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PREPARATION OF SILVER HALIDE EMULSIONS HAVING HIGH COVERING POWER

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ABSTRACT OF THE DISCLOSURE

A method of improving the covering power in a fine-grain silver halide emulsion wherein the halide is predominantly chloride, wherein said method comprises precipitating silver halide crystals and adding an azaindene compound at a concentration of at least 0.5 gram of azaindene per mole of silver to the silver halide emulsion within about 4 minutes after the initial precipitation of said silver halide.

This invention relates to photography and in one aspect relates particularly to improved photographic silver halide emulsions and improved photographic recording elements comprising such emulsions.

It is known that certain purine bases such as adenine, added to a silver halide emulsion at a point during the period of grain growth in making of the emulsion will effectively inhibit grain growth from the time at which the nucleic acid is introduced (see Klein and Moisar, Berichte der Bunsengeselleschaft 67(4), pages 349–55, 1963). It is also known that a very small proportion of certain azaindene compounds added with reactants in the initial silver halide precipitation will inhibit certain types of chemical ripening in making of predominantly bromide photographic silver bromoiodide emulsions, see Wartburg U.S. Pat. No. 3,156,564, patented Nov. 10, 1964, Example 1. Use of certain tetrazaindenes as antifoggant addenda in photographic emulsions is disclosed in U.S. Pat. No. 2,784,091, patented Mar. 5, 1957.

An object of the present invention is to produce fine grain emulsions having increased covering power and improved developed silver density per mole of available silver in a given emulsion. *Covering power* is defined as the ratio of optical density to mass of developed silver per unit area for a developed photographic image. *Silver efficiency* of a silver halide emulsion may be defined as the ratio of the mass of developed silver at D_{max} to the mass of silver available for development in a given emulsion. From these relationships, it will be seen that the value of maximum optical density per mole of available silver as silver halide in a given emulsion, is a function of both covering power and silver efficiency.

I have found that with predominantly silver chloride emulsions, addition of an azaindene grain growth restrainer very early in the grain formation period in the making of silver halide emulsions will increase covering power of the emulsion and that the earlier in the period of grain growth that the restrainer is added, the greater will be the improvement in covering power. However, I find that these restrainers tend to decrease silver efficiency when present initially or very early in the precipitation and conversely, I find that silver efficiency is increased as the time for crystal formation is extended before addition of the restrainer. I find, therefore, that maximum optical density per mole of silver halide available for development in a given emulsion is attained by adding the azaindene at an optimum time after the initial mixing of silver halide forming reactants, that is, after the point at which silver halide precipitation is initiated. I have found that some improvement in density will be obtained by adding the azaindene restrainer at any time within a period from about 5 seconds to about 4 minutes after initial mixing of the reactants, the exact optimum time within this period depending upon the particular emulsion and to some extent upon the mixing means.

In accordance with the present invention therefore, for a given silver chlorohalide emulsion maximum optical density of the developed image is increased by an azaindene compound having an acidic hydrogen on the molecule, available for formation of a silver salt, added to the emulsion within a defined period immediately after precipitation of silver halide has commenced.

Preferably, the silver halide emulsion is one in which silver chloride constitutes at least one-half of the total silver halide present. I may use any azaindene compound which has an acidic hydrogen atom available for formation of the silver salt of the azaindene compound in aqueous solutions. Especially useful are tetrazaindenes of this type, for example, hydroxy tetrazaindenes and amino tetrazaindenes such as those described in U.S. Pats. 2,444,605, 2,444,607, patented July 6, 1948. Also, I may use tetrazaindenes of kinds described in U.S. Pat. No. 2,444,609, patented July 6, 1948 and U.S. Pat. 2,450,397, patented Sept. 28, 1948. Also, I may use pentazaindenes and any other azaindenes that form a silver salt with silver ion in aqueous solution.

My theory of the function of the azaindene is that in solution with silver ion it forms an insoluble silver salt which attaches itself, probably by adsorption, to the silver halide crystal surfaces and there effectively inhibits further crystal development. I have not proved this theory and I do not depend upon this theory for patentability of the invention.

I have found that selected azaindenes I have used have produced optimum developed image density in most cases when added in the period from about 30 seconds to about 2 minutes after initial mixing of the silver halide forming reactants. To achieve any effective improvement, it is usually necessary to use a concentration greater than 0.5 gram of the azaindene per mole silver in the emulsion and in my preferred embodiments I have used concentrations in the range from about 2 to about 5 grams azaindene per mole silver. The invention can be better understood by reference to the following detailed examples which describe specific embodiments of the invention and set forth the best mode now contemplated for carrying out the invention.

