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[54] **PROCESSES FOR OBTAINING POSITIVE IMAGES IN SILVER HALIDE COMPOSITIONS**

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Related U.S. Application Data

[62] Division of Ser. No. 123,005, March 10, 1971, Pat. No. 3,761,276.

[52] **U.S. Cl.** **96/64**

[51] **Int. Cl.** **G03c/5/24**

[58] **Field of Search** 96/64, 107, 108

[56] **References Cited**

UNITED STATES PATENTS

2,497,875	2/1950	Fallesen	96/64
2,588,982	3/1952	Ives	96/64
3,317,322	5/1967	Porter	96/108
3,586,505	6/1971	Ridgway	96/64
3,615,615	10/1971	Lincoln	96/107

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[57] **ABSTRACT**

Improved processes are disclosed for obtaining positive images in an unfogged, silver halide emulsion wherein a photographic element comprising a support and said emulsion are imagewise-exposed and then either (1) developed in a surface developer in the presence of a silver halide fogging agent or (2) given a light flash during development in a surface developer. In one aspect, the silver halide emulsions of this invention are internal-image emulsions comprising silver halide grains which preferably have metal dopants occluded therein and wherein said grains have been chemically sensitized on the surface thereof to a level less than that which would provide a substantial density in Kodak Developer DK-50 after an imagewise exposure when said emulsions are coated at a coverage of between 300 to 400 mg. of silver per ft. 2.

8 Claims, No Drawings

PROCESSES FOR OBTAINING POSITIVE IMAGES IN SILVER HALIDE COMPOSITIONS

This is a division of application Ser. No. 123,005, filed Mar. 10, 1971, now U.S. Pat. No. 3,761,276, issued Sept. 25, 1973.

This invention relates to unfogged silver halide emulsions and methods for forming positive images in unfogged silver halide emulsions. In one aspect, this invention relates to silver halide emulsions comprising unfogged silver halide grains having metal dopants occluded therein, said grains having been chemically sensitized on the surface to a level less than that which will produce substantial density (i.e., *Dmax* of less than 0.25) in a surface developer after an imagewise exposure to light. In another aspect, this invention relates to an improved method for obtaining positive images wherein a silver halide element comprising the emulsion as described next above is imagewise-exposed and then the silver halide element is either developed in a surface developer in the presence of a fogging agent or given a light flash during development.

Processes are known in the art for making positive images in unfogged silver halide emulsions by imagewise exposure followed by fogging developers, etc. Typical processes of this type are disclosed in U.S. Pat. Nos. 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 Patent 1,151,363, and Japanese Patent 29,405/68 issued December 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. Pat. No. 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 *Dmin*, higher *Dmax* and the like are desired to obtain acceptance of this system in many applications of photography.

I have now found that silver halide emulsions containing silver halide grains having metal dopants occluded therein, and wherein said grains have been chemically sensitized on the surface thereof to a level less than that which would provide a substantial density in Kodak Developer DK–50 after imagewise exposure, can be imagewise-exposed and processed in a surface developer in the presence of a fogging agent or by light fogging during development in a surface developer to provide highly improved positive images. This discovery was quite unexpected since one skilled in the art generally avoided conditions or steps where the surface of the emulsion would be chemically sensitized before the imagewise exposure when it was to be used in this process to form a direct-positive image. One attempt to solve this problem was to sensitize the surface chemically after imagewise exposure as disclosed in Ridgway, British Patent 1,178,683. However, I have now found that when the doped emulsions are used to make positive images by this process, a certain amount of surface sensitivity before imagewise exposure is very desirable to produce high-quality positive images.

In one embodiment of this invention, an improved process is provided for making reversal images, the improvement comprising using an unfogged silver halide emulsion containing silver halide grains having metal dopants occluded therein wherein said silver halide grains have been chemically sensitized to a level which would produce a density of less than 0.4 and preferably less than about 0.25 when imagewise-exposed and developed in Kodak Developer DK–50 and to at least a level which would provide a density of 0.5 in an undoped silver halide emulsion of the same grain size and halide composition when exposed and developed in Kodak Developer DK–50, provided said emulsions are coated at a coverage of between 300 to about 400 mg. of Ag/ft.^{2}.

As a highly preferred embodiment according to this invention, the useful silver halide emulsions can be characterized as being a silver halide composition wherein (1) the halide is predominantly bromide, (2) the emulsion comprises grains having metal dopants occluded therein, (3) the emulsions when coated on a film support at a coverage between about 300 to 400 mg. Ag/ft.^{2}, imagewise-exposed to a 500-watt tungsten lamp for 1/100 to 1 second at a distance of 24 inches and processed in a surface developer such as 5 minutes in Kodak Developer DK–50 will have a Dmax of less than 0.25, and (4) when the emulsions are coated and exposed as described as next above and then processed in a fogging developer as described in Ives, U.S. Pat. No. 2,563,785, the emulsion will have a ΔD or (*Dmax*-*Dmin*) of greater than 1.0.

