are compounds 1 to 12 which contain a single substituent or only hydrogen atoms in the 4-position of the pyrazolidone nucleus. The 4,4-dialkyl-3-pyrazolidone compounds are described and claimed in the Allen et al. U. S. patent application Serial No. 372,148 filed concurrently herewith. The ω-hydroxyalkyl-3-pyrazolidones, for example, compounds 18 and 24 above, are also especially useful in concentrated formulas, in replenishers, and in the presence of high salt concentrations where their increased solubility enables obtaining and holding adequate amounts of the pyrazolidone compound in solution. The compounds are described and claimed in the Allen et al. U. S. patent application Serial No. 372,148 filed concurrently herewith and in the Reynolds and Tinker U. S. patent application Serial No. 372,167 filed concurrently.

The ene-diol compound reductone prepared from glucose by the method of Euler and Martius, Ann. 505, 73-87 (1933) and also obtained from sugars such as galactose, fructose, pentose, lactose, 1-arabinose and levulose by treatment with hot alkali, is a reducing sugar especially valuable for use in the developer compositions of our invention since the development rate of the developers containing the compound is appreciably increased by the presence of the 3-pyrazolidone compounds as will be seen from consideration of the data of the following examples.

#### Example 1

A solution of reductone was obtained from 2 grams of glucose by heating the latter with 2 grams of sodium carbonate in 20 cc. of water at 200 to 210° F. for 16 minutes. 80 cc. of a buffer solution containing 0.1 molar sodium sesquicarbonate and 0.2 molar sodium sulfite was added and the resultant solution adjusted to pH 10.0 with alkali. To 50 cc. of the resulting solution was then added 0.04 gram of 1-phenyl-3-pyrazolidone. The resultant developer was found to be very active, full development of an exposed film to a density of 2.0 being obtained in 5 minutes' development at 68° F.

Reductone prepared by the method of Euler and Martius was utilized in pyrazolidone developers of the following composition:

	A	B	C
Reductone.....	0.0025	0.02	0.02
1-phenyl-3-pyrazolidone.....	0.2	0.2	0.0025
Sodium sulfite.....	0.2	0.2	0.2
Sodium carbonate.....	0.2	0.2	0.2

The quantities of the ingredients in the developer compositions A, B and C are given in terms of moles per liter of solution. Each developer solution was adjusted to pH 10 with acetic acid before use in development of a fine-grain positive film for 4 minutes at 68° F. As a result, developer A developed weakly, producing density 0.42 and

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contrast of .44 with little induction period. The reductone developer B developed only after a considerable induction period to a density of 0.08, whereas the reductone-pyrazolidone developer C developed rapidly with little induction period to produce a strong black image of density 2.64 and contrast 1.7.

#### Example 2

A developer composition was prepared which was free of sulfite so as to provide a surface latent image developer, by heating a solution of 2 grams of glucose in 20 cc. of 0.5 molar sodium hydroxide solution for 90 seconds at 200–210° F. 80 cc. of 0.1 molar sodium sesquicarbonate solution was then added. To the cool solution was then added 0.04 gram of 1-phenyl-3-pyrazolidone. The resultant developer solution was used to develop an exposed film, an image density of 2.34 being obtained in 8 minutes' development at 68° F. The results showed that the developer possessed surface latent image development characteristics and did not produce undesirable physical development.

#### Example 3

20-cc. samples of 0.5 normal sodium hydroxide solution were heated to 200–212° F. and 2-gram samples of the sugars indicated below were added. Each solution was heated at this temperature for 90 seconds and 80 cc. of the sulfite-carbonate buffer solution of Example 5 was added. The pH of each solution was then reduced to 10.0 and the solution used alone and with the addition of 1-phenyl-3-pyrazolidone for development of a film. The following table shows the density obtained for the solutions of ene-diol compounds alone (32 minutes' development) and with 1-phenyl-3-pyrazolidone (8 minutes' development):

Reductone from—	Density	
	Alone (32 min.)	With 1-phenyl- 3-pyrazoli- done (8 min.)
Glucose.....	1.30	2.26
Galactose.....	1.30	2.10
l-Arabinose.....	0.88	2.00
Levulose.....	1.34	2.34
Lactose.....	0.90	2.00

A comparable developer containing only 1-phenyl-3-pyrazolidone as the developing agent was used as a comparison and found to develop the same emulsion to a density of only 0.93 in 8 minutes and 1.5 in 32 minutes.

From the description of the above examples it will be apparent that internal latent image developers have been provided in Examples 1 and 3, whereas Example 2 illustrates a surface latent image developer containing the pyrazolidone and reductone developing agents.

Results similar to those exemplified above are obtained when developer compositions, containing or free of silver halide solvents, are prepared from a mixture of at least one of the mentioned

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pyrazolidone compounds and at least one of the reductone compounds. Particularly valuable developer compositions in addition to those exemplified above are those containing reductone and either a 1-tolyl-3-pyrazolidone such as 1-p-tolyl-4,4-dimethyl-3-pyrazolidone or a 1-(p-hydroxyalkylphenyl)-4,4-dialkyl-3-pyrazolidone, such as 1-(p-β-hydroxyethylphenyl)-4,4-dimethyl-3-pyrazolidone, or a 1-(p-hydroxyalkylphenyl)-3-pyrazolidone such as 1-(p-β-hydroxyethylphenyl)-3-pyrazolidone.

It will be understood that our invention as specified by the claims hereinafter, includes the mentioned developer compositions in either the liquid form exemplified above, or in the dry powder form such as packaged developer formulas suitable for dissolving in water to form a liquid developer. Such dry compositions include the mentioned 3-pyrazolidone compounds, the ene-diol compound, and alkaline material such as sodium carbonate, caustic alkali or sodium perborate.

What we claim is:

1. A photographic developer composition comprising an alkaline material, a 3-pyrazolidone silver halide developing agent and a compound of the group consisting of reductone, p-amino-benzoic acid reductone, m-salicylic acid reductone, p-salicylic acid reductone, and sulfanilic acid reductone.

2. A photographic developer composition comprising an aqueous alkaline solution containing a mixture of a 3-pyrazolidone silver halide developing agent and reductone.

3. A photographic developer composition comprising an aqueous alkaline solution containing a mixture of 1-phenyl-3-pyrazolidone and reductone.

4. The developer composition of claim 2 wherein the designated 3-pyrazolidone is a 4,4-dialkyl-3-pyrazolidone.

5. A photographic developer composition comprising an aqueous alkaline solution containing a mixture of a 1-tolyl-3-pyrazolidone and reductone.

6. A photographic developer composition comprising an aqueous alkaline solution containing a mixture of 1-p-tolyl-4,4-dimethyl-3-pyrazolidone and reductone.

7. A photographic developer composition comprising an aqueous alkaline solution containing a mixture of 1-phenyl-4,4-dimethyl-3-pyrazolidone and reductone.

8. A photographic developer composition comprising an aqueous alkaline solution containing a mixture of 1-(p-β-hydroxyethylphenyl)-3-pyrazolidone and reductone.

9. A photographic developer composition comprising an aqueous alkaline solution containing a mixture of 1-p-tolyl-3-pyrazolidone and reductone.

10. A photographic developer composition comprising an aqueous alkaline solution containing a mixture of 1-(p-β-hydroxyethylphenyl)-4,4-dimethyl-3-pyrazolidone and reductone.

No references cited.