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3,531,289

SILVER HALIDE PHOTOGRAPHIC EMULSIONS IMPROVED BY NEW PRECIPITATION METHODS

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19 Claims

ABSTRACT OF THE DISCLOSURE

An improved process for making developing-out-type silver halide photographic emulsions comprising an initial emulsification and a digestion step wherein the silver halide grains are formed in an aqueous medium in the presence of a peptizer, the improvement comprising the use or presence of a combination of a rhodium salt and an organic thioether silver halide solvent during said emulsification step and said digestion step.

This invention relates to photography and particularly to photographic silver halide emulsions and to methods for making such emulsions and to photographic recording elements comprising such emulsions.

In the art of photographic silver halide emulsion-making it is known that presence of a rhodium salt in the emulsion during initial silver halide emulsification and digestion will cause the emulsion to produce an image of higher contrast upon development than if the rhodium salt were not present. However due to a desensitizing effect on the emulsion by the rhodium salts, this improvement in high contrast is usually accompanied by a substantial loss of photographic speed for the emulsion. See British Pat. No. 775,197.

It is also known that certain thioether compounds are effective as speed increasing sensitizers when added to a photographic silver halide emulsion just prior to or during the after-ripening step in preparation of a silver halide emulsion or just prior to coating of the emulsion. See U.S. Pat. No. 3,021,215.

An object of the present invention is to provide photographic silver halide emulsions of the developing-out type having the improved high-contrast characteristics obtained by presence of a rhodium salt in the initial silver halide grain formation step and with the further improvement that the usually expected loss of sensitivity due to presence of rhodium salts during this grain formation step is reduced or eliminated by means of a thioether compound which is also present with the rhodium salt. Further objects are to provide methods for making such emulsions and to provide photographic recording elements comprising such emulsions.

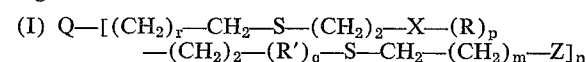
Therefore, in accordance with the objects of the present invention, silver halide photographic emulsions of the developing-out type are prepared by a process comprising an initial emulsification and digestion step wherein silver halide is formed in presence of a rhodium salt and a thioether silver halide solvent. In most of our preferred embodiments, this initial emulsification and digestion occurs in aqueous medium containing gelatin or other suitable peptizer and in our most preferred embodiments the silver halides are silver bromides or silver chlorides or silver chlorobromides or silver bromochlorides. However the objects of the invention will be obtained with various emulsions comprising other combinations of silver bromide, chloride, and iodide. The invention is especially advantageous in making developing-out emulsions and in our most preferred embodiments we prepare projection

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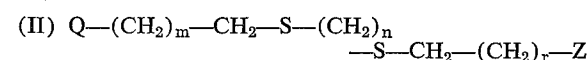
speed silver chlorobromide developing-out emulsions which may be used for making photographic enlarging papers and the like.

A preferred rhodium salt that may be used is ammonium chlororhodate which has the formula $(\text{NH}_4)_3\text{RhCl}_6$. Instead, we may also use any of the other water-soluble rhodium salts which also have the property of increasing contrast in photographic emulsions when present during the initial precipitation of silver halide. Rhodium chloride and rhodium trichloride are other specific examples and other water-soluble salts of rhodium may be used. Usually the rhodium salt is introduced in the emulsion with the soluble halide solution, however, introduction into the precipitation medium by any means will be within the scope of the invention. The rhodium salt will be effective in most cases when used in concentrations ranging from about 0.01 mg. to about 0.25 mg. per mole silver in the emulsion.

