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SILVER HALIDE EMULSIONS

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This invention pertains to the sensitization of colloid silver halide emulsions with mixtures of heavy metal salts. More particularly it pertains to gelatino silver halide emulsions which are sensitized with a mixture of gold, palladium and mercury salts.

An object of this invention is to provide colloid silver halide development type emulsions which have improved speed and contrast. A related object is to produce such emulsions which have relatively low fog levels. A further object is to produce such emulsions with relatively available simple chemicals. Still other objects will be apparent from the following description of the invention.

The photographic emulsions of this invention are of the development type and consist of a silver halide suspension in a hydrophilic colloid binding agent, e. g., gelatin, which contains small amounts of a sulfur sensitizer and very small amounts of gold, palladium and mercury. The sulfur sensitizer may be one of the naturally occurring sulfur compounds which are present in photographic gelatin or they may be added sulfur compounds, e. g., sodium thiosulfate, sodium thiocyanate, allylthiourea, allyl isothiocyanate, etc.

The amount of gold, palladium and mercury salts which may be added to the emulsions will vary. 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.; palladium chloride ($PdCl_2 \cdot 2H_2O$) is used in an amount of 1.0 to 9.33 mg., and mercuric chloride is used in an amount of 1.32 to 1.97 mg. per 765 g. of silver nitrate used in making the original emulsions or based on the silver present in the emulsion (i. e., 486 g.). The mol per cents of the gold, palladium and mercury as elements are respectively .0000723 to .000288 for gold, .000104 to .000975 for palladium, and .000108 to .000162 for mercury. Other salts can be used in chemically equivalent amounts.

The amount of sulfur sensitizer will also vary depending on the chemical constitution of the particular compound used. In the case of sodium

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thiosulfate, the amounts may range from 1.73 to 9.2 mg. per 486 g. of silver in the emulsions. Photographically equivalent amounts of other sulfur sensitizers can be used.

The gold, palladium and mercury salts are added to the colloid silver halide emulsions after the silver salts have been precipitated and the water-soluble salts have been removed. The set and washed emulsion is liquefied, the small amount of sulfur sensitizer is added, and the emulsion adjusted to a pH from 5.5 to 6.5. A mixture of chlorauric acid, palladium chloride and mercuric chloride is added to the emulsion from an aqueous solution. 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 photographic gelatin containing 7.5% silver iodide and 92.5% silver bromide and a sensitizing dye was divided into samples equivalent to 0.15 mol of silver halides each. Additions as tabulated below were made and the samples were digested until they reached the maximum light sensitivity. The resulting 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, developed in a developer of the following composition:

N-methyl-para-aminophenol sulfate	g.	2.5
Hydroquinone	g.	3.0
Sodium sulfite (anhydrous)	g.	75.0
Borax	g.	5.0

Water to 1 liter.

for 9 minutes at 68° F. with the results listed in the following table:

$Na_2S_2O_3$ 6×10^{-5} Molar, cc.	Chlorauric Acid 6×10^{-5} Molar, cc.	Palladium Chloride 6×10^{-5} Molar, cc.	Mercuric Chloride 6×10^{-5} Molar, cc.	Relative Speed	Gam.	Fog
23.0	7.3	16.0	8.1	302	.90	.11
23.0	7.3		16.2	151	1.03	.15
23.0				141	.87	.18
				25	.55	.02

Example II

A silver halide dispersion in inert photographic gelatin containing 7.5% silver iodide and 92.5% silver bromide and a cyanine sensitizing dye was divided into samples equivalent to 0.15 mol of silver halides each. Additions as tabulated below were made and the samples were digested to obtain maximum light sensitivity. The resulting emulsion samples were coated on a cellulose ester film base in a thin layer and dried. Samples of said film elements were thus exposed in a type IB sensitometer, developed in a developer of the following composition:

	Grams
N-methyl-para-aminophenol sulfate	0.8
Hydroquinone	1.0
Sodium sulfite (anhydrous)	90.0
Borax	3.0
Potassium bromide	0.1
Water to 1 liter	

for 10 minutes at 68° with the results listed in the following table:

