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METHOD OF MAKING COLLOID SILVER HALIDE EMULSIONS CONTAINING THALLIUM

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This invention relates to photographic elements, to light-sensitive silver halide emulsions and to their preparation. More particularly it relates to photographic elements bearing a colloid silver halide emulsion layer which contains a small amount of thallium.

An object of this invention is to provide photographic silver halide emulsion layers which are more resistant to local desensitization due to abrasive forces. A related object is to provide flexible photographic elements with silver halide emulsion layers which are more resistant to desensitization due to kinking. A further object is to provide such elements which have good speed and contrast. Still other objects will be apparent from the following description of the invention.

Various metal salts have been added to silver halide emulsions for various purposes including toning of the developed silver image, reducing fog, increasing sensitivity, etc. Among such salts are the salts of thallium. However, the amounts proposed are quite different from those comprehended by the present invention.

It has been found that if very small amounts of thallous salts are present during the formation and growth of silver halide crystals in a colloidal system, the resulting emulsions have increased contrast and good speed. Thin emulsion layers made from such emulsions have a quite marked decrease in local desensitization caused by abrasive forces or kinking of the layers.

Silver halide crystals, when permitted to grow through Ostwald ripening in a pure system, present triangular and hexagonal outlines. In a system using a protective colloid binder, sufficient forces are exerted in the binder to hold the crystals in a rigid position, and any strains set up in this protective media affect the crystals in that portion of the matrix. Rupture of the bonds at the gelatin-crystal interface frequently results in desensitization. This is particularly true when a piece of photographic film is sharply bent or kinked.

The incorporation of small amounts of water-soluble thallium salts in the silver halide crystal distorts the lattice so that during the Ostwald ripening the normal habit of the crystal is no longer discernible under a microscope of 430 $\times$ magnification, and the crystal appears to be more nearly spherical in shape. These more nearly spherical grains are held by the protective colloid with forces equal to that encountered with the hexagonal grains, but are less affected by bends or kinks in films containing them.

The soluble thallous salts are incorporated with

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an aqueous solution of silver nitrate. This solution is added to a water solution of gelatin containing a water-soluble halide, e. g., an alkali metal or ammonium halide whereby silver and thallium halides are precipitated in the gelatin. The emulsions are then ripened, set, washed, digested and sensitized, etc., in the conventional manner.

The water-soluble thallous salts are used in amounts corresponding to 0.005 to 0.05 and preferably 0.01 to 0.02 mol per cent of thallous nitrate based on the silver nitrate used in making the silver halide emulsion. When salts other than thallous nitrate and silver nitrate are used, an amount of such salt to yield the corresponding proper amount of thallium should be used. The amounts of thallium salts just specified are very small and constitute a small fractional part of the amounts prescribed by prior-art investigators for toning, sensitization, fog reduction, etc., and yet give rather surprising and unique results. The small amounts confer an increased contrast to the emulsion and they are markedly less susceptible to desensitization by kinking of thin layers of the emulsions.

Thallous nitrate is most active in gelatino silver iodobromide emulsions, and especially those which are dominantly bromide. They confer an increase in both speed and contrast in addition to the decrease in local desensitization due to kinking photographic films bearing such emulsions in the form of thin layers.

The invention will be further described but is not intended to be limited by the following examples. The operations are carried out in the absence of actinic light.

Example I

Gelatin silver iodobromide emulsions were prepared with 1.7 mols per cent iodide, 0 and 0.01 mol per cent $TlNO_3$ (based on silver halide) being present in the silver nitrate solution. The precipitation was then made by the addition to 3N ammonium bromide and 0.5N KI solutions. The emulsions were given a ripening, washed, given a digestion to bring them to their maximum light sensitivity, and coated onto a cellulose acetate film base. The following effects on kink susceptibility and sensitometric properties were observed.

Mol Percent $TlNO_3$	Relative Speed	Contrast	Kink Susceptibility
0	100	319	60
0.01	151	314	71

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Example II

A photosensitive silver iodobromide emulsion containing 0.0001 mol of thallous nitrate per mol of silver nitrate was prepared by incorporating the thallous salt in the bromide-gelatin solution before the precipitation after the manner set forth in Example I. After the treatments described in Example I, the following sensitometric properties were obtained as compared to the properties of a related emulsion prepared without the thallous salt.

	Relative Speed	Contrast	Fog
Control emulsion.....	100	3.43	.11
Emulsion containing .01 mol per cent TI.....	100	3.89	.13

Example III

After the start of the precipitation with an ammonium bromide and KI solution and ripening but before completion of the precipitation and ripening of one mol of silver iodobromide emulsion in gelatin, 0.0001 mol of thallous nitrate was added in solution form. The finished emulsion, compared to a control emulsion similarly prepared but without thallous nitrate present, possessed the following properties.