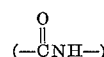
Thioether silver halide solvents that may be present with the rhodium salt during silver halide precipitation are any of the organic thioether silver halide solvents described by C. E. McBride in U.S. Pat. No. 3,271,157 patented Sept. 6, 1966. Aqueous solutions of suitable organic thioether silver halide solvents utilized during the grain growth or formation of the silver halide grains of the present emulsions have a greater solubility for silver chloride than water. More specifically, such thioether silver halide solvents are those which, when utilized in aqueous solutions (60°C.) at 0.02 molar concentration, are capable of dissolving more than twice the amount (by weight) of silver chloride than that which can be dissolved by water at 60°C. These include thioethers having the formulas:



and



wherein: r and m are integers of 0 to 4; n is an integer of 1 to 4; p and q are integers of 0 to 3; X is an oxygen atom ($-\text{O}-$), a sulfur atom ($-\text{S}-$), a carbamyl radical



a carbonyl radical

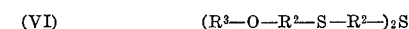
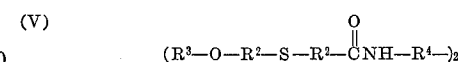
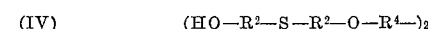
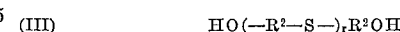


an oxycarbonyl radical



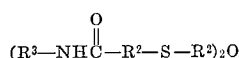
R and R' are ethylene oxide radicals ($-\text{O}-\text{CH}_2\text{CH}_2-$); Q and Z are hydroxy radicals ($-\text{OH}$), carboxy radicals, or alkoxy radicals ($-\text{O}-\text{alkyl}$) wherein the alkyl group has 1 to 5 carbon atoms; and Q and Z can also be substituents described for X linked to form a cyclic compound.

Preferred organic thioether silver halide solvents suitable for forming the emulsions of the invention include compounds represented by the formulas:



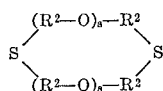
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wherein: r is an integer of 1 to 3; s is an integer of 1 to 2; R^2 is an alkylene radical having 1 to 5 carbon atoms and is preferably ethylene ($-\text{CH}_2\text{CH}_2-$); R^3 is an alkyl radical having 1 to 5 carbon atoms and is preferably ethyl; and R^4 is an alkylene radical having 1 to 5 carbon atoms and is preferably methylene ($-\text{CH}_2-$).

The thioether silver halide solvents are effective in accordance with the objects of the invention in various emulsions wherein the concentration of such thioethers may range from about 1 gram to about 50 grams per mole silver in the emulsion.

The invention will be better understood by reference to the following detailed examples which describe a preferred embodiment of the invention and include our presently most preferred mode of carrying out the invention.

EXAMPLE I

Emulsion A—A 60:40 silver chlorobromide gelatin emulsion was prepared using a conventional "double-jet" emulsification and digestion technique. An aqueous solution of potassium chloride and potassium bromide in ratio of 60 parts chloride, 40 parts bromide, and a second aqueous solution of silver nitrate sufficient to precipitate the halides with slight halide excess were simultaneously added to an aqueous gelatin solution at 75° C. with rapid stirring. The emulsion was then washed by a conventional water rinse method to thoroughly remove soluble components from the emulsion. The emulsion was then re-dispersed with total gelatin content of 300 gm./mole silver and sulfur sensitized with 6 mg. sodium thiosulfate per mole silver. The emulsion was ripened 5 minutes at 60° C., then conventional adjuvants such as hardeners, coating aids and spectral sensitizing dyes were added. Then the emulsion was coated on a paper support at a coverage of 200 mg. of silver per square foot.

Emulsion B was prepared the same as Emulsion A except 0.09 mg. of ammonium chlororhodate, $(\text{NH}_4)_3\text{RhCl}_6$, per mole silver was added to the aqueous solution of potassium chloride and, potassium bromide prior to running into the gelatin solution.

Emulsion C was prepared the same as Emulsion A except 1.0 g. of 1,8-dihydroxy-3,6-dithiaoctane per mole silver was added to the potassium chloride-potassium bromide solution prior to running into the gelatin solution.

Emulsion D was prepared the same as Emulsion A except 0.09 mg. of ammonium chlororhodate and 1.0 g. of 1,8-dihydroxy-3,6-dithiaoctane per mole of silver halide were added to the aqueous solution of potassium chloride and potassium bromide prior to running into the gelatin solution.

