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(54) Photographic silver bromoiodide emulsions, elements and processes.

(57) A photographic silver bromoiodide emulsion comprises a dispersing medium and silver bromoiodide that (a) is octahedral silver bromoiodide; (b) has a grain size within the range of 0.45 to 1.2 microns; (c) contains 1 to 12 mole percent iodide; (d) has a core region (A), a surface region (B) and a subsurface region (C) between core region (A) and surface region (B); wherein (i) subsurface region (C) contains an iodide concentration higher than the iodide concentration of core region (A); and, (e) the silver bromoiodide is prepared by a process comprising, in sequence, (I) a nucleation step comprising mixing bromide or bromoiodide salts and silver salts in a reaction medium; then, (II) a crystal growth step under controlled pBr conditions within the range of 1.75 to 4.2 pBr enabling formation of core region (A) comprising 50% to 90% by weight of the silver bromoiodide; then, (III) addition to the composition from (II) of iodide salt in which 25 to 100 mole percent of the total iodide salt is added to the composition resulting from step (II) within a time period of 1 second to 20 minutes; then, (IV) holding the reaction mixture from step (III) for a time period of 0.5 second to 20 minutes that aids in formation of subsurface region (C); then, (V) addition of silver salts or, optionally, the combination of silver salts and bromide to the reaction mixture from step (IV) until reaction completion forming surface region (B). Such photographic silver bromoiodide emulsions are useful in photographic silver halide materials to provide increased photographic speed of the materials.

PHOTOGRAPHIC SILVER BROMOIODIDE EMULSIONS, ELEMENTS AND PROCESSES

This invention relates to photographic silver bromoiodide emulsions, photographic elements incorporating these emulsions, and processes for the use of the photographic elements.

Photographic emulsions useful in photography typically comprise a dispersing medium, such as gelatin, containing grains of photographic silver halide. Emulsion other than silver bromoiodide have found only limited use in camera speed photographic elements. Silver bromoiodide emulsions and their preparation are described in, for example, such standard texts as Duffin, "Photographic Emulsion Chemistry", Focal Press, 1966 and Mees and James, "The Theory of the Photographic Process", MacMillan Publishing Co., 4th Edition, 1977.

Photographic silver bromoiodide emulsions having various grain sizes and shapes are also known in photography. Illustrative emulsions containing silver bromoiodide grains are described in, for example, European Patent Application 330,508 and U.S. Patents 4,433,048; 4,720,452; 3,505,068 and 4,704,351.

Photographic silver bromoiodide emulsions that contain octahedral silver bromoiodide grains are also known, such as described in U.S. Patents 4,150,994; 4,184,877 and 4,610,958 and published Japanese Patent Application (Kokai) 60-138538 published July 23, 1985.

Octahedral silver bromoiodide emulsions, particularly monodispersed emulsions, are known to have advantages, such as high sensitivity and improved photographic properties. However, it has been desirable to provide the following improvements: (a) improved photographic speed and (b) decreased granularity.

It has been found that such requirements are satisfied by a photographic silver bromoiodide emulsion comprising a dispersing medium and silver bromoiodide that (a) is octahedral silver bromoiodide; (b) has a grain size within the range of 0.45 to 1.2 microns; (c) contains 1 to 12 mole percent iodide; (d) has a core region (A), a surface region (B) and a subsurface region (C) between core region (A) and surface region (B); wherein (i) subsurface region (C) contains an iodide concentration higher than the iodide concentration of core region (A); and, (e) the silver bromoiodide is prepared by a process comprising, in sequence, (I) a nucleation step comprising mixing bromide salts and silver salts in a reaction medium; then, (II) a crystal growth step under pBr conditions within the range of 1.75 to 4.2 pBr, typically 2.0 to 2.8 pBr, enabling formation of core region (A) comprising 50% to 90% by weight of the silver bromoiodide; then, (III) addition to the composition from step (II) of iodide salt in which 25 to 100 mole percent of the total iodide salt is added to the composition from step (II) within a time period of 1 second to 20 minutes, such as, 1 second to 5 minutes; then, (IV) holding the reaction mixture from step (III) for a time period, such as 0.5 second to 20 minutes, that aids in formation of subsurface (C); then, (V) addition of silver salts and, optionally, bromide to the reaction mixture from step (IV) until reaction completion forming surface region (B). The step (III) is described herein as a "dump iodide step". The method steps as described enable the formation of a higher concentration of crystal defects in the silver bromoiodide than would otherwise be expected. This higher concentration of crystal defects is believed to contribute to the unexpectedly higher photographic speed of the resulting octahedral silver bromoiodide as described.

Another aspect of the invention is a photographic element, particularly a color photographic element, comprised of a support bearing at least one photographic silver bromoiodide emulsion layer as described herein.

