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PROCESS FOR PREPARING SILVER HALIDE EMULSIONS

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This invention relates to photography, and more particularly to a process for increasing the low intensity response of light-sensitive silver halide dispersions in a water-permeable colloid. Still more particularly, it relates to a process for increasing the low intensity response to light and/or X-rays of light-sensitive gelatino-silver halide emulsions.

The problem of loss of sensitivity on low intensity exposure of light-sensitive gelatino-silver halide emulsion layers, that is, reciprocity law failure, is well known. This reciprocity law failure is particularly important in photographic films such as X-ray, negative and lithographic films having such light-sensitive layers which are used over a range from low intensity exposures (long time) at which reciprocity failure occurs to relatively high intensity exposures (short time). Present techniques such as sensitization, digestion, etc., for increasing low intensity exposure response have the disadvantages that they result in high fog, instability, etc. Moreover, emulsion preparation techniques which improve general emulsion characteristics are frequently detrimental to the low intensity response.

An object of this invention is to provide a simple and practical process for increasing the low intensity response of light-sensitive silver halide dispersions in water-permeable colloids. Another object is to provide such a process which utilizes readily available and inexpensive materials. Yet another object is to provide such a process which can be carried out in the usual equipment of a photographic emulsion manufacturer. A further object is to provide such a process which is effective and can be carried out by the ordinary technician. A still further object is to provide X-ray sensitive silver halide emulsions and emulsion layers and elements having such layers which are sensitive to very low intensity exposures. Still further objects will be apparent from the following description of the invention.

The novel process of this invention for improving the low intensity response of light-sensitive silver halide emulsions or dispersions wherein a water-permeable organic colloid having protective colloid properties, preferably gelatin, is used as the binding agent for the silver halide grains consists of (1) adjusting the pAg of the precipitated, Ostwald ripened and washed or unwashed and digested aqueous silver halide emulsion or dispersion to a value from 0.2 to 2.0 pAg units greater than the pAg at which digestion is carried out by the addition of a water-soluble halide, e.g., ammonium, lithium, sodium, potassium, cadmium or hydrogen, chloride or bromide, and (2) then subjecting the emulsion of higher pAg to an auxiliary digestion at a temperature from 110° F. to 180° F. for a period of 3 to 30 minutes. After the precipitation, the resulting dispersion of silver halide or emulsion can be bulked up by the addition of the same or a different water-permeable organic colloid and the desired emulsion adjuvants, e.g., sulfur sensitizers, metal or metal compounds, spreading agents, foam inhibitors, etc. added.

As an exemplary procedure, a high speed silver iodobromide or silver bromochloride gelatin emulsion is made by precipitating such a mixed halide in an aqueous solution or dispersion by admixing therewith a soluble silver salt, e.g., silver nitrate, silver sulfamate, silver acetate or

silver citrate, in the form of an aqueous solution, with an aqueous solution of a water-soluble halide or mixture of such halides, e.g., ammonium, lithium, sodium, potassium or cadmium chloride, bromide and iodide. If desired, the emulsion is washed free from soluble salts. The pAg of the emulsion is then adjusted to pAg 6.5 to 8.5 by means of water-soluble halides, e.g., chlorides, bromides and iodides, the cation of which is any of those known by persons skilled in the art to be innocuous to photographic emulsions, including those just mentioned in the precipitation step, to achieve a balance between sensitivity and fog. The emulsion is then digested (after ripened) at a temperature of about 110° F. to 180° F. for a period from 35 to 70 minutes. The pAg is adjusted upwardly by 0.2 pAg units or more so that the final pAg is not greater than about 10.0 and the emulsion is given a second or auxiliary digestion at a temperature from 110° F. to 180° F. or more for a period of about 3 to about 30 minutes. The time period of digestion depends, of course, on the temperature at which the digestion is carried out, and at low temperatures will be longer than at higher temperatures. For example, while the preferred temperatures are 110° F. to 150° F. and times from 5 to 30 minutes, it is possible to digest the emulsions at about 200° F. for about 3 to about 5 minutes without adversely affecting the sensitometric quality of the emulsion. By this procedure, surprisingly, the low intensity response of the emulsion is greatly enhanced without fogging, as compared with a similar emulsion where the pAg was not adjusted by the addition of a water-soluble halide prior to the second digestion.