In one preferred embodiment, the emulsions having the characteristics next above are processed after imagewise exposure in a silver halide surface developer in the presence of a hydrazine fogging agent.

In another preferred embodiment, the emulsions having the characteristics above are processed after imagewise exposure in a silver halide surface developer in the presence of a reactive N-substituted, cycloammonium quaternary salt.

In still another embodiment, the silver halide emulsions of this invention are processed after imagewise exposure with an over-all light flash during development in a silver halide surface developer, for example, as disclosed in Knott and Stevens, U.S. Pat. No. 2,456,953.

In another preferred 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.

Generally, the internal-image silver halide emulsions of my invention comprise those wherein the halide is predominantly bromide and which have a predominant amount of light sensitivity internal to the silver halide grain and when examined according to normal photographic testing techniques by coating a test portion of the emulsion on a transparent support, exposing to a light-intensity scale for a fixed time between 1×10^{-2} and 1 second, and developing for about 5 minutes at 65° F. in Developer Y below (an "internal-type" developer), have a maximum density at least five times the maximum density of an identical test portion which has

been exposed in the same way and developed for 6 minutes at 68° F. in Developer X below (a "surface-type" developer). Preferably, the maximum density in Developer Y is at least 0.5 density unit greater than the maximum density in Developer X and/or the grains of said emulsion have a ratio of total sensitivity to surface sensitivity of greater than 5.

Developer X

N-methyl-p-aminophenol sulfate	2.5	g.
ascorbic acid	10.0	g.
potassium metaborate	35.0	g.
potassium bromide	1.0	g.
water to 1 liter		
pH of 9.6		

Developer Y

N-methyl-p-aminophenol sulfate	2.0	g.
sodium sulfite, desiccated	90.0	g.
hydroquinone	8.0	g.
sodium carbonate, monohydrate	52.5	g.
potassium bromide	5.0	g.
potassium iodide	0.5	g.
water to 1 liter		

Internal-image emulsions which are useful according to this invention are those which contain grains having a metal dopant occluded therein. The metal dopants can be occluded within the grain, for example, by precipitating in the presence of foreign metal ions (i.e., other than silver ions), occluding metallic compounds within the grain, etc. The metal dopants can be introduced by chemically sensitizing a core of a silver halide grain to form a metal or metal salt thereon and then forming a shell or outer region on the core occluding the chemically sensitized site within the grain, etc. Typical useful silver halide emulsions containing grains having metal dopants occluded therein can be prepared by the procedures disclosed in U.S. Pat. Nos. 3,206,313 by Porter et al. issued Sept. 14, 1965; 3,317,322 by Porter et al. issued May 2, 1967; 3,367,778 by Berriman issued Feb. 6, 1968, omitting the surface fogging procedure; 3,447,927 by Bacon et al. issued June 3, 1969; 3,531,291 by Bacon et al. issued Sept. 29, 1970; 3,271,157 by McBride issued Sept. 6, 1966; British Patents 1,027,146 and 1,151,782; and U.S. Ser. No. 65,696 by Motter filed Aug. 20, 1970; and the like.

The silver halides used in the present invention are unfogged. Such emulsions contain 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 0.4.

Generally, the internal-image emulsions useful in this invention comprise silver halide grains having chemical or physical sites internal to the grain for the deposition of photolytic silver. The physical sites can be obtained by employing precipitation conditions which will result in the formation of physical defects in the crystal lattice such as, for example, changing the conditions of the precipitation medium to promote a change in crystal shape, interrupted precipitations, and the like. The chemical sites can be obtained by incorporating foreign metal dopants into the silver halide grain. In certain preferred embodiments, the dopant is a foreign metal ion or a metallic compound. It is understood, of course, that "foreign metal ion" means an ion other than a silver ion, and that "metallic dopants" can include occluded metallic silver, sulfur, sulfur compounds, metallic iridium, metallic gold, metallic platinum, etc. In certain embodiments, the silver halide grains containing occluded metallic compounds can be obtained by precipitating in the presence of the metallic compound or preferably depositing the metal on a core of silver halide and then continuing formation of the grain to build a shell or outer region over the metallic deposit. Typical emulsions of this type are disclosed in Porter et al., U.S. Pat. Nos. 3,206,313 and 3,317,322. In one preferred embodiment wherein the silver halide grains contain occluded metal dopants, the silver halide grains comprise occluded sulfur and noble metal compounds.