A further aspect of the invention is a method of preparing the described silver bromoiodide emulsion including the steps of the process comprising, in sequence, (I) a nucleation step comprising mixing bromide salts, particularly alkali metal bromide salts, and silver salts, particularly silver nitrate, in a reaction medium, such as an aqueous gelatin reaction medium; then, (II) a crystal growth step under pBr conditions within the range of 1.75 to 4.2 pBr, preferably within the range of 2.0 to 2.8 pBr, enabling formation of described core region (A) comprising 50% to 90% by weight of the silver bromoiodide; then, (III) addition to the composition from step (II) of iodide salt in which 25 to 100 mole percent, preferably 50 to 100 mole percent, of the total iodide salt is added to the composition from step (II) within a time period, such as within a time period of 1 second to 20 minutes, such as 1 second to 5 minutes, that enables formation of subsurface region (C); then, (IV) holding the reaction mixture from step (III) until the iodide salt dissolves and reacts, such as for a time period within the range of 2 to 5 minutes; then, (V) addition of silver salts, such as silver nitrate, to the reaction mixture from step (IV) until reaction completion forming surface region (B). The octahedral silver bromoiodide grains that result from the described process are preferably monodispersed grains having a grain size within the range of 0.6 to 1 micron.

A further aspect of the invention is directed to forming a visible photographic image, particularly a color photographic image, by a process comprising processing an exposed photographic element, as described, herein in an aqueous alkaline solution in the presence of a photographic developing agent, particularly a color photographic silver halide developing agent.

The described invention enables unique and unexpected advantages. The described photographic emulsion, element and process enable the improvement of photographic speed and reduced granularity without sacrificing the advantages of an octahedral silver bromoiodide emulsion. The described emulsions are particularly advantageous when chemically sensitized and spectrally sensitized and in color photographic materials designed to form dye images. The described emulsions, elements and processes enable significantly improved photographic speed for color images, especially images that have particularly useful sharpness and speed-grain relationship.

The term octahedral herein includes octahedral and such grains that do not include sharp edges, such as cubooctahedral grains.

The term core region (A) herein means the central portion of the octahedral silver bromoiodide grain according to the invention. This region (A) can contain 0 to 9 mole percent iodide. It comprises 50% to 90%, typically 60% to 80% by weight of the total silver bromoiodide grain.

The term surface region (B) herein means the outer region of the octahedral silver bromoiodide beyond subsurface region (C). This region (B) can contain 0 to 9 mole percent iodide. This typically comprises 10% to 40% by weight of the total silver bromoiodide grain.

The term subsurface region (C) herein means the region of the silver bromoiodide grain according to the invention between the core region (A) and the surface region (B) as described. The subsurface region (C) typically comprises 1% to 20% by weight of the total silver bromoiodide grain. The interfaces between the regions (A), (B) and (C) as described are typically not sharply defined in the silver bromoiodide grain. Each of the regions (A), (B) and (C) may, but typically do not, comprise multiple regions within each of the described regions, that is each region does not typically comprise multiple shells.

In the process as described necessary bromide can be added before or after the described dump iodide step.

The step (IV) can be essentially eliminated or extended depending on the emulsion making equipment capability. Preferably, the hold step (IV) is present and is typically carried out within a period of about 2 minutes to 10 minutes.

In the process of preparation of the silver bromoiodide emulsion it is preferred to carry out a finishing step as known in the photographic art. This finishing step is preferably carried out using at least one spectral sensitizing dye as part of the finishing step. Any spectral sensitizing dye known to be useful in a finishing step can be used for this purpose. In addition it is preferable to use a finishing modifier known in the photographic art in the finishing step, such as a benzothiazolium finish modifier. Such a finishing step using at least one spectral sensitizing dye and a finish modifier, such as a benzothiazolium compound, enables the resulting photographic silver bromoiodide emulsion of the invention to have even higher photographic speed than otherwise would be expected.

The term monodispersed herein means that at least 95%, such as 95% to 99.9%, by weight of the silver bromoiodide grains less than the mean grain diameter and at least 95%, such as 95% to 99.9%, by number of the silver bromoiodide grains larger than than the mean grain diameter must be within 40% of the mean grain diameter. The mean grain diameter means the diameter of a circle equal in area to the mean projected area of the silver bromoiodide grains, especially as viewed in a photomicrograph or an electronmicrograph of an emulsion sample.

The octahedral silver bromoiodide grains as described may have rounded corners and rounded edges.

The grain size and characteristics of the silver bromoiodide grains as described can be readily ascertained by procedures well known in the photographic art. In some instances a concentration of silver halide grains that are not octahedral silver bromoiodide grains can be present in the emulsion and element without adversely affecting the required properties of the silver bromoiodide emulsion as described.

The silver bromoiodide emulsion as described is prepared by controlling the introduction of the iodide salts in the precipitation process. The iodide is added in the process within a reasonably short time and can be termed a "dump iodide process" because the iodide is not run into the reaction mixture over the entire term of the precipitation. The described step (III) is a "dump iodide step".

In the process of preparing the silver bromoiodide emulsion as described typically a dispersing medium, preferably an aqueous gelatin or gelatin derivative composition, is introduced into a conventional reaction vessel designed for silver halide precipitation equipped with an efficient stirring mechanism. The volume of dispersing medium initially present in the reaction vessel can equal or exceed the volume of the silver bromoiodide emulsion present in the reaction at the conclusion of the grain precipitation. The dispersing medium introduced into the reaction vessel is preferably a dispersion of peptizer in water, particularly gelatin in water, optionally containing other ingredients, such as silver halide ripening agents and/or metal dopants. The peptizer, particularly gelatin or a gelatin derivative, is typically initially present in a concentration of at least 0.5%, preferably at least 1%, of the total peptizer present at the completion of the silver bromoiodide precipitation. Additional dispersing medium can optionally be added to the reaction vessel with the silver salts and the alkali metal bromide and iodide salts and also can be introduced through a separate inlet means, such as a separate jet. The proportion of dispersing medium can be adjusted after the completion of the salt introductions or after washing.

