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3,761,267

PHOTOGRAPHIC ELEMENT CONTAINING MONO-DISPERSED, UNFOGGED, DYE SENSITIZED SILVER HALIDE GRAINS METAL IONS SENSITIZED INTERNALLY AND THE USE THEREOF IN REVERSAL PROCESS

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ABSTRACT OF THE DISCLOSURE

Improved processes are disclosed for obtaining positive images in unfogged, silver halide emulsions. In one aspect, the silver halide emulsions of this invention comprise silver halide grains having foreign metal ions and preferably polyvalent metal ions occluded therein.

This invention relates to silver halide emulsions and methods of forming positive images in silver halide emulsions. In one aspect, this invention relates to silver halide emulsions comprising silver halide grains having foreign metal ions, and preferably polyvalent metal ions, occluded therein. In another aspect, this invention relates to an improved method of obtaining positive images wherein a photographic element comprising a silver composition containing silver halide grains having foreign metal ions occluded therein is imagewise-exposed, and then is either given a light flash during development in a surface developer or developed in a surface developer in the presence of a fogging agent to produce a positive image with respect to the imagewise exposure.

Processes are known in the art for making positive images in unfogged silver halide emulsions by imagewise exposure followed by processing in fogging developers, etc. Typical processes of this type are disclosed in U.S. Pats. 2,497,875 by Falleson issued Feb. 21, 1950; 2,588,982 by Ives issued Mar. 11, 1952; and 2,456,953 by Knott and Stevens issued Dec. 21, 1948; British Pat. 1,151,363; and Japanese Patent 29,405/68 issued Dec. 17, 1968. Generally, the prior processes used internal-image silver halide emulsions such as emulsions made by the conversion technique of Davey and Knott, U.S. Patent 2,592,250, emulsions made by the techniques disclosed in British Patent 1,011,062, and the like. The emulsion could be used to make positive images by the above techniques, but improved photographic characteristics such as higher photographic speed, lower D_{min} , higher D_{max} and the like are desired to obtain acceptance of this system in many applications of photography.

We have now found that improved image properties and photographic response characteristics can be obtained in the production of a reversal or positive image when the photographic element comprises an internal-image emulsion which contains silver halide grains having foreign metal ions, and preferably polyvalent metal ions, occluded therein. In one highly preferred embodiment, highly improved results are obtained in producing a positive image when the silver halide emulsions comprising silver halide grains having polyvalent metal ions occluded therein and which grains have desensitizing levels of sensitizing dyes adsorbed thereto can be imagewise-exposed and then (1) developed in a surface developer in the presence of a fogging agent or (2) light-flashed during development in a surface developer. The silver halide emulsions described, next above, can be obtained by precipitating silver halide in the presence of certain ionized metal salts whereby the metal ion is incorporated in the crystal.

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In one preferred embodiment, the silver halide emulsions used in the improved process of this invention contain silver halide grains having lead ions occluded therein.

In another embodiment, the silver halide emulsions used in the improved process of this invention contain silver halide grains having tetravalent or trivalent metal ions occluded therein.

In another embodiment, the silver halide emulsions used in the improved process of this invention contain silver halide grains having trivalent antimony, bismuth, arsenic, gold, iridium or rhodium ions occluded therein.

In another embodiment, the silver halide emulsions used in the improved process of this invention contain silver halide grains having osmium, iridium or platinum ions occluded therein.

In another embodiment, the emulsions of this invention can be used to provide improved direct-positive image transfer systems and processes for forming a transfer image. The emulsions of this invention can comprise at least one layer in an image transfer film unit which additionally comprises an image-receiving layer and a processing composition which can be discharged to facilitate development of the silver halide emulsion by passing the unit through a pair of juxtaposed pressure-applying members. Preferably, a selective fogging agent is located in the film unit whereby it will contact said silver halide upon discharge of the processing composition, such as in one layer of the element or in a rupturable pod.

In still another embodiment, this invention relates to a process for forming a positive image in an unfogged silver halide emulsion comprising silver halide grains having polyvalent metal ions occluded therein wherein a photographic element comprising at least one layer of said emulsion is imagewise-exposed, heated to obtain an emulsion temperature of at least 100° C. for at least 1 second and then developed in a surface developer. Preferably, the emulsion comprises silver halide grains having lead ions occluded therein.

The emulsions of this invention comprise silver halide grains having dopants such as foreign metal ions or polyvalent metal ions occluded therein. The term "foreign metal ion" is understood to mean a metal ion different from the silver ions used to form the silver halide grain. Generally, emulsions of this type can be prepared by forming the silver halide grain in the presence of the metal ion salt. In the case of aqueous precipitations of silver halides, the metal salt is preferably a salt having at least some degree of water solubility at the temperature of the precipitation.