In a preferred embodiment, the silver halide grains are formed in the presence of foreign metal ions and preferably polyvalent metal ions. Generally, when the grains are formed in an aqueous medium, the silver halide grains are formed in the presence of the water-soluble salts of the respective metal, preferably in an acidic medium. Typical useful polyvalent metal ions include divalent metal ions such as lead ions, trivalent metal ions such as antimony, bismuth, arsenic, gold, iridium, rhodium and the like and tetravalent metal ions such as platinum, osmium, iridium and the like. In highly preferred embodiments, the grains are formed in the presence of bismuth, lead or iridium ions. Generally, the silver halide grains contain at least 10^{-9} and preferably at least 10^{-6} mole percent dopant based on silver halide.

The surface of the grains of the doped emulsions of this invention is generally chemically sensitized to a level below that which would produce substantial density (i.e., a density of less than 0.4) in a surface developer such as Kodak Developer DK–50 after exposure when coated at a coverage of between about 300 to 400 mg. Ag/ft.^{2}. By chemical sensitization, I mean sensitization of the type described by Antoine Hautot and Henri Saubenier in *Science et Industries Photographiques*, Vol. XXVIII, January, 1957, pages 1–23, and January, 1957, pages 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 fog appreciably the silver halide, but introduces small specks of metallic silver into the silver halide crystal or grain. In highly preferred embodiments of this invention, I have found that higher amounts of surface sensitivity are desirable in producing good reversal images when the silver halide emulsion comprises silver halide grains having metal dopants occluded therein, and especially when the grains contain polyvalent metal ions occluded therein. However, in certain embodiments the optimum sensitization will also vary with developer composition, e.g., smaller amounts of chemical sensitization are used when the emulsion is to be developed in p-phenylenediamine-containing developing compositions, iodide-containing developing compositions and the like.

The silver halide grains can be chemically sensitized by any of the accepted procedures. The silver halide grains can be digested with naturally active gelatin, sulfur compounds can be added, such as those described in U.S. Pat. Nos. 1,574,944 by Sheppard issued Mar. 2, 1926; 1,623,499 by Sheppard et al. issued Apr. 5, 1927, and, 2,410,689 by Sheppard issued Nov. 5, 1946,

or selenium compounds can be used, such as those described in U.S. Pat. Nos. 3,297,447 by McVeigh, 3,297,446 by Dunn, and the like.

The silver halide grains can also be treated with salts of the noble metals, such as ruthenium, palladium and platinum. Representative compounds are ammonium chloropalladate, potassium chloroplatinate and sodium chloropalladite, which are used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in Smith and Trivelli, U.S. Pat. No. 2,448,060 issued Aug. 31, 1948, and as antifoggants in higher amounts, as described in Trivelli and Smith, U.S. Pat. Nos. 2,566,245 issued Aug. 28, 1951, and 2,566,263 issued Aug. 28, 1951.

The silver halide grains can also be chemically sensitized with gold salts as described in U.S. Pat. Nos. 2,399,083 by Waller et al. issued Apr. 23, 1946, and 2,642,361 by Damschroder et al. issued June 16, 1953. Suitable compounds are potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

The silver halide grains can also be chemically sensitized with reducing agents, such as stannous salts (Carroll, U.S. Pat. No. 2,487,850 issued Nov. 15, 1949), polyamines, such as diethylene triamine (Lowe et al., U.S. Pat. No. 2,518,698 issued Aug. 15, 1950), polyamines, such as spermine (Lowe et al., U.S. Pat. No. 2,521,925 issued Sept. 12, 1950), or bis(β-aminoethyl)sulfide and its water-soluble salts (Lowe et al., U.S. Pat. No. 2,521,926 issued Sept. 12, 1950).

The silver halide grains can also be optically sensitized with cyanine and merocyanine dyes, such as those described in U.S. Pat. Nos. 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 et al.; 2,493,748 by Brooker et al. 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 et al. issued Jan. 19, 1954; 2,734,900 by Heseltine issued Feb. 14, 1956; and 2,739,149 by VanLare issued Mar. 20, 1956; and Kodak Limited British Patent 450,958 accepted July 15, 1936.

In certain embodiments where the surface of the grains has been chemically sensitized at the low end of the specified range, it is desirable to incorporate iodide-releasing compounds in the silver halide element or to use a developer containing iodide ions to obtain certain desired image characteristics. However, as the level of chemical sensitization is increased, the use of the iodide-releasing compounds or iodide in the developer or emulsion becomes less desirable.

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.

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 crack or dissolve the grain to reveal substantial internal image. Low amounts of excess halide are sometimes desirable in the developer 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 the developing bath.

When an over-all flash exposure is used during surface development, it can be of high intensity for a short duration or of low intensity for longer duration. However, the light flash can precede development in certain embodiments, such as those embodiments where the imagewise-exposed emulsion is first contacted with a stabilizer composition.