During precipitation silver salts, preferably silver nitrate, bromide salts, preferably alkali metal bromide salts, and iodide salts, preferably alkali metal bromide salts, are added to the reaction vessel by techniques known in the photographic emulsion making art. Typically an aqueous silver salt solution, preferably an aqueous silver nitrate solution, is introduced into the reaction vessel concurrently with the introduction of bromide alone or bromide and iodide salts. The bromide and iodide salts are typically introduced as aqueous solutions, preferably as aqueous solutions of one or more alkali metal, such as potassium or sodium salts. Alkaline earth metal salts can also be useful, such as calcium and magnesium salts. The silver salt is introduced into the reaction vessel separately from the halide salt. The iodide and bromide salts can be added to the reaction vessel separately or as a mixture.

With the introduction of the silver salts into the reaction vessel the nucleation step of the grain formation is initiated. A population of grain nuclei are formed that are capable of serving as precipitation sites for silver bromide and silver iodide as the introduction of silver, bromide and iodide salts continues. The precipitation of the silver bromide and silver iodide onto the existing grain nuclei constitutes the crystal growth step of grain formation. The permissible latitude of pBr during the growth stage of the precipitation is within the range of 1.75 to 4.2 pBr, preferably within the range of 2.0 to 2.8 pBr. The pBr can be measured and regulated during the precipitation by methods and apparatus known in the photographic art. The pBr is as defined in U.S. Patent 4,434,226 and is the negative logarithm of bromide ion concentration.

Subject to requirements of the process as described the concentrations and rates of silver salt, bromide salt and iodide salt introductions can take any convenient and conventional form useful for forming octahedral silver bromoiodide emulsions. The silver and halide salts are preferably introduced in concentrations within the range of 0.1 to 5 moles per liter. The rate of silver and halide salt introduction can be constant or optionally increased either by increasing the rate at which the silver and halide salt are introduced or by increasing the concentrations of the silver and halide salts being introduced. It is preferred to increase the rate of silver and halide salt introduction, but to maintain the rate of introduction below that at which the formation of new grain nuclei is favored to avoid renucleation. The concentration of iodide in each step is important to enable the higher concentration of iodide in subsurface region (C) as described.

The process can be carried out within controlled pAg conditions using methods and apparatus known in the photographic art. Using measuring techniques, electrodes and conditions known in the photographic art the vAg is, for example, controlled within the range of +5 to +160 mV, preferably within the range of +20 to +80 mV.

The process of preparing the described silver bromoiodide is preferably carried out at a temperature within the range of 25° C to 80° C, such as 45° C.

Modifying compounds can be present during the silver bromoiodide precipitation. Such compounds can be initially in the reaction vessel or can be added with one or more of the salts according to conventional emulsion making procedures. Modifying compounds, such as compounds of copper, iridium, thallium, lead, bismuth, cadmium, zinc, middle chalcogens, such as sulfur, selenium and tellurium, gold, Group VIII noble metals, can be present during the precipitation, as described in, for example, U.S. Patent 4,433,048 and the art described therein.

The individual silver and halide salts or a silver halide source, such as silver iodide seeds, can be added to the reaction vessel through surface or subsurface delivery tubes, by gravity feed or delivery apparatus for maintaining control of the rate of delivery and the pH, pBr, and/or pAg or the reaction vessel contents as is used in the art of photographic emulsion making.

In forming the silver bromoiodide emulsions, a dispersing medium preferably comprises in the reaction vessel initially an aqueous peptizer suspension. The peptizer concentration is typically within the range of 0.2% to 10% by weight, based on the total weight of the emulsion components in the reaction vessel. Typically the concentration of peptizer in the reaction vessel is maintained below about 6%, based on the total weight, prior to and during silver halide formation. The emulsion vehicle concentration is typically adjusted upwardly for optimum coating characteristics by delayed, supplemental vehicle additions. Additional vehicle can be added later to bring the concentration up to as high as 1000 grams per mole of silver halide. Preferably the concentration of vehicle in the finished emulsion is above 50 grams per mole of silver halide. When coated and dried on a support forming a photographic element, the vehicle preferably comprises about 30% to about 70% by weight of the emulsion layer.

Vehicles, including both binders and peptizers, can be selected from those conventionally employed in photographic silver halide emulsions. Preferred peptizers are hydrophilic colloids, that can be used alone or in combination with hydrophobic materials. Useful hydrophilic materials include both naturally occurring substances, such as proteins, protein derivatives, cellulose derivatives, such as cellulose esters, gelatin, such as alkali treated gelatin or acid treated gelatin, gelatin derivatives, such as acetylated gelatin and phthalated gelatin, polysaccharides, such as dextran, gum arabic, zein, casein, pectin, collagen derivatives, agar-agar, arrowroot and albumin and other vehicles and binders known in the photographic art. Gelatin is highly preferred.