In one of the preferred embodiments of this invention, the silver halide emulsions contain silver halide grains having lead ions occluded therein. In certain other embodiments, the occluded ions are polyvalent metal ions or preferably tetravalent or trivalent metal ions. Typical procedures for forming silver halide emulsions with silver halide grains having polyvalent metal ions occluded therein are disclosed in U.S. Pats. 3,271,157 by McBride issued Sept. 6, 1966, 3,447,927 by Bacon et al. issued June 3, 1969, and 3,531,291 by Bacon issued Sept. 29, 1970.

Typical suitable polyvalent metal ions include the divalent metal ions such as lead ions, the trivalent metal ions such as those of antimony, bismuth, arsenic, gold, iridium, rhodium and the like, and tetravalent metal ions such as those of platinum, osmium, iridium and the like. The polyvalent metal ions or mixtures thereof can be suitably added with the water-soluble salt (e.g., silver nitrate) or the water-soluble halide (e.g., sodium or potassium iodide, bromide or chloride) that are combined to precipitate photographic silver halide. Likewise, the polyvalent ions can also be introduced into the silver halide precipitation vessel with a hydrophilic colloid such as gela-

tin. The polyvalent metal ions can be added to the system as water-soluble inorganic salts, as organo-metallic materials, as complexes or as any other form of material that results in the availability of the polyvalent metal ions during the formation of the silver halide. The amount of polyvalent metal utilized can be widely varied, though at least 1×10^{-9} and more generally about 1×10^{-6} to about 2 mole percent based on the silver halide is used. The presence of the polyvalent metal ions in the silver halide grain can be observed analytically by successively washing the precipitated silver halide grains with a silver halide solvent such as an organic thioether or an alkali metal thiocyanate. If the polyvalent metal ions are only contiguous to the surface, substantially all of the ions will be observed in the analysis of the first washings while substantial amounts of polyvalent ions will be found in washings just prior to complete dissolution of the silver halide when the ions are occluded therein.

In certain embodiments of this invention, the silver halide grains can be sensitized on the surface with dyes such as spectral-sensitizing dyes. The dyes can be used in concentrations used in the art or in concentrations which generally caused desensitization with prior-art emulsions. Typical dyes which can be used to sensitize the emulsions include the methine dyes such as cyanine and merocyanine dyes, for example, those described in U.S. Pats. 1,846,301 and 1,846,302, both issued Feb. 23, 1932, and 1,942,854 issued Jan. 9, 1934, all by Brooker; 1,990,507 by White issued Feb. 12, 1935; 2,112,140 issued Mar. 22, 1938, 2,165,338 issued July 11, 1939, 2,493,747 issued Jan. 10, 1950, and 2,739,964 issued Mar. 27, 1956, all by Brooker and White; 2,493,748 by Brooker and Keyes issued Jan. 10, 1950; 2,503,776 issued Apr. 11, 1950, and 2,519,001 issued Aug. 15, 1950, both by Sprague; 2,666,761 by Heseltine and Brooker issued Jan. 19, 1954; 2,734,900 by Heseltine issued Feb. 14, 1956; and 2,739,149 by Van Lare issued Mar. 20, 1956; Kodak Limited British Patent 450,958 accepted July 15, 1936; and U.S. Ser. No. 56,700 by Spence et al. filed July 20, 1970.

In one highly preferred embodiment of this invention, the sensitizing dyes are used at a concentration which would lower the blue-speed sensitivity of an undoped, control sulfur and gold surface-sensitized silver bromoiodide (6 mole percent iodide) emulsion of similar grain size and distribution at least 0.3 log E when developed at 25° C. in a surface developer such as Kodak Developer D-19. In a highly preferred embodiment, silver halide emulsions comprising silver halide grains having lead ions occluded therein are used in combination with desensitizing levels of sensitizing dyes in a photographic element which can be processed by the process disclosed herein to provide a positive image record. In one aspect of this preferred embodiment, a fogging agent from the class of reactive N-substituted cycloammonium quaternary salts is present in at least one layer of the photographic element in water-permeable association with the silver halide emulsion. The term "sensitizing dye" as used herein is intended to include those dyes known to sensitize spectrally silver halide emulsions, and preferably refers to those organic dyes which have a cathodic halfwave potential less positive than -1.0, i.e., -1.5, -2.0, etc. The cathodic halfwave potentials can be calculated as disclosed in Illingsworth, U.S. Pat. 3,501,307 issued Mar. 17, 1970.

The silver halides used in the present invention are unfogged. Such emulsions contain only minimal developable surface latent image wherein processing for 5 minutes at 27° C. in Kodak Developer DK-50 will provide a density of less than 0.4 and preferably less than 0.25. However, the surface of the grains of the doped emulsions of this invention can be chemically sensitized to a level below that which would produce substantial density (i.e., a density of less than 0.25) in a surface developer such as Kodak Developer DK-50 after imagewise exposure when coated at a coverage of between about 300 and 400 mg.