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 nitrobenzimidazoles, benzothiazoles such as 5-nitrobenzothiazole and 5-methylbenzothiazole, heterocyclic thiones such as 1-methyl-2-tetrazoline-5-thione, aromatic and aliphatic mercapto compounds, and the like.

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 Publishing Co., Cleveland, Ohio, page 2,558, and has the following composition:

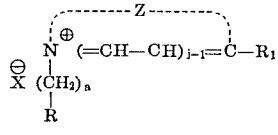
water, about 125° F. (52° C.)	500	cc.
N-methyl-p-aminophenol sulfate	2.5	g.
sodium sulfite, desiccated	30.0	g.
hydroquinone	2.5	g.
sodium metaborate	10.0	g.
potassium bromide	0.5	g.
water to make 1 liter		

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. Pat. Nos. 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;

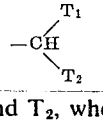
C. *q* represents a positive integer of from 2 to 6;

D. $X^{\ominus}$ represents an acid anion;

E. R represents a member selected from:

1. a formyl radical,

2. a radical having the formula:



wherein each of T_1 and T_2, when taken alone, represents a member selected from an alkoxy radical and an alkylthio radical, and T_1 and T_2, 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. R_1 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 radial, 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 fogging agent in the developer composition; however, the fogging agents 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 1,500 mg. of the subject fogging agents per mole of silver in the silver halide emulsion are useful, with from about 90 to about 1,200 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-sulfophenylhydrazone)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-acetylethyl)-2-benzylbenzothiazolium bromide, 3-(2-acetylethyl)-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, now abandoned hot nucleation procedures as disclosed in Musliner, U.S. Ser. No. 31,351 filed Apr. 23, 1970, now abandoned 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 percent, by weight, of the silver halide grains smaller than the mean grain size and/or no more than about 5 percent, 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 percent. Preferred photographic emulsions of this invention comprise silver halide grains, at least 95 percent, by weight, of said grains having a diameter which is within 40 percent, preferably within about 30 percent, 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 emulsion 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 mulsions 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 the 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. Pat. Nos. 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 Nov. 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. No. 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 such as described in U.S. Pat. No. 2,716,059 by Yutzy et al.; silver salt diffusion transfer systems wherein development of silver halide precedes solution of the silver halide with processes as described in U.S. Pat. Nos. 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. Pat. Nos. 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. No. 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. Pat. Nos. 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. Pat. Nos. 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. No. 2,763,549 by Hanson.

The invention can be further illustrated by the following examples.

EXAMPLE 1

Emulsion A: A silver bromide emulsion is prepared by mixing simultaneously over a period of 28 minutes at a temperature of 70° C. equal molar solutions of silver nitrate and sodium bromide using a controlled silver halide precipitation technique. Upon completion of the precipitation, octahedral crystals having a diameter of 0.5 μ result. The silver bromide grains are chemically sensitized by adding 1.7 mg. of sodium thiosulfate/silver mole and 2.5 mg. of potassium chloroaurate/silver mole and heating for 30 minutes at 70° C. The chemically sensitized grains are further grown in the

same precipitation environment as the first precipitation for an additional 28 minutes, such that the final crystalline structure results in octahedral grains 0.8 μ in diameter.

The emulsion is then split into separate equal portions and chemically sensitized at the surface of the grain as illustrated in Tables 1 and 2.

Emulsion B: A silver bromide emulsion is prepared similar to Emulsion A, except no chemical sensitization is added internally to the silver halide grain. The emulsion is then sensitized at the surface as shown in Tables 1 and 2.

Emulsion C: A silver bromide emulsion is prepared similar to Emulsion A, except at the completion of the first precipitation, the 0.5 μ grains are chemically sensitized by adding 0.18 mg. of dimethyl selenourea/silver mole, 2.57 mg. of sodium thiosulfate/silver mole and 3.83 mg. of potassium chloroaurate/silver mole and heating for 30 minutes at 70° C., and then are grown to 0.8 μ as described in Emulsion A and surface-sensitized as described in Table 1.

EXAMPLE 2

The emulsions described in Example 1 are coated on a polyethylene terephthalate film support at 350 mg. of silver/ft.^{2} and exposed on a Bausch and Lomb Spectrograph. The exposed coatings are then processed in Developer A, an Elon-hydroquinone surface-type developer, and Developer B, a fogging-type developer of the type described in Ives, U.S. Pat. No. 2,563,785. The results as listed in Table 1 are observed.