Other materials commonly used in combination with hydrophilic colloid peptizers as vehicles, including, for example, vehicle extenders such as materials in the form of latices, are also useful in the emulsions as described, such as polymeric peptizers, carriers and/or binders, such as poly(vinyl lactams), acrylamide polymers, poly(vinyl alcohol) and its derivatives, poly(vinyl acetals), polymers of alkyl and sulfoalkyl acrylates and methacrylates, hydrolyzed poly(vinyl acetates), polyamides, poly(vinyl pyridine), acrylic acid polymers, maleic acid copolymers, vinyl amine copolymers, methacrylic acid copolymers, acryloyloxyalkylsulfonic acid copolymers, sulfoacrylamide copolymers, polyalkyleneimine copolymers, polyamines, N,N-dialkylaminoalkyl acrylates, vinyl imidazole polymers and copolymers, vinyl sulfide copolymers, halogenated styrene polymers, amineacrylamide polymers, polypeptides and other vehicles and binders known to be useful in the photographic art, such as described in U.S. Patent 4,433,048.

These added materials need not be present in the reaction vessel during the silver halide precipitation, but rather can typically be added to the emulsion prior to coating on the support. The vehicles and binders, including the hydrophilic colloids, as well as the hydrophobic materials, can be employed alone or in combination, not only in the emulsion layers of the photographic element, but also can be used alone or in combination in other layers, such as overcoat layers, interlayers, and layers positioned between emulsion layers and the support.

Grain ripening can be carried out in preparation of an emulsion as described. Grain ripening agents known to be useful in the photographic art can be useful in the photographic emulsions. For example, a thioether ripening agent can be added to the photographic silver bromoiodide emulsion. Useful thioether ripening agents include, for example, those described in U.S. Patents 3,271,157; 3,574,628; and 3,737,313.

The silver bromoiodide emulsions are preferably washed to remove soluble salts. Any of the processes and compositions known in the photographic art for this purpose can useful for washing the photographic silver bromoiodide emulsions. The soluble salts can be removed by decantation, filtration, and/or chill setting and leaching, coagulation washing, by centrifugation, and by other methods and means known in the photographic art.

If desired, the silver bromoiodide emulsion as described can be blended or otherwise combined with other photographic silver halide emulsions. The octahedral photographic silver bromoiodide emulsions can be, for example, optionally combined with a tabular grain silver halide emulsion, such as one described in U.S. Patent 4,433,048, or optionally combined with a cubic grain silver halide emulsion, such as one described in European Patent Application No. 353,628.

The photographic silver bromoiodide can be chemically sensitized by procedures and by compounds known in the photographic art to be useful for this purpose. For example, the silver bromoiodide can be chemically sensitized with active gelatin, or with sulfur, selenium, tellurium, gold, platinum, palladium, iridium, osmium, rhodium, rhenium, or phosphorous sensitizers or combinations of these sensitizers, such as at pAg levels within the range of 90 to 120 mV and pH levels within the range of 5 to 8 at temperatures within the range of 30° to 80° C. The silver bromoiodide can be chemically sensitized in the presence of finish, also known as chemical sensitization, modifiers, such as compounds known to suppress fog and increase speed during chemical sensitization, such as azaindenes, azapyridazines, azapyrimidines, benzothiazolium salts, and sensitizers having more than one heterocyclic nuclei. Optionally the silver bromoiodide can be reduction sensitized, such as with hydrogen, or through the use of reducing agents, such as stannous chloride, thiourea dioxide, polyamines or amineboranes.

The photographic silver bromoiodide emulsion can be spectrally sensitized by methods and compounds known in the photographic art. The silver halide emulsion can be sensitized in the presence of sensitizing dyes. The photographic silver bromoiodide emulsion can be spectrally sensitized by, for example, dyes of a variety of classes, including the polymethine sensitizing dye class, including cyanines, merocyanines, complex cyanines and merocyanines, oxonols, hemioxonols, styryls, merostyryls and streptocyanines. Combinations of spectral sensitizers are also useful.

The photographic silver bromoiodide emulsions can be used in ways, in photographic element formats and for purposes that silver bromoiodide emulsions have been used in the photographic art.

Photographic silver halide elements comprising a photographic silver bromoiodide emulsion as described can be either single color or multicolor elements. In a multicolor element, a cyan dye-forming coupler is typically associated with a red-sensitive emulsion, a magenta dye-forming coupler is typically associated with a green-sensitive emulsion and a yellow dye-forming coupler is associated with a blue-sensitive emulsion. Multicolor elements typically contain dye-forming units sensitive to each of the three primary regions of the spectrum. Each unit can comprise a single emulsion layer or multiple emulsion layers. The layers of the element and the image-forming units can be arranged in various orders as known in the photographic art.

The photographic element can contain added layers, such as filter layers, interlayers, overcoat layers, subbing layers and other layers known in the photographic art.

The following discussion of illustrative materials that are useful in photographic silver halide materials and processes reference will be made to Research Disclosure, December 1978, Item No. 17643, published by Kenneth Mason Publications Ltd., Dudley Annex, 21a North Street, Emsworth, Hampshire PO10 7DQ, England. The publication will be identified hereafter by the term "Research Disclosure".

Silver halide emulsions that can be employed in combination with the silver bromoiodide emulsion as described can be comprised of silver bromide, silver chloride, silver iodide, silver chloroiodide, silver chlorobromide or mixtures thereof. These silver halide emulsions can include silver halide grains of any conventional shape or size. Specifically the emulsions can be coarse, medium or fine grain. Tabular grain silver halide emulsions are particularly useful in a photographic element as described. The silver halide emulsions that are useful with the silver bromoiodide emulsions can be polydisperse or monodisperse as precipitated. The grain size distribution of these emulsions can be controlled by silver halide grain separation techniques or by blending silver halide emulsions of differing grain sizes. For example, silver bromoiodide or silver bromides of different sizes of the same type and shape can be blended.