Ag/ft.². It is understood that chemical sensitization means sensitization of the type described by Antoine Hautot and Henri Sauvenier in *Science et Industries Photographiques*, Vol. XXVIII, January 1957, pages 1-23, and January 1957, pp. 57-65. Such chemical sensitization includes three major classes, viz., gold or noble-metal sensitization, sulfur sensitization such as by a labile sulfur compound, and reduction sensitization, i.e., treatment of the silver halide with a strong reducing agent which does not appreciably fog the silver halide but introduces small specks of metallic silver into the silver halide crystal or grain.

In accordance with this invention, a simple exposure and development process can be used to form a positive image. In one embodiment, a photographic element comprising at least one layer of a silver halide composition as described above can be imagewise-exposed and then developed in the presence of a fogging agent in a silver halide surface developer. In another embodiment, the element can be given a flash over-all exposure during surface development to provide a positive image. In still another embodiment, the emulsions can be thermally fogged after imagewise exposure by raising the temperature of the emulsion to a temperature of above 100° C. for at least 1 second, which is then followed by development in a surface developer to produce a positive image.

It is understood that the term "surface developer" encompasses those developers which will reveal the surface latent image on a silver halide grain, but will not reveal substantial internal latent image in an internal image-forming emulsion, and conditions generally used develop a surface-sensitive silver halide emulsion. The surface developers can generally utilize any of the silver halide developing agents or reducing agents, but the developing bath or composition is generally substantially free of a silver halide solvent (such as water-soluble thiocyanates, water-soluble thioethers, thiosulfates, ammonia and the like) which will solubilize or crack the grain to reveal substantial internal image. Low amounts of excess halide are sometimes desirable in the developers or incorporated in the emulsion as halide-releasing compounds, but high amounts are generally avoided to prevent substantial cracking of the grain, especially with respect to iodide-releasing compounds.

Typical silver halide developing agents which can be used in the developing compositions of this invention include hydroquinones, catechols, aminophenols, 3-pyrazolidones, ascorbic acid and its derivatives, reductones, phenylenediamines and the like or combinations thereof. The developing agents can be incorporated in the photographic elements wherein they are brought in contact with the silver halide after imagewise exposure; however, in certain embodiments they are preferably employed in a developing bath along with a silver halide fogging and/or nucleating agent.

When an over-all flash exposure is used during surface development, it can be of high intensity for a short duration or low intensity for a longer duration. In one embodiment, a Colight contact printing lamp having a tungsten light source, such as Model 919 available from Colwell Litho Products, Inc., Minneapolis, Minn., can be used to provide a light flash during development.

The developing compositions used in the process of this invention can also contain certain antifoggants and development restrainers, or optionally they can be incorporated in layers of the photographic element. Typical useful antifoggants include benzotriazoles, benzothiazoles such as 5-methylbenzothiazole, 5-methylbenzotriazole and the like, heterocyclic thiones such as 1-methyl-2-tetrazoline-5-thione and the like, aromatic and aliphatic mercapto compounds, etc.

The surface developer referred to herein as Kodak Developer DK-50 is described in the *Handbook of Chemistry and Physics*, 30th Ed. 1947, Chemical Rubber Pub-

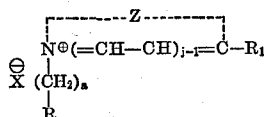
lishing Co., Cleveland, Ohio, page 2558, and has the following composition:

Water, about 125° F. (52° C.)	cc	500
N-methyl-p-aminophenol sulfate	g	2.5
Sodium sulfite, desiccated	g	30.0
Hydroquinone	g	2.5
Sodium metaborate	g	10.0
Potassium bromide	g	0.5
Water to make 1 liter.		

The silver halide emulsions of this invention can be developed in a silver halide surface developer in the presence of a fogging agent to provide good positive images. The fogging agent can be incorporated in at least one layer of the silver halide element, which layer is in water-permeable association with the silver halide emulsion, or it can be contacted with said silver halide emulsion by a separate bath or simultaneously with the surface developer composition by incorporating the fogging agent into the developer composition. Generally, the useful fogging agents of this invention are those which provide nucleation or fog specks which initiate development of the silver halide in the unexposed areas before initiating substantial development in the exposed areas of an internal-image emulsion in a surface developer. Compounds of this type are generally not practical developing agents by themselves for silver halides and are referred to as selective fogging agents; in some documents they have been referred to generally as silver halide fogging agents or nucleating agents. Typical useful selective fogging agents include hydrazine compounds, reactive N-substituted cycloammonium salts and the like.