Film	Relative Speed	Contrast	Fog
Control.....	100	2.93	.08
Emulsion containing .01 mol per cent Thallous Nitrate as a separate solution.....	126	2.96	.05

Example IV

An aqueous solution of $TiNO_3$ was added to separate portions of silver nitrate solution before precipitation of a silver iodobromide emulsion in gelatin after the manner set forth in Example I. The emulsions and one free from $TiNO_3$ were mixed and ripened in the known manner and contained 2.2 mols per cent of AgI. After washing, the emulsion was digested and made orthochromatic by the addition of a pseudocyanine dye.

The quantity of $TiNO_3$ is given below along with photographic results.

Mols $AgNO_3$	Mols $TiNO_3$	Relative Speed	Control	Fog
1.0.....	Control.....	100	1.77	.11
1.0.....	.00010.....	130	1.91	.14
1.0.....	.00020.....	145	2.21	.18

Example V

Two gelatin-iodobromide photographic emulsions were prepared by the method of Example I, except that one emulsion contained 0.02 mol per cent thallous nitrate based on the silver halide present. Prior to coating, these emulsions were pan-chromatized by the addition of a suitable sensitizing dye. The following sensitometric results were obtained.

	Relative Speed	Contrast	Fog
Standard Emulsion.....	100	.89	.20
Emulsion containing .02 mol per cent $TiNO_3$	93	1.05	.20

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Example VI

Three iodobromide photosensitive emulsions were prepared by the method of Example I except that one emulsion contained 0.02 mol per cent of thallous nitrate and one emulsion contained 0.02 mol per cent of hexa-thallium sorbitol. Each emulsion was given the usual ripening, wash, and digestion treatments. After coating, the following sensitometric properties were observed.

	Relative Speed	Contrast	Kink Susceptibility
Control Emulsion.....	100	3.18	.66
Emulsion containing .02 mol per cent $TiNO_3$	114	3.33	.75
Emulsion containing 0.02 mol per cent $Tl_2C_6H_8O_6$	114	3.36	.85

Example VII

Silver iodobromide emulsions were prepared with 0 and 0.02 mol per cent $TiNO_3$ based on silver halide present in the silver nitrate solution. After precipitation after the manner set forth in Example I and ripening, the emulsions were washed, sensitized with 0.12 mg. sodium thiosulfate per kg. of silver halide, treated with 0.27 mg. gold chloride and 0.09 mg. mercuric chloride, digested, brought to their maximum light sensitivity, and coated. The effects observed are tabulated below.

Film	Relative Speed	Contrast	Fog
Without thallous nitrate.....	100	2.51	.02
With thallous nitrate.....	115	2.53	.02

Example VIII

During the initial stages of preparation of one mol of chloro-bromide-gelatin emulsion by precipitation as set forth in Example I, 0.001 mol of thallous nitrate was added. At the same time a similar emulsion without thallous nitrate was also prepared. The effect of the thallous nitrate is tabulated below.

Film	Relative Speed	Contrast	Kink Susceptibility
Without thallous nitrate.....	100	185	.952
With thallous nitrate.....	107	189	.954

The kink susceptibility of the photographic X-ray films described in the foregoing examples was determined as follows: The coated films were kinked in a stainless steel device which had two interfitting parts, each part consisting of a V-shaped groove and an inverted V-shaped projection. The apex of the projections were rounded and one had a radius of curvature of $\frac{1}{32}$ of an inch and the other $\frac{1}{8}$ of an inch. The base of the grooves were 20 mm. wide and the depth of the grooves 10 mm. This tester produced two longitudinal bends in a 35 mm. test strip of film. The films were kinked before normal exposure and were then developed in a standard developer, fixed, washed and dried. The strips exhibited desensitization at the areas of curvature, and the amount of desensitization was a direct function of the susceptibility of the film to desensitization from handling kinks. To assign a numerical value to this susceptibility at the step having a normal net density of 1.0, the ratio of the minimum net density in a kinked

area to the normal net density in the same step of the wedge was selected.

The six-inch 35 mm. X-ray film strips were exposed in contact with a barium-calcium tungstate X-ray intensifying screen which fluoresces chiefly in the blue region of the spectrum. It was excited by radiation from a General Electric KX-8 Model X-ray machine at 70 kvp., 150 ma. for $\frac{1}{16}$ second at 64 inches through a 1.5 mm. aluminum filter, using an XP4.5 tube. Development was for 4 minutes at 68° in a metol-hydroquinone developer. Fixation was for 10 minutes in a thiosulfate fixer containing chrome alum as a hardener. Densities were determined on a stroboscopic photoelectric densitometer (J. Soc. Mot. Picture Engrs., 33, 403 (1939)).