Any coupler known in the photographic art can be used with the silver bromoiodide emulsions as described. Examples of useful couplers are described in, for example, Research Disclosure Section VII, paragraphs D, E, F, and G and in U.S. Patent 4,433,048 and the publications cited therein, as well as in U.S. Patents 4,333,999; 4,443,536; 4,420,556; 4,401,752; 4,777,121; 4,728,598; 4,753,871; 4,782,012; 4,477,563; 4,248,962; 4,409,323 and European Patent Applications 284,239; 271,323; 271,324; 285,274; 193,389; 255,085 and 284,240. Polymeric couplers are also useful with the described silver bromoiodide emulsions, as described in, for example, U.S. Patents 4,804,620; 4,540,654; and 4,576,910. The couplers can be incorporated as described in Research Disclosure Section VII and the publications cited therein.

The photographic emulsions and elements can contain addenda known to be useful in the photographic art. The photographic emulsions and elements can contain brighteners (Research Disclosure Section V), antifoggants and stabilizers (Research Disclosure Section VI), antistain agents and image dye stabilizers (Research Disclosure Section VII, paragraphs I and J), light absorbing and scattering materials (Research Disclosure Section VIII), hardeners (Research Disclosure Section XI), plasticizers and lubricants (Research Disclosure Section XII), antistatic agents (Research Disclosure Section XIII), matting agents (Research Disclosure Section XVI) and development modifiers (Research Disclosure Section XXI).

The photographic emulsions can be coated on a variety of supports as described in, for example, Research Disclosure Section XVII and the references cited therein.

The photographic elements as described can be exposed to actinic radiation, typically in the visible region of the spectrum, to form a latent image as described in Research Disclosure Section XVII and then processed to form a visible image using processes and compositions known in the photographic art, such as described in Research Disclosure Section XIX and U.S. Patent 4,433,048 and the references described therein.

Processing of a color photographic element as described to form a visible dye image includes the step of contacting the element with a color photographic silver halide developing agent to reduce developable silver halide and oxidize the color developing agent. Oxidized color developing agent in turn reacts with at least one coupler to yield a dye.

Preferred color developing agents are p-phenylenediamines. Especially preferred are 4-amino-3-methyl-N,N-diethylaniline hydrochloride; 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)-ethylaniline sulfate hydrate; 4-amino-3-methyl-N-ethyl-N-β-hydroxyethylaniline sulfate; 4-amino-3-β-(methanesulfonamido)ethyl-N,N-diethyl-aniline hydrochloride and 4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluene sulfonic acid.

With the negative working silver bromoiodide emulsion this processing step leads to a negative image. To obtain a positive image (or reversal image), this step can be preceded by development with a non-chromogenic developing agent to develop exposed silver halide, but not form dye, and then uniform fogging of the element to render unexposed silver halide developable.

Development is followed by conventional steps of bleaching, fixing, or bleach-fixing, to remove silver and silver halide, washing and drying.

Improvements in sharpness can be obtained with a photographic silver bromoiodide emulsion and element as described, a photographic silver halide development inhibitor releasing compound or coupler (DIR compound or DIAR compound). Any development inhibitor releasing compound or coupler known in the photographic art is useful with the photographic silver bromoiodide emulsion and element. Particularly useful development inhibitor releasing compounds or couplers are represented by the formula: CAR-TIME-INH wherein CAR is a carrier moiety, preferably a coupler moiety; TIME is at least one timing group; and INH is a development inhibitor moiety.

The DIR compounds that satisfy the formula CAR-TIME-INH are known in the art and are described in, for example, U.S. Patents 4,248,962; 4,409,323; 4,684,604; 4,737,451; 4,546,073; 4,564,587; 4,618,571; 4,698,297; 4,782,012; and U.K Patent 2,099,167 and European Published Patent Applications 167,168 and 255,085 and German OLS 3,307,506, the disclosures of which are incorporated herein by reference.

The carrier moiety (CAR) can be any moiety that, as a result of reaction with oxidized color developing agent, will release the timing group (TIME). Preferably the carrier is a coupler, but it can be another group, such as a hydrazide, a hydrazine or hydroquinone. Coupler moieties can be colored or colorless, diffusible or nondiffusible, reaction product with oxidized color developing agent.

When the carrier moiety is a coupler moiety, the DIR compounds are DIR couplers represented by the formula: COUP-TIME-INH wherein COUP is a coupler moiety.

Preferred timing groups are described in U.S. Patents 4,248,962; 4,409,323; 4,782,012 and European Patent Application 255,085.

The development inhibitor that is released from the DIR compound or coupler during processing of the element can be any of the development inhibitors known in the photographic art. Illustrative INH moieties are mercaptotetrazoles, selenotetrazoles, mercaptobenzolthiazoles, selenobenzothiazoles, selenobenzimidazoles, mercaptobenzimidazoles, mercaptobenzoxazoles, selenobenzoxazoles, benzotriazoles, and benzodiazoles. Particularly preferred are those described in U.S. Patents 4,477,563 and 4,782,012.

The following examples further illustrate the invention.

Example 1:

A series of 4 monodisperse silver bromoiodide octahedral grain emulsions all containing a total of 3 mole percent iodide were prepared. The emulsions differed in the placement and method of introduction of the iodide. Emulsions A and B are comparison emulsions and emulsions C and D are examples of the invention.