Table 1

Emulsion Number	Internal Sensitivity	External Sensitivity (mg./m.)		Surface Developer A (Density)	Fogging Developer B
A	1 + 2	none		less than 0.25	no image
B	none	1	(1.4)	above 0.25	fogged
		2	(2.1)		
C	1 + 2 + 3	1	(1.4)	less than 0.25	good reversal image
		2	(2.1)		
		3	(0.1)		
A	1 + 2	1	(1.4)	less than 0.25	good reversal image
		2	(2.1)		
A	1 + 2	2	(2.1)	no observable image	weak reversal image
A	1 + 2	1	(1.4)	less than 0.25	moderate reversal image
A	1 + 2	1	(1.4)	less than 0.25	good reversal image
		2	(2.1)	—	
		4	(0.1)		
A	1 + 2	2	(2.1)	less than 0.25	weak reversal image
		4	(0.1)	—	

1 — sodium thiosulfate
2 — potassium chloroaurate
3 — dimethyl selenourea
4 — thiourea dioxide

EXAMPLE 3

Emulsions A and B, described in Example 1, are coated with 400 mg. per mole of silver of the fogging agent 2-methyl-3-[3-(p-sulfophenylhydrazone)propyl]benzothiazolium bromide on a film support, exposed as described in Example 2 and processed in an Elon-hydroquinone developer.

Table 2

Emulsion Number	Internal Sensitivity	Surface Sensitivity (mg./m.)		Surface Developer
A	1 + 2	none		no image
B	none	1	(1.4)	fogged
		2	(2.1)	
A	1 + 2	1	(1.4)	good reversal image
		2	(2.1)	

1 — sodium thiosulfate
2 — potassium chloroaurate

It is apparent from the data in Tables 1 and 2 that an emulsion having a combination of internal sensitivity with certain levels of chemically induced surface sensitivity will result in a reversal image under conditions wherein similar emulsions which have not been chemically sensitized on the surface will not provide a reversal image and wherein similar emulsions which have not been internally sensitized but sensitized on the surface of the grain will produce a completely fogged image record.

EXAMPLE 4

A silver bromoiodide emulsion (2.5 mole percent iodide) is prepared by mixing simultaneously, over a period of 55 minutes at a temperature of 70° C., equal molar solutions of silver nitrate and halide salts using a controlled pAg technique. To the precipitation vessel prior to precipitation are added 150 mg. of 1,8-dihy-

droxy-3,6-dithiaoctane per silver mole. Upon completion of the precipitation, cubic crystals having a diameter of 0.8 μ result. The silver bromoiodide grains are then chemically sensitized by adding 2.0 mg. of sodium aurous (I) dithiosulfate dihydrate per silver mole. Two moles of the chemically sensitized grains are further grown by adding 1.0 moles of silver nitrate and halide salts for 20 minutes at 65° C. Prior to the second precipitation, 500 mg. of 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane are added to the precipitation vessel. The final crystalline structure results in cubic grains 0.9 μ in diameter. The surface of the grains is then chemically sensitized by adding 1.0 mg. of sodium aurous (I) dithiosulfate dihydrate per silver mole and finished as shown in the following table. To the emulsion are added 400 mg. of 2-methyl[3-(p-sulfophenylhydrazono)propyl]benzothiazolium bromide/silver mole.

The above finished emulsions are then coated on a film support at 350 mg. of silver/ft.^{2} and exposed on a Bausch and Lomb Spectrograph. The exposed coatings are processed in an Elon-hydroquinone developer containing 50 mg. of 5-methyl benzotriazole per liter. The following results are observed.

Finish Time	Relative Speed	D*max*	D*min*	ΔD
0'/65°	—	.23	.05	.18
10'/65°	100	1.29	.12	1.17
20'/65°	95	1.76	.22	1.54
30'/65°	63	2.30	.40	1.90
40'/65°	38	2.36	.66	1.70

It can be seen from the above data that a more desirable direct-positive image is obtained when controlled amounts of chemical sensitization on the surface of said emulsions are employed. As the amount of surface sensitivity increases to even higher levels, the emulsions become substantially fogged with less image discrimination upon development.

EXAMPLE 5

A halide-covered emulsion prepared similar to that described in Davey et al, U.S. Pat. No. 2,592,250, having an average grain size of 0.8 μ is coated on a polyethylene terephthalate film support at 350 mg. of silver/ft.^{2}.

A second emulsion prepared as Emulsion A in Example 1 is surface-sensitized by adding 1.4 mg. of sodium thiosulfate/silver mole and 2.1 mg. of potassium chloroaurate/silver mole and coated on a separate polyethylene terephthalate film support at 350 mg./ft^2.

To each of the above coated emulsions is added the fogging agent as described in Example 2. After exposing as described in Example 2 and processing in Developer A, a speed advantage of 0.6 log E is noticed with the emulsions of the present invention.

