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SILVER HALIDE EMULSIONS

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This invention pertains to colloid silver halide emulsions of enhanced speed and contrast. More particularly it pertains to colloid silver halide emulsions which contain very small amounts of gold and iron salts and to their preparation.

An object of this invention is to provide new sensitized colloid silver halide emulsions. Another object is to provide such emulsions which have good speed and contrast. A further object is to provide such emulsions from readily available inorganic compounds.

It has been found that colloid silver halide emulsions which have good speed and contrast and low fog levels can be made by adding small amounts of water-soluble iron salts, particularly ferric salts such as ferric nitrate, to colloid silver halide emulsions which contain very small amounts of gold or gold and mercury. The emulsions are further sensitized by the addition of a sulfur sensitizer, e. g., sodium thiosulfate, allyl isothiocyanate, thiourea, or an N-substituted thiourea. In the case of gelatin which contains an adequate amount of naturally occurring sulfur compounds, it is not necessary to add a sulfur sensitizer.

The amount of sulfur sensitizer will vary depending on the chemical constitution of the particular compound used. In the case of sodium thiosulfate, the amounts may range from 1.73 to 9.2 mg. per 765 g. of silver nitrate used in making the emulsion which corresponds to 486 g. of silver based on the element in the final emulsion. Equivalent amounts of other sulfur sensitizers can be used.

The amount of gold and mercury which may be present will vary depending upon the particular salt used. In the case of the preferred salts, chlorauric acid ($AuCl_3 \cdot HCl \cdot 4H_2O$) is used in an amount of 1.34 to 5.33 mg., and mercuric chloride is used in an amount of 1.32 to 1.97 mg. per 765 g. of silver nitrate, or based on the silver present in the emulsion, the mol per cents of the two components are respectively .0000723 to .000288 for gold and .000108 to .000162 for mercury.

It has been found that the amount of iron salts which can be added is not critical. Once the optimum sensitization level is obtained with the gold and iron or gold, mercury and iron salts, the addition of relatively large quantities of iron salts does not result in a decrease in sensitivity. From 3.0 to 200.0 mgs. and, preferably 3.93 to 31.44 mgs. of hydrated ferric nitrate, is used per 765 g. of silver nitrate used in making the emulsion. Based on the amount of silver in the emulsion, the amounts are .0002165 to .0110 mol per cent of iron. In the case of other salts. the amounts are, of course, used in chemically equivalent amounts. Suitable additional salts are ferric chloride, ferric sulfate, ferric ammonium sulfate, ferrous nitrate and ferrous chloride.

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The gold and iron or mixture of gold, iron and mercury are preferably added to the colloid silver halide emulsions after the silver salts have been formed. The washed emulsion is liquefied and the sulfur sensitizer added if necessary. An aqueous solution of chlorauric acid or of chlorauric acid and mercuric chloride, for example are added in an amount sufficient to introduce the above-prescribed quantities of such compounds. An aqueous solution of the water-soluble iron salt, e. g., ferric nitrate, is added. The emulsion is then digested for a suitable time to obtain the maximum sensitivity and coated onto a suitable support to form a thin light-sensitive layer. An optical sensitizing dye, e. g., a cyanine, carbocyanine, merocyanine, pseudocyanine, or styryl dye, can be added to the emulsion prior to or subsequent to digestion, if desired.

The invention will be further illustrated but is not intended to be limited by the following examples:

Example I

A silver halide dispersion in inert gelatin containing 5.0% silver iodide and 95.0% silver bromide and a carbocyanine sensitizing dye was divided into samples equivalent to 0.15 mol of silver halide each. Additions as tabulated below were made and the samples digested to maximum light sensitivity. The emulsion samples were coated on film base in a thin layer and dried. Samples of said film elements were then exposed in a type IB sensitometer, and developed in a developer of the following composition:

	Grams
N-methyl-para-aminophenol sulfate	2.5
Hydroquinone	3.0
Sodium sulfite (anhydrous)	75.0
Borax	5.0
Water to 1.0 liter	

for nine minutes at 68° F. with the results listed in the following table:

[Concentration of solutions: 6×10^{-5} molar]