Samples of each of the above coatings were exposed on an intensity scale sensitometer and processed for 1½ minutes in Kodak D72 developer with the following results:

	Relative Speed	Contrast
Emulsion Type:		
A.....	100	2.60
B.....	77	3.20
C.....	199	1.81
D.....	100	3.10

These results demonstrate that presence of a rhodium salt and an organic thioether silver halide solvent together in the initial emulsification and digestion step of making the emulsion produces increase in contrast with reduction or elimination of speed loss.

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EXAMPLE II

An emulsion was prepared and coated as described for Emulsion D above and Emulsion E was prepared by the same procedure except it was sulfur and gold sensitized using sodium thiosulfate as the sulfur sensitizer as before and 8 mg. potassium chloroaurate per mole silver as a gold sensitizer. A sample of each of the emulsion coatings was exposed and processed as in Example I except the coatings were developed for 5 minutes instead of 1½ minutes. The following results were obtained:

	Relative Speed	Contrast	Development Fog
Emulsion Type:			
D (sulfur sensitized).....	94	4.76	0.18
E (sulfur and gold sensitized).....	123	4.28	0.01

These results demonstrate that the sulfur and gold sensitized emulsion is not only faster than the sulfur sensitized emulsion but also has much lower fog, which was an unexpected advantage.

EXAMPLE III

An emulsion was prepared and coated the same as Emulsion E. A second emulsion coating was made (Emulsion F) in which 10 g. of zinc nitrate and 6 g. of cadmium chloride per mole of silver halide were added to the emulsion just prior to coating. A sample of each coating was exposed and processed as described in Example II with the following results:

	Relative Speed	Contrast
Emulsion Type:		
E.....	125	4.25
F.....	300	4.80

These results demonstrate an unexpected speed increase which was obtained by the addition of a divalent metal salt such as cadmium and zinc salts to the emulsions of the invention.

The silver halide emulsions prepared in accordance with this invention may be sensitized using any of the well-known techniques in emulsion-making, for example, by digesting with naturally-active gelatin or with chemical sensitizers of the "sulfur group" comprising various sulfur, selenium, and tellurium compounds, and also with gold compounds. The emulsions can be sensitized with salts of noble metals of Group VIII of the Periodic Table which have an atomic number greater than 100. Sensitizers of the "sulfur group" mentioned above are described in more detail in U.S. Pat. No. 1,574,944 patented Mar. 2, 1926, U.S. Pat. No. 1,623,499 patented Apr. 5, 1927, and U.S. Pat. 2,410,689 patented Nov. 5, 1956.

If desired, antifoggants can be added to the emulsion either prior to chemical sensitization or after chemical sensitization. Suitable antifoggants include the azaindenes, azoles, nitroindazoles, thiazoles, thiazolium salts, mercury compounds, and the like.

In making silver halide photographic emulsions in accordance with the invention, the emulsification and digestion step as defined may be carried out in any suitable manner, for example, by any of the conventional precipitation mechanisms including those called the *single-jet* method and the *double-jet* method. The rhodium salt and the thioether solvent, either or both, may be present in the mixing vessel from the start or either or both may be introduced in the same stream or separate streams that are introduced into the vessel during the emulsification and digestion process during which the silver halide grains are being formed. The invention is effective in accordance with the objects of the invention in making neutral emul-

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sions, and we intend to cover those ammoniacal emulsions embodying the invention. The invention will be found effective in making many kinds of emulsions of the developing-out type which may be varied or modified by a variety of after-ripening and coating procedures and the like following the initial precipitation and rinsing steps.

Emulsions made in accordance with the invention are subject to most of the known treatments with chemical and optical sensitizers for increasing sensitivity and broadening spectral response of the emulsions. The emulsions may comprise peptizers such as gelatin or other protective colloids and may comprise gelatin as a binder as well as other suitable colloid binders. A variety of photosensitive recording elements may comprise one or more layers of developing-out emulsions made in accordance with the invention, such as photographic printing papers and films, color printing papers and films, and other papers, films and plates adapted for a variety of photographic uses.

It will be understood that modifications and variations may be made within the scope of the invention as described above and as defined in the following claims.