Examples:

Emulsion A - (Iodide introduced uniformly throughout the precipitation)

A monodisperse, octahedral grain, silver bromoiodide (3M% I) emulsion having a grain size of 0.8 micron was prepared in the following manner:

Eight solutions were prepared as follows:

Solution 1A: (Placed in the reaction vessel)

Deionized Gelatin	36 g
Distilled Water	4000 ml

Dissolved at 80°C

Solution 2A:

Sodium Bromide	14.8 g
Potassium Iodide	0.4 g
Distilled Water to	280 ml

Dissolved at room temperature

Solution 3A:

Sodium Bromide	898.2 g
Potassium Iodide	44.8 g
Distilled Water to	4500 ml

Dissolved at room temperature

Solution 4A:

Silver Nitrate (5M solution)	37.8 g
Distilled Water to	225 ml

Solution 5A:

Silver Nitrate (5M solution)	2138 g
Distilled Water to	3181 ml

Solution 6A:

Silver Nitrate (5M solution)	537.6 g
Distilled Water to	800 ml

Solution 7A:

Gelatin	150 g
Distilled Water	800 ml
Dissolved at 80°C	

Solution 8A:

Gelatin	294 g
Distilled Water	1600 ml
Dissolved at 40°C	

To Solution 1A, at 80° C, were added 0.018 g of 1,10-dithio-4,7,13,16-tetraoxacyclooctadecane dissolved in 36 ml of methanol and distilled water (1:1). The pH of the contents of the reaction vessel was determined to be 5.22, and the pBr was adjusted to 2.8 using a 1M sodium bromide solution. Solutions 2A and 4A were then simultaneously run into Solution 1A, with continuous agitation, for 5 minutes using a balanced double jet technique at a flow rate of 15 ml per minute, while maintaining the pBr at 2.8 and the temperature at 80° C. At this point Solution 7A was added and the resulting composition was held for 5 minutes. At 2 1/2 minutes into the hold the pBr was adjusted to 2.2 with Solution 3A. After the completion of the hold, the precipitation was continued by simultaneously adding Solutions 3A and 5A using an accelerated flow balanced double jet technique according to the following profile: 15 minutes at 25 ml per minute, 10 minutes at 35 ml per minute, 10 minutes at 65 ml per minute, 10 minutes at 105 ml per minute, then 155 ml per minute, until Solution 5A was exhausted, while maintaining the pBr at 2.2 and temperature at 80° C. At this point the pump supplying Solution 5A was switched to Solution 6A and the pump supplying Solution 3A was switched off until the pBr was adjusted to 2.5. At this point the salt supply pump was switched on and Solutions 3A and 6A were simultaneously added at a rate of 35 ml per minute until Solution 6A was exhausted. The resulting emulsion was then cooled to 40° C and washed using by diafiltration, with a semipermeable membrane to a pBr of 3.4. Solution 8A was then added and the pH and pBr were adjusted to 5.6 and 3.4 respectively.

Emulsion B - (All of the iodide was introduced uniformly throughout the first 80% of the precipitation, followed by only bromide for the last 20%)

Nine solutions were prepared as follows:

Solution 1B: (Placed in the reaction vessel)

Deionized Gelatin	36 g
Distilled Water	4000 ml

Dissolved at 80°C

Solution 2B:

Sodium Bromide	14.8 g
Potassium Iodide	0.4 g
Distilled Water to	280 ml

Dissolved at room temperature

Solution 3B:

Sodium Bromide	672.3 g
Potassium Iodide	42.3 g
Distilled Water to	3394 ml

Dissolved at room temperature

Solution 4B:

Sodium Bromide	257.3 g
Distilled Water to	1250 ml

Dissolved at room temperature

Solution 5B:

Silver Nitrate (5M solution)	12.6 g
Distilled Water to	75 ml

Solution 6B:

Silver Nitrate (5M solution)	2138 g
Distilled Water to	3181 ml

Solution 7B:

Silver Nitrate (5M solution)	537.6 g
Distilled Water to	800 ml

Solution 8B:

Gelatin	150 g
Distilled Water	800 ml
Dissolved at 80°C	

Solution 9B:

Gelatin	294 g
Distilled Water	1600 ml
Dissolved at 40°C	

To Solution 1B, at 80° C, were added 0.018 g of 1,10-dithio-4,7,13,16-tetraoxacyclooctadecane dissolved in 36 ml of methanol and distilled water (1:1). The pH of the contents of the reaction vessel was determined to be 5.17, and the pBr was adjusted to 2.8 using a 1M solution of sodium bromide. Solutions 2B and 5B were then simultaneously run into Solution 1B, with continuous agitation, for 5 minutes using a balanced double jet technique at a flow rate of 15 ml per minute, while maintaining the pBr at 2.8 and the temperature at 80° C. At this point Solution 8B was added and the resulting composition was held for 5 minutes. At 2 1/2 minutes into the hold the pBr was adjusted to 2.2 with Solution 3B. Solutions 3B and 6B were then simultaneously run into the reaction vessel using the same flow profile described above in Emulsion A while maintaining the pBr at 2.2 until Solution 6B was exhausted. Solution 7B was then added until the pBr reached 2.5. Solutions 4B and 7B were then simultaneously introduced over a period of 85.4 minutes using the same flow profile described in Emulsion A above while maintaining a pBr of 2.5. The resulting emulsion was then cooled to 40° C and washed by diafiltration, with a semipermeable membrane, to a pBr of 3.5. Solution 9B was then added and the pH and pBr were adjusted to 5.6 and 3.4, respectively. The resulting emulsion had a grain size of 0.7 micron.