In one preferred embodiment of the invention, hydrazines are used as the fogging agent, such as the compounds disclosed in U.S. Pats. 2,588,982 by Ives issued Mar. 11, 1952, and 3,227,552 by Whitmore issued Jan. 4, 1966.

In another preferred embodiment, the fogging agents are reactive N-substituted cycloammonium quaternary salts. Typical useful fogging agents of this type are disclosed in U.S. Ser. Nos. 28,041 by Lincoln et al. filed Apr. 13, 1970, 85,706 by Kurtz et al. filed Oct. 30, 1970, and 85,709 by Kurtz et al. filed Oct. 30, 1970, which are incorporated herein by reference. Generally, these compounds can be represented by the formula:



wherein:

(A) Z represents the atoms necessary to complete a heterocyclic nucleus containing a heterocyclic ring of 5 to 6 atoms including the quaternary nitrogen atom, with the additional atoms of said heterocyclic ring being selected from carbon, nitrogen, oxygen, sulfur and selenium;

(B) *j* represents a positive integer of from 1 to 2;

(C) *a* represents a positive integer of from 2 to 6;

(D) X[−] represents an acid anion;

(E) R represents a member selected from:

- (1) a formyl radical,
- (2) a radical having the formula:



wherein each of T₁ and T₂, when taken alone, represents a member selected from an alkoxy radical and an alkylthio radical, and T₁ and T₂, when taken together, represent the atoms necessary to complete a cyclic radical selected from cyclic oxyacetals and cyclic thioacetals having from 5 to 6 atoms in the heterocyclic acetal ring, and

(3) a 1-hydrazonoalkyl radical; and

(F) R₁ represents either a hydrogen atom, an alkyl radical, an aralkyl radical, an alkylthio radical or an aryl radical such as phenyl and naphthyl, and including substituted aryl radicals.

In certain preferred embodiments of this invention, the N-substituted cycloammonium quaternary salts are those which contain N-substituted alkyl radicals having the terminal carbon atom substituted with a hydrazono radical, an acyl radical such as a formyl radical, an acetyl radical or a benzoyl radical, and those which have a dihydroaromatic ring nucleus such as, for example, a dihydropyridinium nucleus.

Generally, the fogging agents can be incorporated in at least one layer of the photographic element in water-permeable association with the silver halide emulsion or they can be contacted with the emulsion before or during development such as by a pre-bath or incorporating the developing agent into the developing composition; however, they are preferably located in at least one layer of the element and in a highly preferred embodiment they are located in the silver halide emulsion layer. Concentrations of from about 75 to about 1500 mg. of the subject fogging agents per mole of silver in the silver halide emulsion are useful, with from about 90 to about 1200 mg. of said compounds or agents per mole of silver being preferred. These ratios are according to conventional practice, however, and with either particular reversal emulsions, fogging compounds of varying chemical activity, or varying processing conditions, more widely varying fogging agent concentrations can be advantageously used.

Typical useful selective fogging agents include

- 2-methyl-3-[3-p-sulfophenylhydrazono)propyl]benzothiazolium bromide,
- hydrazine dihydrochloride,
- phenylhydrazine hydrochloride,
- p-methyl sulfonamide ethyl phenyl hydrazine,
- formyl-4-methyl phenyl hydrazide,
- 3-(2-formyl ethyl)-2-methylbenzothiazolium bromide,
- 3-(2-acetyethyl)-2-benzylbenzothiazolium bromide,
- 3-(2-acetyethyl)-2-benzylbenzoselenazolium bromide,
- 1,2-dihydro-3-methyl-4-phenyl pyrido[2,1-b]benzothiazolium bromide,
- 4,4'-ethylene bis(1,2-dihydro-3-methylpyrido[2,1-b]benzothiazolium bromide),
- 2-methyl-3-[(3-p-nitrophenyl hydrazono)propyl]naphtho[2,1-d]thiazolium iodide,

and the like.

The silver halide emulsions of this invention can be made by any of the precipitation and ripening procedures used for making silver halide grains having metal dopants or metal ions occluded therein. Typical procedures include single-jet procedures, double-jet procedures, procedures utilizing automatic proportional control means to maintain specified pAg and pH, procedures using ripening agents such as thiocyanates, thioethers and/or ammonia, procedures utilizing an increase in flow rates as disclosed in Wilgus, U.S. Ser. No. 11,838 filed Feb. 16, 1970, hot nucleation procedures as disclosed in Musliner, U.S. Ser. No. 31,351 filed Apr. 23, 1970, and the like.