EXAMPLE 6

A silver bromide emulsion is prepared by mixing simultaneously over a period of 28 minutes at a temperature of 70° C. equal molar solutions of silver nitrate and sodium bromide. Upon completion of the precipitation, octahedral crystals having a diameter of 0.5 μ result. The silver bromide grains are chemically sensitized by adding 1.7 mg. of sodium thiosulfate/silver mole and 2.5 mg. of potassium chloroaurate/silver mole and heating for 30 minutes at 70° C. The chemically sensitized grains are further grown in the same precipitation environment as the first precipitation for an additional 28 minutes, such that the final crystalline structure results in octahedral grains 0.8 μ in diameter. The emulsion is then chemically sensitized at the surface of the grains by adding 1.4 mg. of sodium thiosulfate/silver mole and 2.1 mg. of potassium chloroaurate/silver mole and finished by heating to 65° C. as described in the following table. The emulsions are then coated on a film support at 350 mg. of silver/ft.^{2} and exposed on a Bausch and Lomb Spectrograph. The exposed coatings are processed in a fogging-type developer (Developer B) of the type described in Ives, U.S. Pat. No. 2,563,785. Example 3 is processed in said fogging developer which contains 20 mg./liter of potassium iodide. The results are as follows:

Example	Time of Finish	Developer	D*max*
1	20'/65° C.	B	1.80
2	0'/65° C.	B	1.12
3	0'/65° C.	B + KI	1.88

It can be seen from the above table that adding some iodide to the developer produces improved D*max* in an emulsion which has been chemically sensitized on the surface to a low level of sensitivity.

EXAMPLE 7

A silver bromide emulsion (Emulsion D) is prepared by mixing simultaneously equal molar solutions of silver nitrate and sodium bromide to obtain octahedral crystals having an average grain size of 0.9 micron. The silver bromide grains are chemically sensitized by adding 1.7 mg. of sodium thiosulfate/silver mole and 2.5 mg. of potassium chloroaurate/silver mole and heated for 15 minutes at 80° C. The chemically sensitized grains are further grown by adding additional silver nitrate and sodium bromide as described above to obtain a covered-grain emulsion having octahedral grains having an average diameter of about 1.3 microns. The covered-grain emulsion is then chemically sensitized by adding 0.85 mg. of sodium thiosulfate/silver mole and 0.85 mg. of potassium chloroaurate/silver mole and finished at the times indicated in the following table.

A comparison emulsion (Emulsion E) having a chemically sensitized core and a chemically sensitized shell is prepared in the same manner as described in Porter et al., U.S. Pat. No. 3,317,322, Example 1.

The above emulsions are then coated on a film support at 300 mg. of silver/ft.^{2}, exposed on an Eastman 1B Sensitometer and processed as follows:

Table 3

Emulsion	Finish Time	D*max* Surface Developer
D	0'/60° C.	.06
D	10'/60° C.	.06
D	20'/60° C.	.06
D	30'/60° C.	.06
D	40'/60° C.	.06
E	25'/70° C.	1.20

Samples of the above-described coated emulsions are exposed on an Eastman 1B Sensitometer and processed in a fogging developer of the following composition for 1 minute at 38° C.

Elon	5.0	g.
hydroquinone	10.0	g.
sodium sulfite	75.0	g.
sodium hydroxide	10.5	g.
5-methylbenzotriazole	.02	g.
diglycolic acid	13.4	g.
sodium phosphate	75.0	g.
p-methyl sulfonamide ethyl phenylhydrazine	2.0	g.
distilled water to 1 liter		

Table 4

Emulsion	Finish Time	*Dmin*	*Dmax*	ΔD
D	0'/60° C.	.18	.29	.11
D	10'/60° C.	.18	.48	.30
D	20'/60° C.	.18	1.02	.84
D	30'/60° C.	.18	2.04	1.86
D	40'/60° C.	.18	2.42	2.24
E	25'/70° C.	3.02	3.15	.13

It is apparent from the above tables that the emulsions which have been sufficiently chemicallly sensitized but have a *Dmax* in a surfaces developer of less than 0.25 produce a more acceptable ΔD (i.e., at least 0.50) in a fogging developer than emulsions which are surface-sensitized to a level which will provide a high *Dmax* in a nonfogging surface developer, i.e., greater than 0.50. It is of interest to note that the *Dmax* areas of Table 3 become the *Dmin* areas of Table 4.

EXAMPLE 8

The emulsions preferably contain metal dopants occluded in the grains such as, for example, iridium, osmium, gold, lead, sulfur plus gold, sulfur plus selenium, and the like. The surface of the grains is preferably chemically sensitized with sulfur, gold, sulfur and gold or gold and reduction sensitization.

A 0.2 cubic-grain internal-image silver bromoiodide monodispersed emulsion (2.5 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 100 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. A similar emulsion is prepared except potassium hexachloroiridate is omitted and 11.25 mg. of osmium trichloride/silver mole are added. The above emulsions are then chemically sensitized by adding 33 mg. of sodium thiosulfate/silver mole and 6.6 mg. of potassium chloroaurate/silver mole and heated to 15' at 65° C. The emulsions are coated on a film support at 100 mg. silver/ft.², image-exposed on an Eastman 1B Sensitometer and developed in an Elon-hydroquinone developer such as Kodak Developer D–19 for 3 minutes. During development, the film samples are over-all flashed for 30 seconds using a 15-watt bulb at a distance of 2 feet. Positive images having the following photographic characteristics are observed.