Emulsion C - (All of the iodide was introduced at one finite time during the precipitation)

Ten solutions were prepared as follows:

Solution 1C: (Placed in the reaction vessel)

Deionized Gelatin	40 g
Distilled Water	4000 ml
Dissolved at 80°C	

Solution 2C:

Sodium Bromide	51 g
Distilled Water to	2000 ml
Dissolved at room temperature	

Solution 3C:

Sodium Bromide	611.8 g
Distilled Water to	2400 ml
Dissolved at 40°C	

Solution 4C:

Sodium Bromide	191.2 g
Potassium Iodide	3.3 g
Distilled Water to	500 ml
Dissolved at 40°C	

Solution 5C:

Silver Nitrate (5M solution)	145.2 g
Distilled Water to	17.28 ml
Dissolved at room temperature	

Solution 6C:

Silver Nitrate (5M solution)	1868 g
Distilled Water to	2224 ml
Dissolved at room temperature	

Solution 7C:

Silver Nitrate (5M solution)	941 g
Distilled Water to	1120 ml
Dissolved at room temperature	

Solution 8C:

Preformed Silver Iodide emulsion grains having a grain size of 0.05 micron	492 g (0.22 mole)
Dissolved at 40°C	

Solution 9C:

Gelatin	200 g
Distilled Water	800 ml
Dissolved at 80°C	

Solution 10C:

Gelatin	240 g
Distilled Water	1600 ml
Dissolved at 40°C	

The pH of the reaction vessel was determined to be 5.82, and the pBr was adjusted to 2.8 using a 1M solution of sodium bromide. Solutions 2C and 5C were then simultaneously run into Solution 1A in the reaction vessel, with constant agitation. The addition was performed over a 5-minute period, using a balanced double jet technique at a flow rate of 24 ml per minute while maintaining the pBr at 2.8 and the temperature at 80 ° C. The precipitation was then stopped and Solution 9C was added and the reaction vessel and the resulting composition was held for 5 minutes. At 2 1 2 minutes into the hold the pBr was adjusted to 2.2 with Solution 2C. After completion of the hold, the precipitation was continued by simultaneously Solutions 2C and 5C using an accelerated flow balanced double jet technique at flow rates of 24 ml per minute for 1 minute and 690 ml per minute until Solution 5C was exhausted. Solutions 3C and 6C were then introduced using flow rates of 24 ml per minute for 10 minutes, 40 ml per minute for 10 minutes, 65 ml per minute for 10 minutes, 105 ml per minute for 10 minutes and 155 ml per minute until Solution 6C was exhausted while maintaining a pBr of 2.2. Solution 4C was then dumped into the reaction vessel and the resulting composition was held for 2 minutes, at which time Solution 8C was dumped into the reaction vessel and the composition was again held for 2 minutes. Solution 7C was then introduced at a flow rate of 77 ml per minute for 10 minutes, then 33 ml per minute until a pBr of 2.5 was reached. The emulsion was then cooled to 40 ° C and washed using by diafiltration, with a semipermeable membrane to a pBr of 3.5. Solution 10C was then added and the pH and pBr were adjusted to 5.6 and 3.4 respectively The emulsion had a grain size of 0.7 micron.

Emulsion D - (The introduction of the iodide was partly accomplished in a uniform manner during the run phase of the precipitation and partly during a finite time in the precipitation)

The emulsion was prepared using the same procedure described above for Emulsion C with the following differences in composition of the solutions:

Solution 2D:

As Solution 2C plus 1.4 g Potassium Iodide

Solution 3D:

As Solution 3C plus 16.5 g Potassium Iodide

Solution 8D:

As Solution 8C except only 0.12 moles of the preformed silver iodide emulsion.

The emulsion had a grain size of 0.6 micron.

The series of monodisperse octahedral grain silver bromoiodide emulsions described above were spectrally sensitized to the red region of the visible spectrum then optimally sulfur and gold chemically sensitized in the presence of sodium thiocyanate and the finish modifier N-[N-(methyl-sulfonyl)-carbamoylethyl]benzothiazoliumtetrafluoroborate. The emulsions were separately coated in a single-layer cyan dye-forming format on a cellulose triacetate film support. Each of the coated elements comprised the respective emulsion at 0.8 g Ag/m^2, gelatin at 3.2 g/m^2, a solvent dispersion of the cyan dye image-forming coupler (Coupler A) at .97 g/m^2 and the DIR coupler (Coupler B) at 0.03 g m^2. An overcoat layer comprising gelatin at 4.3 g/m^2 and the hardener bis(vinylsulfonylmethyl)ether at 1.75% based on the total gelatin weight was applied.