The silver halide compositions made for use in the systems of this invention are preferably monodispersed, and in some embodiments are preferably large-grain emulsions made according to Wilgus, U.S. Ser. No. 11,838, which is incorporated herein by reference. The monodispersed emulsions are those which comprise silver halide grains having a substantially uniform diameter. Generally, in such emulsions, no more than about 5%, by weight, of the silver halide grains smaller than the mean grain size and/or no more than about 5%, by number, of the silver halide grains larger than the mean grain size vary in diameter from the mean grain diameter by more than

about 40%. Preferred photographic emulsions of this invention comprise silver halide grains, at least 95%, by weight, of said grains having a diameter which is within 40%, preferably within about 30%, of the mean grain diameter. Mean grain diameter, i.e., average grain size, can be determined using conventional methods, e.g., such as projective area as shown in an article by Trivelli and Smith entitled "Empirical Relations Between Sensitometric and Size-Frequency Characteristics in Photographic Emulsion Series" in the *Photographic Journal*, Vol. LXXIX, 1939, pp. 330-338. The aforementioned uniform size distribution of silver halide grains is a characteristic of the grains in monodispersed photographic silver halide emulsions. Silver halide grains having a narrow size distribution can be obtained by controlling the conditions at which the silver halide grains are prepared using a double-run procedure. In such a procedure, the silver halide grains are prepared by simultaneously running an aqueous solution of a water-soluble silver salt, for example, silver nitrate, and a water-soluble halide, for example, an alkali metal halide such as potassium bromide, into a rapidly agitated aqueous solution of a silver halide peptizer, preferably gelatin, a gelatin derivative or some other protein peptizer. The pH and the pAg employed in this type of procedure are interrelated. For example, changing one while maintaining the other constant at a given temperature can change the size frequency distribution of the silver halide grains which are formed. However, generally the temperature is about 30 to about 90° C., the pH is up to about 9, preferably 4 or less, and the pAg is up to about 9.8. Suitable methods for preparing photographic silver halide emulsions having the required uniform particle size are disclosed in an article entitled "Ia: Properties of Photographic Emulsion Grains," by Klein and Moisar, *The Journal of Photographic Science*, Vol. 12, 1964, pp. 242-251; an article entitled "The Spectral Sensitization of Silver Bromide Emulsions on Different Crystallographic Faces," by Markocki, *The Journal of Photographic Science*, Vol. 13, 1965, pp. 85-89; an article entitled "Studies on Silver Bromide Sols, Part I. The Formation and Aging of Monodispersed Silver Bromide Sols," by Ottewill and Woodbridge, *The Journal of Photographic Science*, Vol. 13, 1965, pp. 98-103; and an article entitled "Studies on Silver Bromide Sols, Part II. The Effect of Additives on Sol Particles," by Ottewill and Woodbridge, *The Journal of Photographic Science*, Vol. 13, 1965, pp. 104-107.

The photographic emulsions and elements described in the practice of this invention can contain various colloids alone or in combination as vehicles, binding agents and various layers. Suitable hydrophilic materials include both naturally occurring substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water-soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like.

The described photographic emulsion layers and other layers of a photographic element employed in the practice of this invention can also contain, alone or in combination with hydrophilic, water-permeable colloids, other synthetic polymeric compounds such as dispersed vinyl compounds such as in latex form and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described, for example, in U.S. Pats. 3,142,568 by Nottorf issued July 28, 1964; 3,193,386 by White issued July 6, 1965; 3,062,674 by Houck et al. issued November 6, 1962; 3,220,844 by Houck et al. issued Nov. 30, 1965; 3,287,289 by Ream et al. issued Nov. 22, 1966; and 3,411,911 by Dykstra issued Nov. 19, 1968; particularly effective are those water-insoluble polymers or latex copolymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, those which have cross-linking sites which facilitate hardening or curing, those having

recurring sulfobetaine units as described in Canadian Patent 774,054 by Dykstra, and those described in U.S. Pat. 3,488,708 by Smith issued Jan. 6, 1970.

The photographic layers and other layers of a photographic element employed and described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials, as well as glass, paper, metal and the like. Typically, a flexible support is employed, especially a paper support, which can be partially acetylated or coated with baryta and/or an alpha-olefin polymer, particularly a polymer of an alpha-olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylenebutene copolymers and the like.

This invention may be used with elements designed for colloid transfer processes such as described in U.S. Pat. 2,716,059 by Yutzy et al.; silver salt diffusion transfer processes wherein development of the silver halide precedes solution of the silver halide with processes as described in U.S. Pats. 2,352,014 by Rott, 2,543,181 by Land, 3,020,155 by Yackel et al. and 2,861,885 by Land; color image transfer processes such as described in U.S. Pats. 3,087,817, 3,185,567 and 2,983,606 by Rogers, 3,253,915 by Weyerts et al., 3,227,550 by Whitmore et al., 3,227,551 by Barr et al., 3,227,552 by Whitmore and 3,415,644, 3,415,645 and 3,415,646 by Land; and imbibition transfer processes as described in U.S. Pat. 2,882,156 by Minsk.