Chemical Sensitization of Core	Chemical Sensitization of Shell	*Dmax*	*Dmin*
iridium	none	.05	.04
iridium	sulfur + gold	1.28	.10
osmium	none	.08	.04
osmium	sulfur & gold	1.19	.22

Similar improvements are obtained when a core emulsion is sulfur and noble metal-sensitized followed by forming a shell or outer region on the core of the grains to occlude the dopants therein; however, a lower amount of chemical sensitization on the shell is generally used to obtain good image discrimination.

EXAMPLE 9

The compositions and processes of this invention can be employed to make improved image transfer systems. A film unit adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members is prepared according to the following procedure.

A silver bromide emulsion is prepared by mixing simultaneously over a period of 50 minutes at a temperature of 70° C. equal molar solutions of silver nitrate and sodium bromide using a controlled silver halide precipitation technique. Upon completion of the precipitation, octahedral crystals having a diameter of 0.9 μ result. The silver bromide grains are chemically sensitized by adding 1.7 mg. of sodium thiosulfate/silver mole and 2.5 mg. of potassium chloroaurate/silver mole and heating for 15 minutes at 70° C. The chemically sensitized grains are further grown in the same precipitation environment as the first precipitation for an additional 40 minutes, such that the final crystalline structure results in octahedral grains 1.3 μ in diameter.

The grains are then chemically sensitized on the surface by adding 0.40 mg. of sodium thiosulfate/silver mole and 0.40 mg. of potassium chloroaurate/silver mole and heating for 10 minutes at 65° C. The emulsion is divided into three portions and one portion is spectrally sensitized in the green region of the spectrum, another is spectrally sensitized to the red region of the spectrum, and another is sensitive only in the blue region of the spectrum.

A multilayer photographic element is then prepared using the above emulsion by coating the following layers in order on a transparent cellulose acetate film support:

1. image-receiving layer of methyl-tri-n-dodecyl ammonium p-toluenesulfonate (22.5 mg./ft.²), N-n-hexadecyl-N-morpholinium ethosulfate (150 mg./ft.²) and gelatin (743 mg./ft.²);
2. light-reflecting layer of TiO_2 (3,000 mg./ft.²) and gelatin (300 mg./ft.²);
3. opaque scavenger interlayer of 1-hydroxy-N-[α-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide (100 mg./ft.²), gelatin (360 mg./ft.²), tricresyl phosphate (50 mg./ft.²) and carbon black (300 mg./ft.²);
4. red-sensitive gelatin-silver bromide emulsion (120 mg. gelatin/ft.² and 100 mg. silver/ft.²), cyan image transfer coupler 1-hydroxy-4-{4-[α-(3-pentadecylphenoxy)butyramido]phenoxy}-N-ethyl-3',5'-dicarboxy-2-naphthanilide (75 mg./ft.²) and fogging agent formyl-4-methylphenylhydrazide (0.5 g./mole of silver bromide);
5. scavenger interlayer of 1-hydroxy-N-[α-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide (45 mg./ft.²),

tricresyl phosphate (22 mg./ft.²) and gelatin (65 mg./ft.²);

6. green-sensitive gelatin-silver bromide emulsion (90 mg. gelatin/ft.² and 100 mg. silver/ft.²), magenta image transfer coupler 1-phenyl-3-(3,5-disulfobenzamido)-4-(6-hydroxy-4-pentadecylphenylazo)-5-pyrazolone, dipotassium salt (75 mg./ft.²) and fogging agent formyl-4-methylphenylhydrazide (0.5 g./mole of silver bromide);

7. scavenger and yellow filter layer of 1-hydroxy-N-[α-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide (45 mg./ft.²), tricresyl phosphate (22 mg./ft.²), Yellow Carey Lea Silver (10 mg./ft.²) and gelatin (65 mg./ft.²);

8. blue-sensitive gelatin-silver bromide emulsion (100 mg. gelatin/ft.² and 100 mg. silver/ft.²), yellow image transfer coupler α-pivalyl-α-[4-(N-methyl-N-n-octadecylsulfamyl)phenoxy]-4-sulfoacetanilide potassium salt (120 mg./ft.²) and fogging agent formyl-4-methylphenylhydrazide (0.5 g./mole of silver bromide);

9. overcoat layer of gelatin (50 mg./ft.²).