EXAMPLE I

A series of silver chloride emulsions were prepared by a continuous process. Into a mixing chamber were continuously added an aqueous solution of sodium chloride in one stream and an aqueous solution of silver nitrate in another stream. The aqueous solution of sodium chloride contained 35 g. sodium chloride plus 125 g. of gelatin per liter of solution. The aqueous solution of silver nitrate contained 97 g. silver nitrate and 127 g. gelatin per liter of solution. Flow rates of each solution to the mixing chamber were 1,000 ml. per minute at 110° F. In the mixing chamber, the solutions were thoroughly mixed causing formation of silver chloride crystals. When filled, the mixing chamber contained about 100 ml. The silver halide gelatin emulsion was removed continuously from the chamber at a flow rate of 2,000 ml. per minute at 105° F. The emulsion was pumped to storage, and just prior to entry of the emulsion stream into storage tanks, about 30 seconds after leaving the mixing chamber, there was added to the emulsion stream at a rate of 3 g. per mole silver, the compound 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, added in aqueous solution as the sodium salt.

A photographic element comprising the emulsion just described was prepared by first coating on a paper sup-

port a gelatin layer containing incorporated developing agents at a laydown at 164 mg. gelatin, 3.7 mg. phenyl-3-pyrazolidone and 28 mg. of hydroquinone per square foot. Over this incorporated developer layer was coated the silver halide emulsion prepared as described above which was removed from storage after several hours. The emulsion was coated at a laydown of 125 mg. gelatin and 45 mg. sliver per square foot. The emulsion coatings were chill set and dried and samples cut from the coated element were tested photometrically by exposing in a sensitometer, processing in an alkaline bath for about 3 seconds at 75° C., and stabilizing in aqueous thiosulfate solution, as described in Broughton and Woodward U.S. Pat. 2,614,917. A control emulsion was made coated and tested exactly as just described, except no tetrazaindene was added in the emulsion. An appreciable increase in D_{max} and covering power, caused by the tetrazaindene, is illustrated by the following sensitometric results obtained with the test and control emulsions in the tests just described.

	Contrast	Relative speed	D_{max}	Covering power
Control	.48	100	0.75	16.7
Tetrazaidene added	.79	44	1.15	25.7

Other known grain growth restrainers such as cadmium nitrate and 1-phenyl-5-mercaptotetrazole were substituted for tetrazaindene in the process and the samples were tested by exactly the same procedures described above and no increase in D_{max} and covering power was observed. Other emulsions were made, coated and tested as described except varying the concentration of sodium chloride in the reaction mixture and in every case the azaindene produced increase in covering power.

EXAMPLE II

Instead of the continuous process of Example I, a batch process was used to prepare a silver chloride-gelatin emulsion. To 1000 ml. of 15 percent gelatin aqueous solution at 110° F. were added simultaneously and rapidly, also at 110° F., two 1500 ml. aqueous solutions, the first such solution being a mixture of 400 ml. of 17.5 percent NaCl aqueous solution and 1100 ml. of 15 percent gelatin aqueous solution, the second being a mixture of 300 ml. of 65 percent $AgNO_3$ aqueous solution and 1200 ml. of 15 percent gelatin aqueous solution. A portion of this emulsion was separated and to this portion 3 grams of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene per mole silver was added two minutes after first mixing of the solutions. The two emulsions were coated and tested as described in Example I, with the following results.

	Contrast	Relative Speed	D_{max}	Covering Power
Control sample (no azaindene)	.31	100	0.56	14.5
Test sample (tetrazaindene added as described)	.56	269	1.05	13.4

Improved D_{max} and covering power, obtained by addition of azaindenes as demonstrated in the above examples, is similarly obtained by use of other azaindenes having acidic hydrogen on the molecule, for example, by use of:

4-hydroxy-6-methyl-1,2,3,3a,7-pentazaindene,
4-hydroxy-6-methyl-2-methylmercapto-1,3,3a,7-tetrazaindene,
adenine, and the like.

The relative improvement in covering power increases generally as the concentration of azaindene increases from about 0.5 gram to about 5 grams per mole silver in the silver halide emulsion. At concentrations below this range, the improvement is hardly appreciable. Increase in concentration above this range does not normally cause a corresponding further increase in covering power, although such increased concentrations beyond 5 grams per mole silver may cause some increase in photographic speed.