Concentration 6×10^{-5} Molar				Relative Speed	Gam.	Fog
$Na_2S_2O_3$, cc.	Chlorauric Acid, cc.	Palladium Chloride, cc.	Mercuric Chloride, cc.			
15.3	14.6	----------	----------	71	.48	.07
15.3	7.3	----------	8.1	107	.56	.05
23.0	7.3	8.0	8.1	132	.63	.07
23.0	7.3	16.0	8.1	141	.61	.07
30.7	7.3	16.0	8.1	174	.64	.07

Example III

A gelatino-silver iodobromide emulsion of the type disclosed in Example II was prepared using inert gelatin and the additions listed in the following table made. The emulsions were coated and tested as in Example II with the results tabulated below:

[All adjuvants are 6×10^{-5} molar in H_2O.]

Emul. No.	Sodium thiosulfate, cc.	Chlorauric acid, cc.	Palladium chloride, cc.	Mercuric chloride, cc.	Relative speed	Gam.	Fog
1	----------	----------	----------	----------	25	.45	.01
2	23	----------	----------	----------	141	1.11	.14
3	23	22	----------	----------	76	.79	.06
4	23	7.3	16	4	214	1.08	.06
5	----------	7.3	16	4	20	.45	.01

Samples of the above emulsions were aged for a period of one week at 120° F. with the results given in the following table.

Emulsion No.	Relative Speed	Gamma	Fog
1	15	.45	.03
2	76	.84	.32
3	123	.78	.12
4	174	.85	.14
5	19	.45	.03

Example IV

A silver iodobromide dispersion in photographic gelatin containing naturally occurring sulfur sensitizers containing 6.0 mol per cent silver iodide and 94 mol per cent silver bromide was prepared, coated, and tested as in Example I but with the following adjuvants. The results are set forth in the following table:

[Adjuvants are 6×10^{-5} molar in H_2O.]

Chlorauric acid, cc.	Palladium chloride, cc.	Mercuric chloride, cc.	Relative speed	Gamma	Fog
----------	----------	----------	107	.78	.13
14.6	32	4	186	.78	.13

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, polyclycuronic 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.

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 increases in speed are obtained which do not entirely disappear on aging. A still further advantage resides in the fact that increased speed and contrast are attained without an undesirable increase in fog.

As many widely different embodiments of this 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 salts of gold, palladium and mercury in such proportions that the emulsion contains .000723 to .000288 mol per cent of gold,

.000104 to .000975 mol per cent of palladium, and, .000108 to .000162 mol per cent of mercury, based on the silver.

2. A gelatin silver halide emulsion containing water-soluble salts of gold, palladium and mercury in such proportions that the emulsion contains .0000723 to .000288 mol per cent of gold, .000104 to .000975 mol per cent of palladium, and, .000108 to .000162 mol per cent of mercury based on the silver content.

3. A gelatin silver iodobromide emulsion predominating in silver bromide containing water-soluble salts of gold, palladium and mercury in such proportions that the emulsion contains .0000723 to .000288 mol per cent of gold, .000104 to .000975 mol per cent of palladium, and .000108 to .000162 mol per cent of mercury, based on the silver.

4. A gelatin silver halide emulsion containing water-soluble salts of gold, palladium and mercury in such proportions that the emulsion contains .0000723 to .000288 mol per cent of gold, .000104 to .000975 mol per cent of palladium, and

.000108 to .000162 mol per cent of mercury, and further containing .00027 to .00135 mol per cent of an added sulfur sensitizer, based on the silver.

5. A gelatin silver halide emulsion containing a naturally occurring sulfur sensitizer, and water-soluble salts of gold, palladium and mercury in such proportions that the emulsion contains .0000723 to .000288 mol per cent of gold, .000104 to .000975 mol per cent of palladium, and, .000108 to .000162 mol per cent of mercury, based on the silver.

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