Sample	Sodium Thiosulfate	Chlorauric Acid	Ferric Nitrate	Mercuric Chloride	Relative Speed	Gamma	Fog
	Cc.	*Cc.*	*Cc.*	*Cc.*			
1					31	.45	.01
2	23.0				151	1.08	11
3	23.0	22.0			76	.63	.06
4	23.0	7.3	30.0		263	.93	.05
5	23.0	7.3	30.0	2.7	282	1.02	.05
6	23.0	7.3	15.0	2.7	246	.79	.04
7	23.0	7.3	15.0		302	.79	.06
8	23.0		30.0		162	1.03	.12
9			30.0		33	.45	.02
10		7.3	30.0		19	.42	.01

The samples described in the above table were aged in an oven maintained at a temperature

of 120° F. for one week with the results given in the resulting table:

Emulsion No.	Relative Speed	Gamma	Fog
1	17	.40	.02
2	123	.86	.10
3	151	.67	.06
4	214	.69	.10
5	246	.77	.12
6	214	.61	.10
7	238	.59	.14
8	123	.82	.13
9	15	.30	.02
10	14	.31	.02

Example II

An emulsion similar to that of Example I was prepared and divided into separate portions. Ferric nitrate was added to one portion in the same quantity as described in Example I. Ferrous sulfate in an equivalent quantity on a valence basis was added to another portion. The emulsions were then coated, exposed and developed as in Example I. The sensitometric results obtained on testing the film samples are set forth in the following table:

Sensitizing Adjuvant	Relative Speed	Gamma	Fog
$FeSO_4$	229	.76	.10
$Fe(NO_3)_3$	229	.74	.10

It will be seen from the table that the ferrous and ferric salts give substantially identical data.

This invention is not limited to the use of gelatin as the binding agent for the silver halides. On the contrary, other hydrophilic colloids can be used. Suitable colloids include agar-agar, polyglycuronic acids, zein, collodion, water-soluble cellulose derivatives, such as substantially hydrolyzed cellulose acetate, cellulose esters of hydroxy monocarboxylic acids, e. g., lactic or glycolic acids, alkali metal salts of cellulose esters of dicarboxylic acids, such as phthalic acid, polyvinyl alcohol, partially hydrolyzed polyvinyl acetate and interpolymers thereof with unsaturated materials such as styrene, maleic acid, etc., water-soluble polyvinyl acetals and other hydrophilic synthetic or natural resins and polymeric compounds. Suitable hydrophilic colloids of the above types are described in United States Patents 2,110,491, 2,276,322, 2,276,323, 2,286,215 and 2,211,323.

The invention moreover is not limited to the specific light-sensitive material described in the above-detailed examples. On the contrary various other simple and mixed silver halides may be used as the light-sensitive materials in like manner. Mixtures of silver bromides, chlorides, and/or iodides can be made by adding mixtures of soluble salts of these halides in like manner.

An advantage of the invention is that it provides a simple and effective method of increasing the speed and contrast of photographic emulsions. A further advantage is that the increase of speed obtained does not disappear on aging. A still further advantage is that increases in speed and contrast are attained without increases in fog.

As many widely different embodiments of the invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited except as defined by the claims.

What is claimed is:

1. A colloid silver halide emulsion containing water-soluble gold and iron salts in such proportions that the emulsion contains .0000723 to .000288 mol per cent of gold and .0002165 to .0110 mol per cent of iron, based on the silver content of such emulsion.

2. A gelatin silver halide emulsion containing water-soluble gold and iron salts in such proportions that the emulsion contains .0000723 to .000288 mol per cent of gold and .0002165 to .0110 mol per cent of iron, based on the silver content of such emulsion.

3. A gelatin silver halide emulsion containing water-soluble gold and iron salts in such proportions that the emulsion contains .0000723 to .000288 mol per cent of gold, .0002165 to .0110 mol per cent of iron, and further containing .00027 to .00135 mol per cent of a sulfur sensitizer, based on the silver content of such emulsion.

4. A gelatin silver halide emulsion containing water-soluble gold, mercury and iron salts in such proportions that the emulsion contains .0000723 to .000288 mol per cent of gold, .000108 to .000162 mol per cent of mercury, .0002165 to .0110 mol per cent of iron, and further containing .00027 to .00135 mol per cent of sodium thiosulfate, based on the silver content of such emulsion.

5. A gelatin silver iodobromide emulsion predominating in silver bromide and containing water-soluble gold, mercury and iron salts in such proportions that the emulsion contains .0000723 to .000288 mol per cent of gold, .000108 to .000162 mol per cent of mercury, .0002165 to .0110 mol per cent of iron, and further containing .00027 to .00135 mol per cent of sodium thiosulfate, based on the silver content of such emulsion.

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