The resulting photographic elements were imagewise exposed at 1 100 of a second through a 0 - 4.0 density step tablet plus a Wratten No. 29 filter (Wratten is a trademark of Eastman Kodak Co., U.S.A.) to a 600W, 5500 K tungsten light source. Processing was accomplished at 37.7 ° C in a color process of the type described in the British Journal of Photography Annual 1979, pages 204 -206, at a development time of 3 minutes 15 seconds. The processed photographic elements were then evaluated for speed and relative granularity position. The results are given in following Table I:

TABLE I

Element/ Emulsion (Grain Size)	Δ Log E vs. Element I	Granularity Position Relative to Element I
I-A (0.8 Micron)	——	——
II-B (0.7 Micron)	-.04	+2 grain units
III-C (0.7 Micron)	+.25	-5 grain units
IV-D (0.6 Micron)	+.08	-4 grain units

When radiation-sensitive silver halide emulsions differing in mean grain size are optimally sensitized, there is a predictable relationship between photographic speed and granularity. It is generally recognized that each doubling of photographic speed results in an increase of 5 - 7 granularity units. When emulsions of differing speed also differ in granularity by a predicted number of granularity units, the emulsions are said to exhibit the same speed-granularity relationship. An emulsion which shows increased speed without a proportional increase in granularity units is not only a faster emulsion, but an emulsion exhibiting a superior speed-granularity relationship. An emulsion which exhibits reduced granularity without a proportionate loss of speed also exhibits an improved speed-granularity relationship.

It is clearly demonstrated in Table I that emulsions C and D of the present invention exhibit an improved speed granularity relationship relative to comparative emulsions A and B.

Claims

1. A photographic silver halide emulsion comprising a dispersing medium and silver bromoiodide that
   (a) is octahedral silver bromoiodide;
   (b) has a grain size within the range of 0.45 to 1.2 microns;
   (c) contains 1 to 12 mole percent iodide;
   (d) has a core region (A) comprising 50% to 90% by weight of the silver bromoiodide, a surface region (B) and a subsurface region (C) between core region (A) and surface region (B); wherein
   (i) subsurface region (C) contains an iodide concentration higher than the iodide concentration of core region (A); and,
   (e) the silver bromoiodide is prepared by a process comprising, in sequence:
      (I) a nucleation step comprising mixing bromide salts or bromoiodide salts and silver salts in a reaction medium; then,
      (II) a crystal growth step under pBr conditions with the range of 1.75 to 4.2 pBr enabling formation of core region (A) comprising 50% to 90% by weight of the silver bromoiodide; then,
      (III) addition to the composition resulting from step (II) of iodide salt in which 25 to 100 mole percent of the total iodide salt is added to the composition from step (II) within a time period of 1 second to 20 minutes; then,
      (IV) holding the reaction mixture resulting from step (III) that aids in formation of subsurface region (C); then,
      (V) addition of silver salts and, optionally, bromide to the reaction mixture resulting from step (IV) until reaction completion forming surface region (B).

2. A photographic silver halide emulsion as claimed in claim 1 wherein the dispersing medium is gelatin or a gelatin derivative.

3. A photographic silver halide element comprising a support bearing at least one photographic silver halide emulsion layer comprising a photographic silver bromoiodide emulsion as defined in claim 1.

4. A photographic silver halide element as claimed in claim 3 that is a color photographic silver halide element.

5. A photographic silver halide element as claimed in claims 3 - 4 comprising at least one photographic silver halide development inhibitor releasing compound or coupler.

6. A process of forming a visible photographic image in an exposed photographic silver halide element as defined in claims 3-5 comprising developing the element in an aqueous alkaline solution in the presence of a photographic silver halide developing agent.

7. A method of preparing an octahedral silver bromoiodide emulsion wherein the octahedral silver bromoiodide grains have a grain size within the range of 0.45 to 1.2 microns; contain 1 to 12 mole percent iodide; and have a core region (A), a surface region (B) and a subsurface region (C) wherein the subsurface region (C) between core region (A) and surface region (B) contains an iodide concentration higher than the iodide concentration of each of core region (A) and surface region (B); wherein the process comprises, in sequence:

(I) a nucleation step comprising mixing bromide salts or bromoiodide salts and silver salts in a reaction medium; then,

(II) a crystal growth step under pBr conditions with the range of 1.75 to 4.2 pBr enabling formation of core region (A) comprising 50% to 90% by weight of the silver bromoiodide; then,

(III) addition to the composition from step (II) of iodide salt in which 25 to 100 mole percent of the total iodide salt is added to the composition from step (II) within a time period of 1 second to 20 minutes; then,

(IV) holding the reaction mixture resulting from step (III) that aids in formation of subsurface region (C); then,

(V) addition of silver salts and, optionally, bromide to the reaction mixture resulting from step (IV) until reaction completion forming surface region (B).

8. A method as claimed in claim 7 wherein the temperature is maintained within the range of 25 °C to 80 °C.

9. A method as claimed in claim 7 or 8 in which an alkali metal bromide and silver nitrate are mixed in step (I), the pBr in step (II) is in the range 2.0 to 2.8, an alkali metal iodide is added in step (III) and only silver nitrate is added in step (V).

European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 20 3208

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 152 822 (AGFA-GEVAERT AKTIENGESELLSCHAFT) * claims * – – –	1-9	G 03 C 1 035 G 03 C 1 015 G 03 C 7 30
Y	EP-A-0 340 168 (ILFORD AKTIENGESELLSCHAFT) * the whole document * – – –	1-9	
A	DE-B-1 169 290 (AGFA AKTIENGESELLSCHAFT) * example 5 * – – – – –	1-9	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	12 March 91	BUSCHA A.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same catagory
A : technological background
O : non-written disclosure
P : intermediate document
T : theory or principle underlying the invention

E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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