The azaindenes, used as described, are effective for increasing covering power and contrast and D_{max} of emulsions hypersensitized with various chemical and spectral sensitizers, e.g. emulsions sensitized with thiourea sensitizers and other sulfur-type sensitizers, sensitizing dyes such as sulfo- and carboxy-substituted merocyanine dyes, various cyanine and carbocyanine sensitizing dyes, and the like.

Silver chlorohalide emulsions exhibiting improved covering power as a result of practicing this invention can contain, in addition to the azaindene, various other addenda such as various hardeners, toners, desensitizers, spectral sensitizers, cationic, anionic, and non-ionic surfactants, chemical sensitizers to increase speed or contrast or both, and the like.

The improvement in covering power is most pronounced in silver halide emulsions containing high concentrations of silver chloride, preferably more than 50 mole percent of the total silver halide present in the emulsion. These include 100 percent chloride emulsions as well as mixtures of bromide or iodide or both with chloride.

Compounds such as rhodium ammonium chloride may be present in the emulsion at the time the silver salts are initially precipitated or added later as modifiers of sensitometric characteristics. Also, if desired, other compounds such as toners, hardeners, surfactants, and the like may be added to the emulsions.

The invention comprises use of the azaindenes for improving covering power of silver halide emulsions made with gelatin and with other film-forming colloids useful as peptizers or binders for silver halide emulsions, for example, with various vinyl copolymers that include acrylamide or comprise polymerized vinyl compounds such as water-insoluble polymers of alkyl acrylates or methacrylates and with other suitable natural and synthetic polymeric vehicles, and the like.

Emulsions made in accordance with this invention may be coated on any suitable photographic support, such as glass, film and paper supports, including such supports having suitable subbing layers, adhesive layers, antistatic layers, antihalation layers, and the like. In the examples we have shown a preferred embodiment in which the emulsion is coated on a support comprising an incorporated developer layer. Instead of the incorporated developing agent shown we may use any developing agent suitable for use in incorporated developer layers, such as hydroquinone and substituted hydroquinones, aminophenols and substituted aminophenols, phenylenediamines, heterocyclic ring developing agents, and the like.

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. A method of improving covering power and maximum developed density per mole silver available in a fine-grain silver halide photographic emulsion in which silver chloride constitutes at least 50 mole percent of the total silver halides present said method comprising the steps of

(A) precipitating silver halide crystals in aqueous emulsion comprising a colloid binder and

(B) adding to said emulsion within about 4 minutes after initial formation of silver halide crystals therein, an azaindene compound having an acidic hydrogen atom available for formation of a silver salt of the azaindene compound, at a concentration of at least about 0.5 gram azaindene per mole silver.

2. The method defined by claim 1 wherein said azaindene is a hydroxy azaindene.

3. The method defined by claim 2 wherein said azaindene is a hydroxy tetrazaindene.

4. The method defined by claim 2 wherein said azaindene is a hydroxy pentazaindene.

5. The method defined by claim 3 wherein said azaindene is 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene.

6. The method defined by claim 1 wherein said azaindene is an amino azaindene.

7. The method defined by claim 6 wherein said azaindene is adenine.

8. The method of claim 1 wherein said silver halide emulsion is a silver chloride emulsion.

9. The method of claim 1 wherein said binder is gelatin.

10. The method defined by claim 1 wherein said azaindene is added in the period from 5 seconds to 4 minutes after initial mixing of the silver halide forming reactants.

11. The method of claim 1 wherein said azaindene compound is added in a period from 30 seconds to two minutes after initial mixing of the silver halide forming reactants.

12. The method of claim 1 wherein said silver halide consists essentially of silver chloride, said colloid binder

consists essentially of gelatin, and said azaindene is 4-hydroxy-6-methyl-1,3,3a,1-tetrazaindene which is added from 30 seconds to 2 minutes after initial mixing of the silver halide forming reactants.

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J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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Inventor(s) Raymond L. Halwig

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 32, "Bunsengeselleschaft" should read --Bunsengesellschaft--. Column 3, line 8, "sliver" should read --silver--; line 14, after "made", insert --,--; line 56, in the table, under heading of Dmax, "0.56" should read --0.65--; line 58, in the table, under heading of Covering Power, "13.4" should read --23.4--. Column 4, line 62, after "present", insert --,--. Column 6, line 2, that portion of formula reading "-1,3,3a,1-" should read -- -1,3,3a,7- --.

SIGNED AND
SEALED
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(SEAL)
Attest:

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