This invention may be used with elements designed for color photography, for example, elements containing color-forming couplers such as those described in U.S. Pats. 2,376,679 by Frohlich et al., 2,322,027 by Jelley et al., 2,801,171 by Fierke et al., 2,698,794 by Godowsky, 3,227,554 by Barr et al. and 3,046,129 by Graham et al.; or elements to be developed in solutions containing color-forming couplers such as those described in U.S. Pats. 2,252,718 by Mannes et al., 2,592,243 by Carroll et al. and 2,950,970 by Schwan et al.; and in false-sensitized color materials such as those described in U.S. Pat. 2,763,549 by Hanson.

The invention can be further illustrated by the following examples.

EXAMPLE 1

A 0.2 cubic-grain internal-image silver bromide emulsion (2.6 mole percent iodide) is prepared by adding simultaneously an aqueous solution of silver nitrate and an aqueous solution of potassium bromide and potassium iodide to a rapidly agitated aqueous gelatin solution containing 10.7 mg. of potassium hexachloroiridate per silver mole. The precipitation is carried out in an acidic medium for 60 minutes at 70° C. at a pAg of 8.9. After precipitation, the emulsion is noodle-washed and chilled. Spreading and hardening agents are added to the emulsion and it is coated at .006" wet thickness on a subbed cellulose acetate support. The dried coating is exposed to an image for 5 seconds, using a 100-watt tungsten lamp at a distance of 4 feet, and then immersed in a surface developer having the following composition:

	G.
Sodium sulfite -----	10
Hhydroquinone -----	10
2.5 N sodium hydroxide -----	10
Water to 1 liter.	

While the coating is immersed in the developer, a uniform white-light exposure is given, using a 100-watt lamp at a distance of 3 feet for 20 seconds, that results in a direct-positive image.

EXAMPLE 2

A silver chlorobromide emulsion containing bismuth ions in the core of the silver halide crystal is prepared as described in Example 18 of Bacon and Barbier, U.S.

Pat. 3,447,927. After coating on a cellulose acetate support, the emulsion is exposed for $\frac{1}{2}$ second with a slit width of 1.0 mm. in a Bausch and Lomb Spectrograph, then bleached for 1 minute in a solution of potassium ferricyanide. After washing, the coating is immersed in an Elon-hydroquinone developer and given an over-all flash to a photoflood lamp for 10 seconds. The flash exposure completely fogs the unexposed areas but not the image areas, thus resulting in a positive image.

EXAMPLE 3

The following internal-image emulsions are prepared similar to Example 1, except various levels of lead nitrate (0, 5, 25, 125, 600 and 3000 mg./mole silver nitrate) are substituted for the iridium salt. A sample of each emulsion is coated on a cellulose acetate film support with suitable spreading and hardening agents. Separate strips of each coating are exposed on a Bausch and Lomb spectrograph for $\frac{1}{125}$ of a second at a slit width of 1.0 mm., then immersed in an Elon-hydroquinone developer and exposed uniformly for 5 seconds to a 100-watt tungsten lamp. The coatings remain in the developing solution for an additional 2 minutes and the following results are observed.

The coating containing no lead at the time of precipitation does not yield a positive image, while the emulsions precipitated in the presence of lead show increased ability to form good positive images as the level of lead nitrate increases. A desirable level appears to be 125 mg. lead nitrate/mole of silver halide formed in the precipitation.

EXAMPLE 4

An internal-image emulsion containing 125 mg./silver mole of lead nitrate is prepared as described in Example 3. To the emulsion are added 400 mg./silver mole of the sensitizing dye 5-[5,6-dichloro-1- β -diethylaminoethyl-3-ethyl-2-benzimidazolinyldene)ethylidene] - 3 - ethyl rhodanine. The coating is coated on a cellulose acetate film support and exposed in a Bausch and Lomb Spectrograph for $\frac{1}{1000}$ of a second at a slit width of 1.0 mm. The coating is immersed in an Elon-hydroquinone developer and exposed uniformly for 5 seconds to a 100-watt tungsten lamp. A high-speed, positive image is obtained.

EXAMPLE 5

An emulsion is prepared and coated as described in Example 4. The coating is then exposed in a Bausch and Lomb spectrograph for $\frac{1}{1000}$ of a second at a slit width of 1.0 mm. and heated on an aluminum block for 5 seconds at 200° C. A positive image results on subsequent processing in an Elon-hydroquinone surface developer.

EXAMPLE 6

Comparison of lead-doped emulsion with halide conversion emulsion

The following two emulsions are prepared:

Emulsion A: A lead-doped emulsion is prepared as described in Example 3 using 125 mg. lead nitrate/mole of silver.

