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PROCESS FOR PREPARING SILVER HALIDE EMULSIONS COMPRISING THE ADDITION OF EXCESS CHLORIDE ION

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ABSTRACT OF THE DISCLOSURE

Radiation-sensitive emulsions and elements particularly suitable for use in high intensity oscillographs are prepared by adding to a colloid-silver halide emulsion of the developing-out type or direct-writing type, a large amount of a water soluble chloride salt of the order of about 160 mole percent based on the silver halides after digestion and prior to coating the emulsion on a support.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to radiation-sensitive photographic elements comprising colloid-silver halide emulsion layers for oscillographic recording purposes having improved development and sensitometric characteristics. The present invention constitutes an improvement in the wet-development response of both developing-out and photodevelopable direct writing radiation-sensitive elements which are exposed in high-intensity oscillographic recording instruments. This improvement is brought about by adding after digestion and prior to coating based on the silver halide, from 80 to 240 mole percent and preferably 130 to 170 mole percent of a water-soluble chloride salt. The addition of a large amount of chloride ions prior to coating produces an improved wet-development response by minimizing the desensitization effect of the ambient flare light to subsequent imaging exposure. This produces higher effective sensitivity to oscillographic traces and timing lines in the high-intensity oscillographic recording instruments in use today. The addition of large amounts of chloride ions prior to coating also produces many other advantages, especially in direct-writing radiation-sensitive elements which are photodevelopable.

Description of the prior art

The addition of halide ions (chloride, bromide and iodide) to photographic gelatino-silver halide emulsions is known. Further it is known to add at least 50% to 100% or more of excess bromide ions based on the silver halide to direct writing emulsions to decrease the background density. Light-developable, direct writing oscillographic recording papers are described in U.S. Pats. 3,033,678; 3,033,682; 3,178,293; 3,183,088; 3,189,456; 3,249,440 and others. In these patents there are described layers and processes of manufacture which provide radiation sensitive elements for recording the high intensity light traces from oscillographic recording instruments. Such elements require no chemical processing and are developed by exposure to a source of radiation of lower intensity than the image forming, high intensity source.

Emulsions for the direct-writing elements of the above patents are made by precipitating silver halides in a macromolecular colloid, e.g., gelatin, coagulating, washing the coagulated emulsions, redispersing, digesting and either during or after digestion adding a powerful halogen acceptor, and usually an excess of bromide ions and a background stabilizer and coating the emulsion. Preferably the silver halides, e.g., silver chloride as in the case of U.S. Pat. 3,178,293, are precipitated in the presence of a plumbous ion and then sufficient soluble bromide is added to convert a substantial portion (approximately 90%) of the silver chloride to silver bromide. The emulsion is coagulated, washed and redispersed in the manner described in U.S. Pat. 2,772,165. A halogen acceptor, e.g., stannous ion, frequently as stannous chloride is added and the emulsion digested and after the addition of final adjuvants, e.g., hardener, buffers, etc., the emulsion is coated. The water-permeable colloids in the listed patents can be used.

One of the difficulties with the above and similar systems which are photodevelopable is that they are adversely affected by the relatively high level of ambient flare light which exists in the exposure region of the currently commercially available high intensity oscillographs. This is due to light scatter from the high intensity exposing lamps (mercury arc/xenon) employed in producing images of grid lines, timing lines and oscillographic trace information. This flare light tends to produce an over-all low level exposure of the emulsion layer both before and after the trace exposure. In addition to producing an undesired background density which reduces image contrast, this low level exposure, particularly when it occurs prior to the high intensity imaging exposure, can desensitize the emulsion to the subsequent imaging exposure resulting in high background density which is observed after wet processing and a loss of writing speed and/or loss of timing line trace density. In addition, where stannous chloride is used as the halogen acceptor it is necessary to use special liquid developers where it is desired to wet process the exposed elements.

SUMMARY OF THE INVENTION

This invention pertains to an improved process for making colloid-siver halide emulsions for oscillograph recording elements which comprises:

(1) admixing silver nitrate with an acidified solution of a water-soluble chloride containing a water-permeable, macro-molecular organic colloid binding agent for the silver halide grains,
(2) ripening the precipitated emulsion for about 5 to about 50 minutes at about 100° F. to 160° F.,
(3) mixing with dispersion 50–160 mole percent of a water-soluble bromide,
(4) setting the resulting emulsion and washing and redispersing it,
(5) digesting the redispersed emulsion for 5 to 30 minutes at 110° to 130° F. and prior to completion of digestion admixing a halogen acceptor;

characterized in that there is added to the digested emulsion from 80 to 240 mole percent of a water-soluble chloride, all percentages being based on silver. An important point is that the soluble chloride salt be added after digestion and prior to coating. During the precipitation step 0.33 to 10 mole percent of a water-soluble plumbous salt may be present per mole of silver.

The emulsion is coated on a suitable support. Emulsions made by the above process have several advantages over the silver halide emulsions of the prior art when used in high-intensity oscillographic recording instruments.

The precipitation can be accomplished by using any of the water-soluble silver salts and water-soluble halides described in the patents listed above, e.g., lithium, sodium, potassium, calcium, magnesium and ammonium, chloride, bromide and iodide listed in Hunt U.S. Pat. 3,183,088. The precipitation is preferably carried out as described in Bigelow U.S. Pat. 3,178,293 by admixing silver nitrate and a plumbous salt in aqueous solution with an aqueous acidified solution of the colloid and water-soluble halide. After

precipitating and ripening, the emulsion is washed, preferably in the manner described in Moede U.S. Pat. 2,772,165. The emusion is redispersed and digested in the conventional manner. At this point or prior to completion of digestion, optical sensitizers may be added to increase the spectral response of the emulsion for use in instruments employing a variety of light sources. Gold salts and a small amount of an alkali metal thiocyanate may be added during digestion. A plumbous salt, e.g., plumbous nitrate or plumbous acetate may be aded as described in Hunt U.S. 3,033,682.

In the case of silver halide emulsions for photo-developable direct writing elements which require the presence of a halogen acceptor, suitable compounds comprise stannous chloride, salts providing iodide and thiocyanate ions, molecular iodine, alkali-metal nitrites, phenylenediamine, aminophenols, hydroquinones, 3-pyrazolidones and other known halogen acceptors such as those disclosed in U.S. Kitze 3,241,971; McBride 3,271,157; 3,207,136 and 3,287,137 and Fix 3,326,689. The optical sensitizing dyes of such patents may be used.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The preferred halogen acceptors for this invention, where it is desired to use photodevelopable direct-writing emulsions which may be wet-processed, are alkali-metal and ammonium iodides and thiocyanates. In general, from .03 to 2.0 mole percent based on the silver halide present in the emulsion of the above iodides or thiocyanates may be used. The silver halide emulsions of this invention are preferably of the silver halide emulsions of this invention are preferably of the silver bromide or silver chlorobromide type although a silver iodobromide can also be used. While there are many useful soluble chloride salts, those which are readily available and least expensive are preferred, e.g., alkali metal and amonium chlorides. The preferred quantity is approximately 160 mole percent of chloride ion based on the silver halide. The viscosity of the emulsion may be adjusted by the addition of gelatin and/or other coloid. In general, the ratio of coloid to silver halide is 2:1 although this is not at all critical. The emulsions are coated to give a dry coating weight equivalent to about 30 mg. AgBr/dm.^{2}.

In order to more specifically illustrate the features of this invention, the following examples are set forth below. They are not intended to limit the scope of the invention except as set forth in the claims.

EXAMPLE I

A gelatino-silver chlorobromide emulsion was made by slowly adding an aqueous solution containing a mixture of 0.15 mole of silver nitrate and 0.005 mole of plumbous nitrate to a gelatin solution containing 0.15 mole of potassium chloride and acidified with 0.005 mole of hydrochloric acid. The precipitation was carried out under Wratten Series 1 red safelight manufactured by the Eastman Kodak Company. The temperature at precipitation and for 40 minutes thereafter was held at 140° F. After the ripening, an aqueous solution of 0.24 mole of potassium bromide was added while the mixture was held at 140° F. the resulting emulsion was coagulated, washed and redispersed in a manner similar to that described in Moede U.S. Pat. 2,772, 165. To the redispersed silver chlorobromide emulsion there was added 25 grams of inert gelatin and the emulsion was digested in the presence of 0.006 mole of potassium thiocyanate and 4.6×10^{-5} mole of auric chloride for 40 minutes at 140° F. After digestion, the emulsion was divided into 8 portions and halide ions in the form of potassium chloride, potassium bromide and potassium iodide were added to the various portions as indicated in the table below. Final adjuvants, e.g., hardeners, wetting agents, etc., were added and the layers were coated on paper supports in an amount of approximately 30 mg./dm.^{2}(expressed as AgBr). The coatings were dried in a conventional manner.

To determine the sensitometric characteristics of the material it was exposed through a power of 2 step wedge in an electronic flash sensitometeer, Edgerton, Germeshausen and Grier Mark VI, using a Xenon flash tube at $\frac{1}{10,000}$ sec. After photodevelopment, which was performed by exposure to black light fluorescent tube for 4 minutes at 50 meter candles intensity, the sensitometric speed is expressed as the number of steps visible. The maximum densities obtainable and the background densities were measured with a reflection densitometer (Mabeth Quanta Log Densitometer Model RD–100 14). Chemical development was 1 minute at 68° F. in a developer having the following composition:

	Grams
N-methyl-p-aminophenol sulfate	1.5
Hydroquinone	6.0
Sodium sulfite (anhydrous)	19.5
Sodium carbonate (anhydrous)	28.0
Potassium bromide	0.8
Water to make 1.0 liter.	

The developed strips were rinsed and then immersed for 5 minutes in a fixing solution having the following composition:

	Grams
Sodium thiosulfate	240
Sodium sulfite (anhydrous)	15
Acetic acid, 28%	47
Potassium aluminum sulfate	1.0
Water to make 1.0 liter.	

The test strips were washed and dried and read on a densitometer as described above.

To determine the characteristics of photographic elements of this invention when used in commercial oscillographs, samples of test material were exposed in a normal manner in a commercial mercury arc oscillograph identified as Honeywell Viscorder Model 1612 at a transport speed of 0.4 inch per second. The exposed samples were developed, fixed, washed and dried and the densities read as described above. The emulsion sensitivity was measured by a visual comparison of the timing line trace densities.

The results of testing as described above are shown in the following table.

TABLE I.—COMPARISON OF EFFECT OF EXCESS HALIDE ION

	Moles of soluble halides/moles of silver halides			Sensitometry						Wet processed oscillographic test	
				Photolyzed			Wet processed				
Ctg.	Cl-	Br-	I-	Visible steps	D-max.	B.G.	Visible steps	D-max.	B.G.	B.G. density	Timing lines
A	0.8	0	0	7	.26	.19	8	.98	.02	.04	Weak.
B	1.6	0	0	6	.20	.14	10	1.17	.01	.04	Stong.
C	2.4	0	0	6	.19	.12	10	1.14	.01	.05	Do.
D	0	0.8	0	7	.12	.06	7	1.11	.00	.21	None.
E (control	0	0	0.01	8	.43	.19	7	1.13	.01	.04	Weak.
F	0.8	0	0.01	7	.45	.20	7	1.15	.01	.05	Medium.
G	1.6	0	0.01	7	.40	.17	8	1.17	.01	.06	Strong.

Note that effect of chloride ion is observed in absence of other halides (B) but it is preferred to include iodide ion (G) for effect on photolyzed response (halogen acceptor). Amounts of chloride above approx. 1.6 may be used but are not necessary.

B.G.=Background density which is the difference between white paper and developed sample.

EXAMPLE II

An emulsion was made as described in Example I and two portions were treated to give an emulsion like (G) in Example I, that is, there was added to the emulsions just prior to coating 1.6 moles of chloride ion and 0.01 mole of iodide ion. One portion was coated as such and was used as a control. To the other portion there was added the amount shown in the following table of the optical sensitizing dye:

5-(3-methyl-2-thiazolinylidene-isopropylidene)-3-ethylrhodanine.

The results are shown below:

TABLE II

Ctg.	Sensitometry: Photolyzed Visible steps	Photolyzed D-max.	Photolyzed B.G.	Wet processed Visible steps	Wet processed D-max.	Wet processed B.G.	Wet processed oscillographic test: B.G. density	Timing lines
H (like G above in Ex. I)----	7	.43	.20	8	1.11	.01	.08	Strong.
I (like G plus 0.005 g. dye)----	8	.45	.24	10	1.17	.01	.10	Very strong.

NOTE.—Optical sensitizing dyes increase speed.

Low levels of bromide combined with high chloride levels produced higher wet speed while retaining low flare light sensitivity. High levels of bromide in absence of chloride produces higher flare sensitivity.

In place of the gelatin binding agent used in the foregoing examples there can be substituted other natural or synthetic water-permeable organic colloid binding agents, including the binding agents listed in Hunt U.S. Pat. 3,033,682.

Suitable supports for the novel photographic emulsions of this invention include those used in the prior art on oscillographic recording elements. The preferred support is a photographic grade paper but may be a hydrophobic film composed of a cellulose ester, e.g., cellulose acetate or a polymer, e.g., polyester films disclosed in Alles et al., U.S. 2,627,088 and Alles U.S. 2,779,684.

Radiation-sensitive elements coated with the emulsions made according to this invention show a significant reduction in oscillographic flare light sensitivity when wet processed without loss of sensitivity to the oscillographic trace thus providing a higher trace density and a cleaner background. There is also an increase in timing line density when wet processed which is believed to be due to reduced flare light desensitization. There is also a reduced background density when the exposed element is photodeveloped in ambient room lighting of lower intensity than the oscillographic image exposing intensity. The emulsions prepared according to this invention also show improved aging stability.

EXAMPLE III

Two portions of the emulsion of Example I were prepared, one of which was digested in the presence of 4.6×10^{-5} mole of auric chloride as a chemical sensitizer, and potassium thiocyanate as described in Example I. No auric chloride was added to the second portion of the emulsion which was otherwise treated similarly. Both portions contained 1.6 mole of chloride ion and 0.01 of iodide ion added just prior to coating. The results are shown in the table.

TABLE III

Ctg.	Moles of soluble halides/moles of silver halides: Cl-	Br-	I-	Sensitometry: Photolyzed Visible steps	Photolyzed D-max.	Photolyzed B.G.	Wet processed Visible steps	Wet processed D-max.	Wet processed B.G.	Wet processed oscillographic test: B.G. density	Timing lines
J----------	1.06	0	0.01	7	.52	.26	11	1.13	.00	.08	Strong.
				Auric chloride digestion							
K----------	1.6	0	0.01	7	.44	.26	9	1.08	.01	.04	Do.
				Like K, but no gold salt was present							

Chemical sensitization with a gold salt can be used to increase chemically developed speed without loss of chloride effect on timing line response. Chemical sensitization is not necessary for the chloride effect.

EXAMPLE V

For portions of a silver halide emulsion were prepared as in Example I and potassium chloride, bromide and iodide were added just before coating to provide halide ions as indicated in the following table along with the sensitometric results.

TABLE IV.—MIXTURES OF HALIDES

Ctg.	Moles of soluble halides/moles of silver halides: Cl-	Br-	I-	Sensitometry: Photolyzed Visible steps	Photolyzed D-max.	Photolyzed B.G.	Wet processed Visible steps	Wet processed D-max.	Wet processed B.G.	Wet processed oscillographic test: B.G. density	Timing lines
L----------	1.6	0	0.01	7	.59	.31	7	1.27	.02	.02	Weak.
M----------	1.6	0.4	0.01	7	.56	.27	8	1.24	.03	.05	Strong.
N----------	1.6	0.8	0.01	7	.52	.26	10	1.26	.02	.06	Do.
O----------	0	0.8	0.01	6	.32	.15	9	1.22	.00	.23	Do.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for preparing photographic silver bromide emulsions comprising

(1) admixing silver nitrate with an acidified solution

of a water-soluble chloride containing a water-permeable, macromolecular organic colloid binding agent for the silver halide grains,

(2) ripening the precipitated emulsion for about 5 to about 50 minutes at about 100° F. to 160° F.,

(3) mixing with the dispersion 50–160 mole percent of a water-soluble bromide selected from the group consisting of lithium, sodium, potassium, calcium, magnesium and ammonium bromide,

(4) setting the resulting emulsion and washing and redispersing it,

(5) digesting the redispersed emulsion for 5 to 30 minutes at 110° F. to 130° F. and prior to completion of digestion admixing a halogen acceptor;

characterized in that there is added to the digested emulsion from 80 to 240 mole percent of a water-soluble chloride, all percentages being based on silver.

2. A process according to claim **1** wherein prior to completion of digestion there is incorporated with the silver halide based on the silver at least one of the following constituents:

(a) up to 120 mole percent of a water-soluble bromide and

(b) up to 5 mole percent of plumbous nitrate or acetate.

3. A process according to claim **1** wherein said binding agent embodies gelatin.

4. A process according to claim **1** wherein said water-soluble chloride is potassium chloride.

5. A process according to claim **1** wherein said halogen acceptor is potassium thiocyanate.

6. A process according to claim **1** wherein nitrate or acetate is present during precipitation of silver halide.

7. A process according to claim **1** whrein iodide ions are present from the halogen acceptor.

8. A process according to claim **1** wherein the emulsion contains "an optical sensitizing dye."

References Cited

UNITED STATES PATENTS

3,033,678	6/1962	Hunt	96—108X
3,178,292	4/1965	Fix	96—108
3,178,293	4/1965	Bigelow	96—108
3,183,088	5/1965	Hunt	96—45.2
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