The proportions of thallous salts in mol per cent of the silver nitrate correspond to 0.005 to 0.05 and preferably 0.01 to 0.02 mol per cent of thallium based on the silver present in the emulsions. The thallium is probably present in the form of thallous halide.

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. Other useful soluble halides include potassium bromide, potassium iodide, sodium and potassium chlorides and iodides, etc. Other useful soluble silver salts include silver sulfamate, silver sulfate, silver citrate, and silver acetate. Similarly, in place of the thallous salts described in the examples one may use the following additional salts: thallous acetate, thallous chlorate, thallous sulfate, thallous cyanide, thallous fluoride, and thallous oxalate.

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.

During the digestion stage or prior thereto, various types of sensitizing agents, e. g., sulfur sensitizers, such as allylthioureas, thiocyanates, or allylthiocyanates, can be used. In addition, various types of optical sensitizing dyes which modify the spectral characteristics of the resulting emulsions can be added. Suitable sensitizing dyes are described in United States Patents 2,010,388, 2,079,376, 2,202,990, 2,202,991, 2,202,992, 2,278,461, 2,265,908, etc.

An advantage of the invention is that it provides a simple and effective method for increasing the contrast of photographic silver halide emulsions. Another advantage is that it provides an effective and economical method for reducing the kink susceptibility of photographic films. This

is important in large sheets of X-ray and portrait film. In the former, the markings may lead to confusion in the interpretation of radiographs.

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 method of making a colloid silver halide emulsion which comprises adding to an aqueous colloid solution a water-soluble silver salt and a water-soluble thallous salt, precipitating silver and thallous halides, ripening the resulting emulsion and preparing the ripened emulsion for coating, said water-soluble thallous salt being used in an amount of 0.005 to 0.05 mol per cent based on the water-soluble silver salt.

2. A method of making a light-sensitive colloid silver halide emulsion which comprises adding to an aqueous water-permeable colloid solution containing at least one water-soluble inorganic halide, a water-soluble silver salt and a water-soluble thallous salt to precipitate silver and thallous halides in said colloid, ripening the resulting emulsion and preparing the ripened emulsion for coating, said water-soluble thallous salt being used in an amount of 0.005 to 0.05 mol per cent based on the water-soluble silver salt.

3. A method of making a light-sensitive gelatin silver halide emulsion which comprises adding to an aqueous gelatin solution containing at least one water-soluble inorganic halide an aqueous solution of a water-soluble silver salt and a water-soluble thallous salt to precipitate silver and thallous halides in the gelatin, ripening the resulting gelatin emulsion and preparing the ripened emulsion for coating, said water-soluble thallous salt being present in an amount of 0.005 to 0.05 mol per cent based on the water-soluble silver salt.

4. A method of making a light-sensitive gelatin silver halide emulsion which comprises adding to an aqueous gelatin solution containing ammonium bromide and potassium iodide, an aqueous solution of a water-soluble silver salt and a water-soluble thallous salt to precipitate silver and thallous halides in the gelatin, ripening the resulting gelatin emulsion and preparing the ripened emulsion for coating, said water-soluble thallous salt being present in an amount of 0.005 to 0.05 mol per cent based on the water-soluble silver salt.

5. A method of making a colloid silver halide emulsion which comprises adding to an aqueous colloid solution containing a water-soluble inorganic halide silver nitrate and thallous nitrate in an amount of 0.005 to 0.05 mol per cent based on silver nitrate, to precipitate silver and thallous halides, ripening the resulting emulsion and preparing the resulting emulsion for coating.

6. A method of making a light-sensitive gelatin silver halide emulsion which comprises adding to an aqueous solution of gelatin containing at least one water-soluble inorganic halide an aqueous solution of silver nitrate and thallous nitrate in an amount of 0.005 to 0.05 mol per cent based on silver nitrate to precipitate silver and thallous halides, ripening the resulting emulsion and preparing the resulting emulsion for coating.

7. A method of making a light-sensitive gelatin silver halide emulsion which comprises adding to an aqueous solution of gelatin containing ammonium bromide and potassium iodide an

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aqueous solution of silver nitrate and thallous nitrate in an amount of 0.005 to 0.05 mol per cent based on silver nitrate, to precipitate silver and thallous halides, ripening the resulting emulsion and preparing said emulsion for coating.

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