I claim:

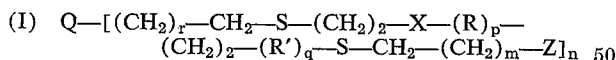
1. In a process of making a developing-out-type silver halide photographic emulsion comprising an initial emulsification and digestion step wherein silver halide grains consisting of at least one silver halide selected from silver chlorobromide, silver bromochloride and silver chloride are formed in aqueous medium in presence of a peptizer, the improvement wherein there are present together in said solution during said emulsification and digestion step a rhodium salt and an organic thioether silver halide solvent, an aqueous solution of said thioether at a 0.02 molar concentration being capable of dissolving more than twice the amount of silver chloride than that which can be dissolved by water at 60° C.

2. A method defined by claim 1 further comprising the step, following said emulsification and digestion step and before any further ripening, of thoroughly rinsing away water-soluble materials present in the emulsion by means of a water rinse.

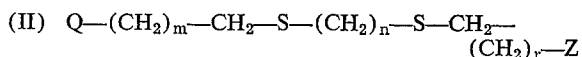
3. A method defined by claim 1 wherein said rhodium salt is ammonium chlororhodate.

4. A method defined by claim 1 wherein said rhodium salt is rhodium chloride.

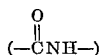
5. A method defined by claim 1 wherein said thioether silver halide solvent is selected from compounds having the formulas:



and



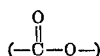
wherein: r and m are integers of 0 to 4; n is an integer of 1 to 4; p and q are integers of 0 to 3; X is an oxygen atom ($-O-$), a sulfur atom ($-S-$), a carbamyl radical



a carbonyl radical



or an oxycarbonyl radical

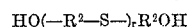


R and R' are ethylene oxide radicals ($-O-CH_2CH_2-$); Q and Z are hydroxy radicals ($-OH$), carboxy radicals or alkoxy radicals ($-O-alkyl$) wherein the alkyl group

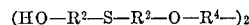
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has 1 to 5 carbon atoms; and Q and Z can also be substituents described for X to form a cyclic compound, and

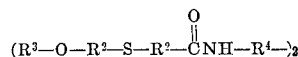
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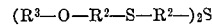
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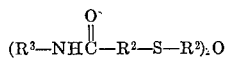
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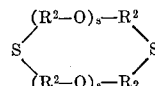
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and

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wherein: r is an integer of 1 to 3; s is an integer of 1 to 2; R^2 is an alkylene radical having 1 to 5 carbon atoms; R^3 is an alkyl radical having 1 to 5 carbon atoms; and R^4 is an alkylene radical having 1 to 5 carbon atoms.

6. A method defined by claim 1 wherein said thioether solvent is 1,8-dihydroxy-3,6-dithiaoctane.

7. A method defined by claim 1 wherein said rhodium salt is present in concentrations in the range from 0.01 to 0.25 mg. per mole silver in the emulsion.

8. A method defined by claim 1 wherein said organic thioether silver halide solvent is present in a concentration in the range from about 1 to about 50 grams per mole silver in the emulsion.

9. A method defined by claim 1 wherein chloride and bromide are present in the ratio of 60 mole percent chloride, 40 mole percent bromide expressed as percentages of the total silver halide present in the emulsion.

10. A photographic silver halide emulsion prepared by a method defined by claim 1.

11. A photographic silver halide emulsion prepared by a method defined by claim 1, said emulsion also being one which has been chemically sensitized by a sulfur group chemical sensitizer.

12. An emulsion defined by claim 11 wherein said chemical sensitizer is a sulfur compound.

13. An emulsion defined by claim 11 wherein said chemical sensitizer is a selenium compound.

14. An emulsion defined by claim 11 wherein said chemical sensitizer is a tellurium compound.

15. An emulsion defined by claim 11 and further being one also chemically sensitized by presence of a gold compound sensitizer.

16. A photographic silver halide emulsion prepared by a method defined by claim 1 and further being one sensitized by presence of at least one divalent metal salt.

17. An emulsion defined by claim 16, said divalent metal salt being selected from zinc and cadmium salts.

18. An emulsion defined by claim 17 wherein said divalent metal salt is zinc nitrate.

19. An emulsion defined by claim 18 wherein said divalent metal salt is cadmium chloride.

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J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

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