The element is exposed to a graduated-density multicolor test object. The following processing composition is employed in the processing pod:

water	100	ml.
benzyl alcohol	0.5	ml.
piperidino hexose reductone	0.025	g.
5-nitrobenzimidazole	0.005	g.
sodium hydroxide	1.25	g.
4-amino-N-ethyl-N-β-hydroxyethylaniline	1.5	g.
hydroxyethylcellulose	2.5	g.

The processing solution is spread from the pod between the exposed surface of the element and an opaque poly(ethyleneterephthalate) film support coated with a polyacrylic acid layer and a polyvinyl acetate timing layer by passing the transfer "sandwich" between a pair of juxtaposed pressure rollers. After 3 minutes at about 20° C., a multicolor reproduction of the test object is observed on a white background when viewed through the transparent film support side of the element. When the above element is compared with an element prepared and processed in a similar manner using the emulsion as described in Knott et al., U.S. Pat. No. 2,592,250, a 0.6 log E increase in photographic speed is observed.

Similar results can be obtained when using the above prepared silver halide emulsions in the film units described in U.S. Ser. Nos. 27,990 and 27,991, both filed Apr. 13, 1970, which are incorporated herein by reference.

EXAMPLE 10

A silver bromide emulsion is prepared by mixing simultaneously equal molar solutions of silver nitrate and sodium bromide to obtain octahedral crystals having an average grain size of 0.9 micron. The silver bromide grains are chemically sensitized by adding 1.7 mg. of sodium thiosulfate/silver mole and 1.7 mg. of potassium chloroaurate/silver mole and finished for 10 minutes at 70° C. The grains are further grown by adding silver nitrate and sodium bromide as described above to 1.3 microns and sensitized by adding 0.85 mg. of sodium thiosulfate/silver mole and 0.85 mg. of potassium chloroaurate/silver mole. The emulsion is heated to 70° C. and 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 hydrazine fogging agent, formyl-4-methylphenyl hydrazine, at 0.5 g./silver mole as described in Whitmore et al., U.S. Pat. No. 3,227,550. The photographic element is then exposed and processed by squeegeeing a pod between samples of the photosensitive element and a receiving element as described in Example 1 of Beavers et al., U.S. Pat. No. 3,445,228. A positive image in the transfer dye area having a relative speed of 398 is observed. When a halide conversion emulsion of the type described in Example 5 of Whitmore et al., U.S. Pat. No. 3,227,550, is substituted for the instant emulsion and processed as described, a direct-positive image having a speed of 100 is observed.

Similar results are obtained when the hydrazine fogging agent is present in the processing pod.

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.

I claim:

1. A process for producing a positive image in a silver halide photographic element comprising (1) imagewise-exposing a photographic element comprising a support and coated thereon at least one layer of silver halide emulsion which comprises silver halide grains which have metal dopants occluded therein and which have been chemically sensitized on the surface thereof (a) to a level which will provide a density of less than 0.4 when developed in Kodak Developer DK–50 for 5 minutes at 27°C after imagewise exposure when the emulsion is coated at a coverage of between about 300 to about 400 mg of silver per square foot and (b) to at least a level which would provide a density of 0.5 in an undoped silver halide emulsion of the same grain size and halide composition when coated, exposed and developed in like manner, and then (2) either (a) developing in a silver halide surface developer in the presence of a fogging agent or (b) light-flashing the exposed silver halide emulsion during development in a silver halide surface developer.

2. A process according to claim **1** wherein the metal dopant is comprised of sulfur and gold.

3. A process according to claim **1** wherein the metal dopants are polyvalent metal ions.

4. A process according to claim **1** wherein the silver halide grains have been chemically sensitized on the surface thereof with sulfur, gold or sulfur and gold containing compounds.

5. A process according to claim **1** wherein said fogging agent is a hydrazine compound.

6. A process according to claim **1** wherein said fogging agent is a reactive N-substituted, cycloammonium quaternary salt.

7. A process according to claim **1** wherein said silver halide emulsion is a monodispersed silver halide emulsion.

8. A process comprising (1) chemically sensitizing a silver halide emulsion which comprises silver halide grains wherein the halide is predominantly bromide and which have metal dopants comprised of sulfur and gold occluded therein, wherein said grains are chemically sensitized on the surface thereof with a sulfur compound (a) to a level which will provide a density of

less than 0.25 in Kodak Developer DK–50 after imagewise exposure when said emulsion is coated at a coverage of between about 300 to about 400 mg of silver per square foot and (b) to at least a level which would provide a density of greater than 0.5 in an undoped silver halide emulsion of the same grain size, coating coverage and halide composition when similarly exposed and developed in Kodak DK–50, (2) coating said emulsion as a layer in a photographic element, (3) imagewise exposing said photographic element and (4) either (a) developing said exposed silver halide emulsion in a silver halide surface developer containing a silver halide fogging compound or (b) light-flashing said exposed silver halide emulsion during development in a silver halide surface developer.

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