Emulsion B: A converted silver halide emulsion is prepared as described in Example 1 of Davey et al., U.S. Pat. 2,592,250.

To the above emulsions is added the fogging agent 2 - methyl-[3 - (p-sulfophenylhydrazono)propyl]benzothiazolium bromide at 400 mg./silver mole. Various levels (0, 100, 200, 400 and 800 mg./mole of silver) of the dye described in U.S. Pat. 2,917,516, Example 7, are added to each emulsion to determine the optimum level of spectral sensitization for each emulsion. The emulsions are then coated at .006" wet thickness on a subbed cellulose acetate support and exposed on a Bausch and Lomb spectrograph for $\frac{1}{1000}$ of a second at a slit width of 1.0 mm. After processing in an Elon-hydroquinone developer, the following results are determined.

The optimum level of spectral sensitization for Emulsion A occurs at 400 mg. dye/silver mole, while the optimum level for Emulsion B occurs at 200 mg. dye/silver mole. It is further noticed that in the spectrally sensitized regions of each emulsion (460-610 nm.), Emulsion A is 0.6 log E faster.

Similar advantages in photographic speed and other photographic properties are obtained with the lead-doped emulsions of this example when compared with emulsions prepared according to Porter et al., U.S. Pat. 3,206,313, Example 2.

EXAMPLE 7

Three silver bromiodide (5 mole percent iodide) emulsions are prepared by slowly adding simultaneously an aqueous silver nitrate solution and a solution of alkali metal halides to an agitated aqueous gelatin solution at 35° C. and a pH of about 2.0 wherein osmium trichloride has been added to the gelatin solution prior to precipitation in concentrations of 0.45 mg./silver mole, 4.5 mg./silver mole and 45 mg./silver mole to be precipitated respectively. The emulsions are washed and then coated on a film support, exposed and processed as described in Example 1. A positive image is formed after processing in each of the photographic elements containing the respective emulsions with improved image discrimination and better photographic speed with increasing levels of osmium trichloride.

A control emulsion prepared by the same procedure without osmium trichloride in the precipitation vessel is coated, exposed and developed by the same procedure. The control does not yield a positive image record which is discernible to the eye.

EXAMPLE 8

A silver bromiodide emulsion is prepared as described in Example 1 with the provision that H_2PtCl_6 is substituted for the iridium salt. The emulsion is coated and processed as described in Example 1 to produce a good positive image.

EXAMPLE 9

A silver bromiodide emulsion is prepared as described in Example 1 with the provision that 4.5 mg. of rhodium trinitrate per mole of silver is substituted for the iridium salt. The emulsion is coated and processed as described in Example 1 to produce a good positive image.

Similar results are obtained when the metal dopants palladium ions, ruthenium ions and gold ions are occluded in the grains.

EXAMPLE 10

An internal-image emulsion is prepared according to Example 3 with 125 mg. of lead nitrate per a mole of silver to be formed added to the precipitation vessel before the start of the precipitation. The emulsion is washed and then coated on a film support, exposed $\frac{1}{50}$ second on an Eastman 1B sensitometer and developed for 1 minute at 27° C. in a fogging developer of the type described in Ives, U.S. Pat. 2,588,982. After washing and drying, a reversal image having excellent photographic characteristics is observed.

Similar results are obtained when the fogging agent 2-methyl-3 - (3 - phenylhydrazonopropyl)benzothiazolium bromide is incorporated in the photographic element at .027 mg./ft.² and then developed after imagewise exposure in a surface developer.

EXAMPLE 11

The compositions and processes of this invention can be employed to make improved image transfer systems.

An internal-image silver bromiodide emulsion is prepared with the addition of 125 mg. of lead nitrate per silver mole to the precipitation vessel prior to precipitation. After washing, the emulsion is coated on a paper support at 100 mg. silver/ft.². To the photosensitive layer are added 107 mg. of the coupler described in Example 2

of U.S. Ser. No. 483,807 and a fogging agent, formyl-4-methylphenyl hydrazine, as described in Whitmore et al., U.S. Pat. 3,227,550. The photographic element is then exposed and processed by squeegeeing a pad between samples of the photosensitive element and a receiving element as described in Example 1 of Beavers et al., U.S. Pat. 3,445,228. An excellent positive image in the transfer dye area is observed.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. In an unfogged photographic, silver halide element which can be imagewise-exposed and then either (1) developed in a silver halide surface developer in the presence of a fogging agent selected from the group consisting of hydrazine compounds and reactive N-substituted cycloammonium quaternary salts or (2) light-flashed during development in a silver halide surface developer to provide a positive image with respect to the exposure, the improvement comprising at least one layer in said photographic element comprising monodispersed silver halide grains (A) having polyvalent metal ions occluded therein (B) containing at least one sensitizing dye used at a concentration which would lower the blue-speed sensitivity of an undoped, control sulfur and gold surface-sensitized silver bromiodide emulsion, containing 6 mole percent iodide, of similar grain size and distribution at least 0.3 log E when developed at 25° C. in a surface developer and (C) containing only minimal developable surface latent images wherein processing for 5 minutes at 27° C. in Kodak Developer DK-50 will provide a density of less than 0.25 when coated at a coverage of between about 300 and 400 mg. of silver per square foot.