It has been found that the low intensity response may be even further enhanced by the addition of a suitable sulfur sensitizing compound, e.g., $Na_2S_2O_3$, thiourea, allyl thiocarbamaide and allyl thiourea just prior to the second digestion. The amount of sulfur sensitizer added may be varied over a wide range but is preferably used in the range of 0.25×10^{-6} to 6.5×10^{-6} moles of available sulfur per mole of silver halide. This sulfur is in addition to any sulfur compounds normally added or available (sulfur containing gelatin) as emulsion sensitizers.

With regard to the value pAg, it is defined as the logarithm of the reciprocal of the silver ion concentration. The silver ion concentration is measured with a standard cell using a silver and a calomel electrode. For the method of calculating pAg, see Getman, F. H., and Daniels, F., Outlines of Theoretical Chemistry, 6th Ed. (New York, 1937), page 433.

The invention will be further illustrated by, but is not to be limited to, the following examples.

Example I

A high speed gelatino-silver iodobromide photographic emulsion containing approximately 1.5 mol percent silver iodide and 98.5 mol percent silver bromide is prepared by precipitation in aqueous gelatin solution in the conventional manner. After Ostwald ripening and a normal digestion for 48 minutes at 143° F., and at a pAg of 8.75, the pAg of the emulsion is adjusted to 10.0 by using a 3 N potassium bromide solution. The emulsion is then divided into four portions, a control sample and three samples which are subjected to a second digestion for periods indicated in the following table. The control sample and the three samples of this invention are coated onto a gelatin sublayer on a cellulose acetate film base and dried. All samples are given an X-ray screen exposure (through a 0.5 mil aluminum filter) of 63 milliampere seconds (7 milliamperes for 9 seconds), using an aluminum step wedge at a distance of 55 inches from the

source of the X-ray. The response to this low intensity exposure is as shown in the following table:

Second Digestion, Time in Minutes	Speed	Contrast	Fog
0	1,000	2.49	.04
5	1,150	2.52	.04
10	1,320	2.42	.05
15	1,490	2.46	.06

Example II

Example I is repeated except sodium thiosulfate ($Na_2S_2O_3$) is added to one of the emulsion samples at the beginning of the second digestion. The response to low intensity exposure is as follows:

Second Digestion, Time in Minutes	Moles $Na_2S_2O_3$ per mole AgIBr	Speed	Contrast	Fog
0	0	1,000	2.13	.05
10	0	1,310	2.27	.08
10	1.16×10^{-6}	1,450	2.33	.07

Example III

A silver halide emulsion containing 1.5 mol percent silver iodide and 98.5 mol percent silver bromide is prepared as described in Example I of Moede, U.S. patent application Ser. No. 354,410, filed May 11, 1953, except the emulsion, prior to being coated, is adjusted to a pAg of 9.25 with 3 N potassium bromide solution and divided into two samples, one of which is given a second digestion at 143° F. for periods of 10 minutes. The emulsion is coated and dried in the usual manner and subjected to a low intensity exposure of 63 milliampere-seconds as described in Example I.

The response is as follows:

Second Digestion, Time in Minutes	Speed	Contrast	Fog
0	1,000	2.36	.04
10	1,530	2.49	.05

Example IV

Example III is repeated except that a conventional antifogging agent was added after the second digestion as indicated in the following table. The response to a low intensity exposure of 63 milliampere seconds, as described in Example I, is as shown in the following table.

Second Digestion, Time in Minutes	Contains Antifoggant	Speed	Contrast	Fog
0	No	1,000	2.36	.04
10	No	1,530	2.49	.05
0	Yes	980	2.23	.05
10	Yes	1,290	2.46	.05

Example V

An intermediate speed (negative type) silver iodobromide, blue-sensitive, photographic emulsion containing approximately 3.7 mol percent silver iodide and 96.3 mol percent silver bromide is prepared by precipitation in an aqueous gelatin in the conventional manner. After Ostwald ripening and a normal digestion for 47 minutes at 132° F., and at a pAg of 7.80, the pAg of the emulsion is adjusted to 8.75 using a 3 N potassium bromide solution. The emulsion is then divided into three portions, a control sample and two samples, which are subjected to a second digestion for periods indicated in the following table. A sulfur sensitizer (1.3 mg.) having available sulfur as shown in the table is added to one of the samples. The control sample and the two samples which were subjected to auxiliary digestion are coated onto a gelatin sublayer on a cellulose acetate film base and dried. All samples are given a 20-second exposure through a 78B Wratten filter and a neutral density 0.60 filter by a standard lamp positioned at a distance of 49 inches from the film. The response to this low intensity exposure is as shown in the following table:

Second Digestion, Time in Minutes	Sulfur sensitizer moles of available sulfur per mole Silver Iodobromide	Speed	Contrast	Fog
0	0	1,000	1.27	.01
20	0	1,300	1.28	.03
20	$6.25=10^{-6}$	1,500	1.33	.03

Example VI

Example V is repeated except the emulsion is optically sensitized in the usual manner so that sensitivity extends to about 670 millimicrons (panchromatic), the second digestion is carried out at 138° F., and a neutral density 1.20 filter is substituted for the 0.60 filter. The response to low intensity exposure is as follows:

Second Digestion, Time in Minutes	Speed	Contrast	Fog
0	1,000	1.27	.03
20	1,225	1.21	.05

Example VII

A silver bromochloride emulsion (lithographic type) containing 20-mol percent silver bromide and 80-mole percent silver chloride is prepared by precipitation in an aqueous gelatin solution in the conventional manner. After Ostwald ripening and a normal digestion for 70 minutes at 114° F. at a pAg of 7.00, the pAg of the emulsion is adjusted to 7.75 using a 3 N cadmium chloride solution. The emulsion is then divided into two portions, a control sample and a sample which is subjected to a second digestion for a period indicated in the following table. The samples are coated onto a gelatin sublayer on a cellulose acetate film base and dried.

Both samples are given an exposure of 480 seconds at a distance of 49 inches through a Corning 5900 filter and a neutral density 1.00 filter. The response to this low intensity exposure is shown in the following table:

Second Digestion, Time in Minutes	Speed	Contrast	Fog
0	1,000	8.80	.01
17	1,100	8.76	.01

The invention is, of course, not limited to the silver iodobromide and silver bromochloride emulsions of the foregoing examples as silver bromide and mixed silver chloride, silver bromide and/or iodide emulsions can be treated as described above. These emulsons can be made in the conventional way by precipitation, Ostwald ripening, chilling, shredding, washing, redispersion and digestion and then, after adjusting the pAg by means of a water-soluble inorganic halide as set forth above, given a second or auxiliary digestion, with or without the addition of a sulfur sensitizer.

Prior to digestion and preferably immediately after precipitation of the silver halide, the emulsions having the enhanced pAg can be sensitized with the gold salts, e.g., chlorauric acid, potassium chloroaurite, auric trichloride or other gold salts as described in U.S. Patents 2,399,083, 2,597,856 and 2,597,915.

The emulsions may also be sensitized with salts of noble metals of group VIII of the periodic table, e.g., ruthenium, rhodium, palladium, iridium, platinum, or with mixtures of such salts and the gold salts referred to above. The metal salts should be used in amounts below that which produces significant fog inhibition.

In addition to the metal salt sensitizers mentioned above or in place of such sensitizers, there may be added to the emulsions resulting from the second digestion treatment of this invention sensitizing amounts of (*a*) various polyoxyalkylene compounds or polyalkylene glycols and derivatives thereof, e.g., ethers, esters and condensation products of hexitol ring dehydration products with ethylene oxide or propylene oxide containing at least 6 oxyalkylene groups, having a molecular weight or an average molecular weight of at least 400 to 8000 or more, including the compounds of these types disclosed in U.S. Patents 2,423,549, 2,441,389, 2,240,472, 1,970,570 and 2,400,532 and/or sensitizing or stabilizing amounts of tetrazaindene stabilizers described in Z. fur Wiss Phot. 47, pp. 2–21 (1952).

The preparation and coating of the silver halide emulsions of the above examples were carried out in the absence of significant actinic radiation.

While the above examples are concerned with the use of gelatin as the binding agent for the silver halide grains, other water-permeable amphoteric protein protective colloids, e.g., alubumin and casein can be used.

Photographic films, plates and papers can be made by coating onto a suitable support the emulsions of this invention having enhanced low-intensity responses. Suitable supports include cellulose esters, e.g., cellulose acetate, cellulose nitrate, cellulose acetate butyrate, cellulose propionate; super polymers, e.g., nylon, polymethylene terephthalates, polyvinyl chloride, poly(vinyl chloride co vinyl acetate) and vinylidene chloride copolymers with vinyl acetate, acrylonitrile, etc.; metal sheets or foils, e.g., aluminum and zinc; and paper, including resin-coated and baryta-coated paper; as well as glass plates inter alia.

An advantage of this invention is that it provides photographic silver halide emulsions of improved properties. A more specific advantage is that of photographic silver halide emulsions and emulsion layers of markedly improved response to low intensity exposure. The invention has the further advantage that it provides a process for improving the response to low intensity exposure of colloid silver halide emulsions and emulsion layers without adversely affecting other sensitometric characteristics of such emulsions.

The X-ray-screen sensitive photographic silver emulsion layers and elements have the important commercial advantage that due to their enhanced sensitivity to very low intensity exposure, the life of the exposure devices used, e.g., X-ray tubes, will be greatly extended since exposure time and/or tube current required for exposure will be reduced. Still further advantages will be apparent to those skilled in the art.

I claim:

1. A process for improving the low intensity response of a light-sensitive silver halide dispersion having a pAg from 6.5 to 8.75 in a water-permeable organic colloid that has been ripened and digested at a temperature from about 110° F. to 180° F. for 35 to 70 minutes which comprises (1) adjusting the pAg of the precipitated, ripened and digested aqueous dispersion upwardly by 0.2 to 2.0 pAg units by the addition of a water-soluble inorganic halide taken from the group consisting of hydrogen, ammonium, lithium, sodium, potassium and cadmium chloride and bromide and (2) subjecting the resulting dispersion to an auxiliary digestion at a temperature of 110° F. to 200° F. for a period of about 3 to about 30 minutes prior to coating.

2. A process as set forth in claim 1 wherein the dispersion predominates in silver bromide.

3. A process as set forth in claim 1 wherein said inorganic halide is an alkali metal bromide.

4. A process as set forth in claim 1 wherein said colloid is gelatin.

5. A process as set forth in claim 1 wherein said dispersion is silver iodobromide.

6. A process as set forth in claim 1 wherein a sulfur sensitizer is admixed with the dispersion prior to the auxiliary digestion.

7. A process for improving the low intensity response of a ripened and digested aqueous gelatino-silver iodobromide emulsion having a pAg between 6.5 and 8.5 that has been ripened and digested at a temperature from about 110° F. to 180° F. for 35 to 70 minutes which comprises adjusting the pAg to a higher value of 0.2 to 2.0 pAg units by the addition of a water-soluble alkali metal bromide and subjecting the resulting dispersion to an auxiliary digestion at a temperature from 130° F. to 160° F. for a period of 5 to 30 minutes prior to coating.

8. A process as set forth in claim 7 wherein said water-soluble inorganic bromide is potassium bromide.

9. A process for improving the low intensity response of ripened and digested aqueous gelatino-silver iodobromide emulsion having a pAg between 6.5 and 8.5 that has been ripened and digested at a temperature from about 110° F. to 180° F. for 35 to 70 minutes which comprises adjusting the pAg to a higher value of 0.2 to 2.0 pAg units by the addition of a water-soluble alkali metal bromide and by the further addition of a sulfur sensitizer in an amount from 0.25×10^{-6} to 6.5×10^{-6} moles of available sulfur per mole of silver bromide and subjecting the resulting emulsion to a further digestion at a temperature from 130° F. to 160° F. for a period of 5 to 25 minutes prior to coating.

10. A process as set forth in claim 9 wherein said water-soluble alkali metal bromide is potassium bromide.

11. A process for improving the low intensity response of a ripened and digested aqueous gelatino-silver bromochloride emulsion having a pAg between 6.5 and 8.5 that has been ripened and digested at a temperature from about 110° F. to 180° F. for 35 to 70 minutes which comprises adjusting the pAg to a higher value of 0.2 to 2.0 pAg units by the addition of water-soluble ammonium chloride and subjecting the resulting dispersion to an auxiliary digestion at a temperature from 130° F. to 160° F. for a period of 5 to 30 minutes prior to coating.

References Cited in the file of this patent

UNITED STATES PATENTS

2,005,837	Arens	June 25, 1935
2,401,051	Crouse et al.	May 28, 1946
2,490,751	Hanson	Dec. 6, 1949
2,552,230	Stauffer et al.	May 8, 1951
2,592,250	Davey et al.	Apr. 8, 1952
2,618,556	Hewitson et al.	Nov. 18, 1952
2,717,833	Wark	Sept. 13, 1955
2,743,183	Lowe et al.	Apr. 24, 1956
2,768,079	Russell	Oct. 23, 1956
2,839,405	Jones	June 17, 1958