2. A photographic silver halide element according to claim 1 wherein said fogging agent is a hydrazine compound.

3. A photographic silver halide element according to claim 1 wherein said fogging agent is a reactive N-substituted cycloammonium quaternary salt.

4. A photographic element according to claim 1 wherein said polyvalent metal ions are lead ions.

5. A photographic element according to claim 1 wherein said polyvalent metal ions are tetravalent metal ions.

6. A photographic element according to claim 1 wherein said polyvalent metal ions are tetravalent metal ion.

7. A photographic element according to claim 1 wherein said silver halide grains were formed in the presence of trivalent or tetravalent metal ions in an acidic medium.

8. A photographic element according to claim 1 wherein said polyvalent metal ions are iridium ions.

9. A photographic element according to claim 1 wherein said hydrazine compound or said reactive N-substituted cycloammonium salt are located in at least one layer of said element and in water permeable association with said layer containing silver halide.

10. An unfogged, photographic, silver halide element comprising (1) a support, (2) at least one layer thereon of a silver halide composition comprising monodispersed silver halide grains (A) having lead ions occluded therein (B) containing at least one sensitizing dye used at a concentration which would lower the blue-speed sensitivity of an undoped, control sulfur and gold surface-sensitized silver bromiodide emulsion, containing 6 mole percent iodide, of similar grain size and distribution at least 0.3 log E when developed at 25° C. in a surface developer and (C) containing only minimal developable surface latent images wherein processing for 5 minutes at 27° C. in Kodak Developer DK-50 will provide a density of less than 0.25 when coated at a coverage of between about 300 to 400 mg. of silver per square foot, and

(3) at least one layer containing a fogging agent selected from the group consisting of hydrazine compounds and reactive N-substituted cycloammonium quaternary salts in water-permeable association with said layer containing silver halide.

11. A photographic film element according to claim 10 wherein said fogging agent is a reactive N-substituted cycloammonium quaternary salt.

12. A process of forming a positive image in an unfogged photographic, silver halide element, comprising (1) imagewise-exposing a layer of said element which comprises a silver halide emulsion containing monodispersed silver halide grains (A) having polyvalent metal ions occluded therein (B) containing at least one sensitizing dye used at a concentration which would lower the blue-speed sensitivity of an undoped, control sulfur and gold surface-sensitized silver bromiodide emulsion, containing 6 mole percent iodide, of similar grain size and distribution at least 0.3 log E when developed at 25° C. in a surface developer and (C) containing only minimal developable surface latent images wherein processing for 5 minutes at 27° C. in Kodak Developer DK-50 will provide a density of less than 0.25 when coated at a coverage of between about 300 to 400 mg. of silver per square foot and then (2) either (a) developing said element in a silver halide surface developer in the presence of a fogging agent selected from the group consisting of hydrazine compounds and reactive N-substituted cycloammonium quaternary salts, (b) flash-exposing said element during development in a silver halide surface developer, or (c) heating the exposed emulsion to a temperature of at least 100° C. followed by developing in a silver halide surface developer.

13. A process according to claim 12 wherein said element is developed in the presence of a fogging agent which is a hydrazine compound.

14. A process according to claim 13 wherein said hydrazine compound is located in at least one layer of the photographic element in water-permeable association with said silver halide emulsion.

15. A process according to claim 13 wherein said hydrazine compound is present in the developing solution.

16. A process according to claim 12 wherein said element is developed in the presence of a fogging agent which is a reactive N-substituted cycloammonium salt.

17. A process according to claim 16 wherein said N-substituted cycloammonium salt is located in at least one layer of said element in water-permeable association with said silver halide emulsion.

18. A process according to claim 12 wherein said polyvalent metal ions are lead ions.

19. A process according to claim 12 wherein said polyvalent metal ions are trivalent or tetravalent metal ions.

20. A process according to claim 12 wherein said polyvalent metal ions are iridium ions.

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U.S. Cl. X.R.

96—108

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,761,267 Dated September 25, 1973

Inventor(s) Paul Brewster Gilman and Ronald George Raleigh

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 11, line 45, claim 5, "tetraivalent" should read
--trivalent--;

Column 11, line 47, claim 6, "ion"
should read --ions--.

Signed and sealed this 30th day of July 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents