United States Patent [19]

Evans

[11] 3,923,513

[45] Dec. 2, 1975

[54] **DIRECT POSITIVE PROCESSING OF SILVER HALIDE WITH METAL DOPANTS IN DIFFUSION TRANSFER FILMS**

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[22] Filed: **Aug. 9, 1974**

[21] Appl. No.: **496,433**

Related U.S. Application Data

[60] Continuation-in-part of Ser. No. 324,611, Jan. 18, 1973, abandoned, which is a division of Ser. No. 123,005, March 10, 1971, Pat. No. 3,761,276.

[52] **U.S. Cl.** ..... **96/29 D;** 96/3; 96/29 R; 96/64; 96/73; 96/74; 96/76 R; 96/77; 96/107; 96/108

[51] **Int. Cl.²** .. **G03C 7/00;** G03C 5/54; G03C 5/24; G03C 1/40

[58] **Field of Search** ..... 96/3, 29 D, 77, 76 R, 64, 96/107, 73, 108, 74

[56] **References Cited**

UNITED STATES PATENTS

3,761,267	9/1973	Gilman et al.	96/64
3,761,276	9/1973	Evans	96/64
3,850,637	11/1974	Evans	96/64

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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/ft.².

23 Claims, No Drawings

DIRECT POSITIVE PROCESSING OF SILVER HALIDE WITH METAL DOPANTS IN DIFFUSION TRANSFER FILMS

This application is a continuation-in-part of U.S. Ser. No. 324,611 filed Jan. 18, 1973, now abandoned, which in turn is a divisional application of 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 images exposure followed by fogging developers, etc. Typical processes of this type are disclosed in U.S. Pat. No. 2,497,875 by Falleson issued Feb. 21, 1950, U.S. Pat. No. 2,588,982 by Ives issued Mar. 11, 1952, and U.S. Pat. No. 2,456,953 by Knott and Stevens issued Dec. 21, 1948, British Pat. Specification No. 1,151,363, and Japanese Pat. No. 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. Pat. No. 2,592,250, emulsions made by the techniques disclosed in British Pat. Specification No. 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 Pat. Specification No. 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 sec. at a distance of 24 in. and processed in a surface developer such as 5 min. 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 overall 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 sec., and developing for about 5 min. 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 min. 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. No. 3,206,313 by Porter et al issued Sept. 14, 1965; U.S. Pat. No. 3,317,322 by Porter et al issued May 2, 1967; U.S. Pat. No. 3,367,778 by Berriman issued Feb. 6, 1968, omitting the surface fogging procedure; U.S. Pat. No. 3,447,927 by Bacon et al issued June 3, 1969; U.S. Pat. No. 3,531,291 by Bacon et al issued Sept. 29, 1970; U.S. Pat. No. 3,271,157 by McBride issued Sept. 6, 1966; and U.S. Pat. No. 3,703,584 by Motter; and British Pat. Specification Nos. 1,027,146 and 1,151,782; 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 min. 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, pp. 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 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. No. 1,574,944 by Sheppard issued Mar. 2, 1926, U.S. Pat. No. 1,623,499 by Sheppard et al issued Apr. 5, 1927, and U.S. Pat. No. 2,410,689 by Sheppard issued Nov. 5, 1946, or selenium compounds can be used, such as those described in U.S. Pat. No. 3,297,447 by McVeigh, U.S. Pat. No. 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. No. 2,566,245 issued Aug. 28, 1951, and U.S. Pat. No. 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. No. 2,399,083 by Waller et al issued Apr. 23, 1946, and U.S. Pat. No. 2,642,361 by Damschroder et al issued June 16, 1953. Suitable compounds are potassium chloraurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurósulfobenzothiazole 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 diethylenetriamine (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 U.S. Pat. No. 1,942,854 issued Jan. 9, 1934, all by Brooker; U.S. Pat. No. 1,990,507 by White issued Feb. 12, 1935; U.S. Pat. No. 2,112,140 issued Mar. 22, 1938, U.S. Pat. No. 2,165,338 issued July 11, 1939, U.S. Pat. No. 2,493,747 issued Jan. 10, 1950, and U.S. Pat. No. 2,739,964 issued Mar. 27, 1956, all by Brooker et al; U.S. Pat. No. 2,493,748 by Brooker et al issued Jan. 10, 1950; U.S. Pat. No. 2,503,776 issued Apr. 11, 1950, and U.S. Pat. No. 2,519,001 issued Aug. 15, 1950, both by Sprague; U.S. Pat. No. 2,666,761 by Heseltine et al issued Jan. 19, 1954; U.S. Pat. No. 2,734,900 by Heseltine issued Feb. 14, 1956; and U.S. Pat. No. 2,739,149 by VanLare issued Mar. 20, 1956; and Kodak Limited British Pat. Specification No. 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 iodidereleasing 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 iodidereleasing 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 overall 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 iodidereleasing 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 overall 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.

Generally improved results are obtained when the direct-positive emulsions are processed in the presence of certain antifoggants as disclosed in U.S. Pat. No. 2,497,917, which is incorporated herein by reference.

Typical useful antifoggants include benzotriazoles, such as benzotriazole, methylbenzotriazole, ethylbenzotriazole and the like, benzimidazoles such as 6-nitrobenzimidazole, 5-nitrobenzimidazole and the like, benzothiazoles such as 5-nitrobenzothiazole, 5-methylbenzothiazole and the like, heterocyclic thiones such as 1-methyl-2-tetrazoline-5-thione and the like, triazines such as 2,4-dimethylamino-6-chloro-5-triazine and the like, benzoxazoles such as ethylbenzoxazole and the like, and pyrroles such as 2,5-dimethylpyrrole and the like.

In certain embodiments, good results are obtained when the emulsions are processed in the presence of high levels of the antifoggants mentioned above. When antifoggants such as benzotriazoles are used, good results can be obtained when the processing solution contains up to 5 g./l. and preferably 1 to 3 g./l.; when they are incorporated in the photographic element, concentrations of up to 1,000 mg./mole of Ag and preferably concentrations of 300 to 500 mg./mole of Ag are employed.

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

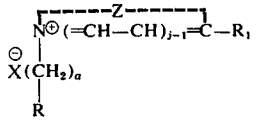
ber Publishing Co., Cleveland, Ohio, p. 2558, and has the following composition:

water, about 125° F. (52° C.)	500 cc.
sodium sulfite, desiccated	30.0 g.
N-methyl-p-aminophenol sulfate	2.5 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.

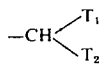
In one preferred embodiment of the invention, hydrazines are used as the fogging agent, such as the compounds disclosed in U.S. Pat. No. 2,588,982 by Ives issued Mar. 11, 1952, and U.S. Pat. No. 3,227,552 by Whitmore issued Jan. 4, 1966.

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. Pat. No. 3,615,615 by Lincoln et al, U.S. Pat. No. 3,719,494 by Kurtz et al issued Mar. 6, 1973, U.S. Pat. No. 3,734,738 by Kurtz et al issued May 22, 1973, and U.S. Pat. No. 3,718,470, which are incorporated herein by reference. Generally, these compounds can be represented by the formula:



wherein:

1. Z represents the atoms necessary to complete a heterocyclic nucleus containing a heterocyclic ring of five to six atoms including the quaternary nitrogen atom, with the additional atoms of said heterocyclic ring being selected from carbon, nitrogen, oxygen, sulfur and selenium;
2. *j* represents a positive integer of from 1 to 2;
3. *a* represents a positive integer of from 2 to 6;
4. $\ominus_X$ represents an acid anion;
5. R represents a member selected from:
   a. a formyl radical,
   b. 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 five to six atoms in the heterocyclic acetal ring, and

   c. a 1-hydrazonoalkyl radical; and

6. 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 radical, an acyl radical such as 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 at least 0.5 mg. and preferably from about 75 to about 1,500 mg. of the subject fogging agents per mole of silver in the silver halide emulsion are useful. 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. When the compounds of U.S. Pat. Nos. 3,615,615 or 3,718,470 are used, the concentration of the fogging agent is preferably from 0.5 to 10 mg./mole of Ag when incorporated in the photographic element and from about 0.1 to about 2 g./l. of solution when incorporated in the developer solution.

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-dihydro3-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, proce-

dures 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%, 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 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 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. No. 3,142,568 by Nottorf issued July 28, 1964; U.S. Pat. No. 3,193,386 by White issued July 6, 1965; U.S. Pat. No. 3,062,674 by Houck et al issued Nov. 6, 1962; U.S. Pat. No. 3,220,844 by Houck et al issued Nov. 30, 1965; U.S. Pat. No. **3,287,289** by Ream et al issued Nov. 22, 1966; and U.S. Pat. No. **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 Canadiam Pat. No. 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 two to 10 carbon atoms such as polyethylene, polypropylene, ethylenebutene copolymers and the like.

The 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. No. 2,376,679 by Frohlich et al, U.S. Pat. No. 2,322,027 by Jelley et al, U.S. Pat. No. 2,801,171 by Fierke et al, U.S. Pat. No. 2,698,794 by Godowsky, U.S. Pat. No. 3,227,554 by Barr et al and U.S. Pat. No. 3,046,129 by Graham et al; or elements to be developed in solutions containing colorforming couplers such as those described in U.S. Pat. No. 2,252,718 by Mannes et al, U.S. Pat. No. 2,592,243 by Carroll et al and U.S. Pat. No. 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.

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. No. 2,352,014 by Rott, U.S. Pat. No. 2,543,181 by Land, U.S. Pat. No.

3,020,155 by Yackel et al and U.S. Pat. No. 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, U.S. Pat. No. 3,253,915 by Weyerts et al, U.S. Pat. No. 3,227,550 by Whitmore et al, U.S. Pat. No. 3,227,551 by Barr et al, U.S. Pat. No. 3,227,552 by Whitmore, U.S. Pat. Nos. 3,415,644, 3,415,645 and 3,415,646, all by Land, U.S. Pat. Nos. 2,543,181 and 3,635,707, Canadian Pat. No. 674,082, and Belgian Pat. Nos. 757,959 and 757,960, both issued Apr. 23, 1971; and imbibition transfer processes as described in U.S. Pat. No. 2,882,156 by Minsk; all of which are incorporated herein by reference.

Generally, the image-transfer film units in accordance with this invention comprise:

1. a photosensitive element comprising a support having thereon at least one layer containing a direct-positive silver halide emulsion preferably having associated therewith an image dye-providing material,
2. an image-receiving layer which can be located on a separate support and superposed or adapted to be superposed on said photosensitive element, or preferably can be coated as a layer in the photosensitive element,
3. means containing an alkaline processing composition adapted to discharge its contents within said film unit and wherein said film unit contains a silver halide developing agent and said direct-positive silver halide emulsion comprises unfogged silver halide grains which have metal dopants 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 photosensitive composition is coated at a coverage of between about 300 to about 400 mg. of silver/ft.^{2} and
   b. to at least a level which would provide a density of 0.5 using undoped silver halide grains of the same grain size and halide composition when coated, exposed and developed in like manner, and
4. a fogging agent located in said film unit whereby it will be in contact with said photosensitive composition upon discharge of said processing composition.

In highly preferred embodiments, the film units of this invention contain a support having thereon a layer containing a blue-sensitive emulsion having associated therewith a yellow image dye-providing material, a red-sensitive silver halide emulsion having associated therewith a cyan image dye-providing material, and a green-sensitive emulsion having associated therewith a magenta image dye-providing material, and preferably all of said image dye-providing materials are initially immobile image dye-providing materials.

The term "image dye-providing material" as used herein is understood to refer to those compounds which either (1) do not require a chemical reaction to form the image dye or (2) undergo reactions encountered in photographic imaging systems to produce an image dye, such as with color couplers, oxichromic compounds and the like. The first class of compounds is generally referred to as preformed image dyes and includes shifted dyes, etc., while the second class of compounds is generally referred to as dye precursors.

The terms "initially diffusible" and "initially immobile" as used herein refer to compounds which are incorporated in the photographic element and, upon contact with an alkaline processing solution, are substantially diffusible or substantially immobile, respectively.

In one preferred embodiment, the silver halide emulsions of the invention are used in association with immobile image dye-providing compounds, wherein said compounds undergo oxidation followed, in certain instances, by hydrolysis to provide an imagewise distribution of a mobile image dye. Compounds of this type can be used with direct-positive emulsions to form negative image records in the exposed photographic element and will provide a positive image in diffusible dye for transfer to an image-receiving layer, such as in an image-transfer film unit. Typical useful compounds of this type are disclosed in Canadian Pat. No. 602,607 by Whitmore et al issued Aug. 2, 1960, U.S. Ser. No. 351,673 by Fleckenstein et al and Ser. No. 351,700 by Fleckenstein, both filed Apr. 16, 1973, and U.S. Pat. No. 3,698,897 by Gompf et al, U.S. Pat. No. 3,728,113 by Becker et al, U.S. Pat. No. 3,725,062 by Anderson et al, U.S. Pat. No. 3,227,552 by Whitmore, U.S. Pat. Nos. 3,443,939, 3,443,940 and 3,443,941, and the like, all of which are incorporated herein by reference. Where the receiver layer is coated on the same support with the photosensitive silver halide layers, the support is preferably a transparent support, an opaque layer is preferably positioned between the image-receiving layer and the photosensitive silver halide layer, and the alkaline processing composition preferably contains an opacifying substance such as carbon or a pH-indicator dye which is discharged into the film unit between a dimensionally stable support or cover sheet and the photosensitive element.

In certain embodiments, the cover sheet can be superposed or is adapted to be superposed on the photosensitive element. The image-receiving layer can be located on the cover sheet. In certain preferred embodiments where the image-receiving layer is located in the photosensitive element, a neutralizing layer is located on the cover sheet.

A means for containing the alkaline processing solution can be any means known in the art for this purpose, including rupturable containers positioned at the point of desired discharge of its contents into the film unit and adapted to be passed between a pair of juxtaposed rollers to effect discharge of the contents into the film unit, frangible containers positioned over or within the photosensitive element, hypodermic, syringes, and the like.

It is known in the art that neutralizing layers containing acidic materials, such as polymeric acids, monomeric acids, hydrolyzable materials and the like, can be positioned within an image-transfer film unit to effect shutdown of development of silver halide and transfer of the image dye-providing substance. Neutralizing layers can also be used in the film units of the present invention, including acid layers positioned behind timing layers to delay neutralization of the element, acid layers positioned near the image-receiving layer, acid layers on a cover sheet used to distribute the processing composition uniformly over the photosensitive element, acid layers within the photosensitive element, and the like.

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 min. 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 micron 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 min. at 70° C. The chemically sensitized grains are further grown in the same precipitation environment as the first precipitation for an additional 28 min., such that the final crystalline structure results in octahedral grains 0.8 micron 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-micron 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 min. at 70° C., and then are grown to 0.8 micron 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./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
		2 (2.1)	reversal image

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 min. 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-dihydroxy-3,6-dithiaoctane/silver mole. Upon completion of the precipitation, cubic crystals having a diameter of 0.8 micron result. The silver bromoiodide grains are then chemically sensitized by adding 2.0 mg. of sodium aurous (I) dithiosulfate dihydrate/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 min. 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 micron in diameter. The surface of the grains is then chemically sensitized by adding 1.0 mg. of sodium aurous (I) dithiosulfate dihydrate/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/liter. The following results are observed.

Finish Time	Relative Speed	Dmax	Dmin	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 micron 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 3. 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 min. 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 micron 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 min. at 70° C. The chemically sensitized grains are further grown in the same precipitation environment as the first precipitation for an additional 28 min., such that the final crystalline structure results in octahedral grains 0.8 micron 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 if processed in said fogging developer which contains 20 mg./liter of potassium iodide. The results are as follows:

Example	Time of Finish	Developer	Dmax
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 Dmax 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 min. at 70° 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	Dmax 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 min. 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 chemically sensitized but have a Dmax in a surface 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/silver mole. The precipitation is carried out in an acidic medium for 60 min. 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 Elonhydroquinone developer such as Kodak Developer D-19 for 3 min. During development the film samples are overall flashed for 30 sec. using a 15-watt bulb at a distance of 2 ft. 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 min. 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 micron 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 min. at 70° C. The chemically sensitized grains are further grown in the same precipitation environment as the first precipitation for an additional 40 min., such that the final crystalline structure results in octahedral grains 1.3 micron 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 min. 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 (3000 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-methyl-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-hydroxyethyl-aniline	1.5	g.
hydroxyethylcellulose	2.5	g.
water to 1 liter		

The processing solution is spread from the pod between the exposed surface of the element and an opaque poly(ethylene terephthalate) 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 min. 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, and now abandoned, 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 min. 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. Pat. No. 3,476,563 issued Nov. 4, 1969, 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.

EXAMPLE 11

The direct-positive emulsions of this invention are especially useful in image-transfer film units wherein the direct-positive emulsion has associated therewith an immobile image dye-providing material which releases an image dye as a function of oxidation.

A silver halide emulsion is prepared as described in Example 9, with the provision that (1) the precipitation medium contains 150 mg. of 1,10-dithio-4,7,13,16-tetraoxacyclooctadecane/silver mole, (2) the pH and pAg during the precipitations are kept constant and (3) the silver halide grains are surface-sensitized only with sodium thiosulfate.

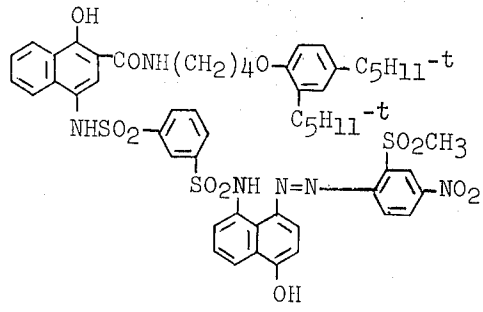
The emulsion is divided into three portions and one portion is spectrally sensitized in the green region of the spectrum, another is spectrally sensitized in the red region of the spectrum, and another is sensitive only in the blue region of the spectrum.

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

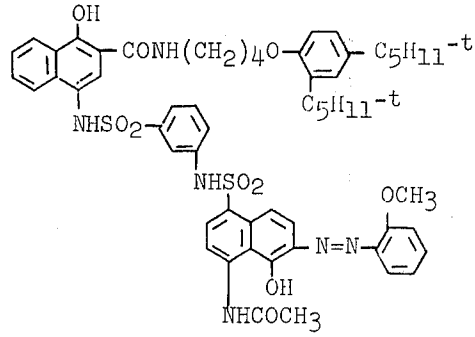
1. image-receiving layer of copoly[styrene-N-benzyl-N,N-dimethyl-N-(3-maleimidopropyl)ammonium chloride] (200 mg./ft.²) and gelatin (100 mg./ft.²);
2. reflecting layer of titanium dioxide (2,000 mg./ft.²) and gelatin (200 mg./ft.²);
3. opaque layer of carbon black (250 mg./ft.²) and gelatin (312 mg./ft.²);
4. Dye Releaser I (65 mg./ft.²) dissolved in diethyl lauramide at 50 mg./ft.² and gelatin (100 mg./ft.²);
5. red-sensitive, internal-image gelatin-silver chlorobromide emulsion (100 mg. gelatin/ft.² and 125 mg. silver/ft.²), 2,5-di-sec-dodecylhydroquinone (25 mg./ft.²) and nucleating agent formyl 4-methylphenylhydrazine (1 g./mole of silver);
6. interlayer of gelatin (100 mg./ft.²) and 2,5-di-sec-dodecylhydroquinone (50 mg./ft.²);
7. Dye Releaser II (150 mg./ft.²) dissolved in diethyl lauramide at 120 mg./ft.² and gelatin (175 mg./ft.²);
8. green-sensitive, internal-image gelatin-silver chlorobromide emulsion (125 mg. gelatin/ft.² and 150 mg. silver/ft.²), 2,5-di-sec-dodecylhydroquinone (50 mg./ft.²) and nucleating agent formyl-4-methylphenylhydrazine (1 g./mole of silver);
9. interlayer of gelatin (100 mg./ft.²) and 2,5-di-sec-dodecylhydroquinone (50 mg./ft.²);
10. Dye Releaser III (100 mg./ft.²) dissolved in diethyl lauramide at 100 mg./ft.² and gelatin 150 mg./ft.²);
11. blue-sensitive, intenal-image gelatin silver chlorobromide emulsion (100 mg. gelatin/ft.² and 150 mg. silver/ft.²), 2,5-di-sec-dodecylhydroquinone (50 mg./ft.²) and nucleating agent formyl-4-methylphenylhydarzine (1 g./mole of silver); and
12. overcoat of gelatin (82.5 mg./ft.²).

The Dye Releasers I, II and III are described in further detail in Eleckenstein et al., U.S. Ser. no. 351,673 filed Apr. 16, 1973; the specific compounds referred to in the examples are as follows:

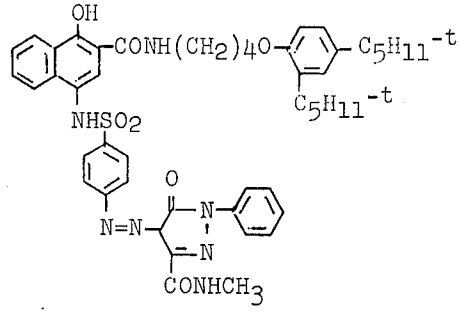
Dye Releaser I — cyan dye-releasing:



Dye Releaser II — magenta dye-releasing:



Dye Releaser III — yellow dye-releasing:



The above-prepared photosensitive element is then exposed to a graduated-density multicolor test object. The following processing composition is employed in a pod and is spread between the photosensitive element and an opaque cellulose acetate sheet by passing the transfer "sandwich" between a pair of juxtaposed pressure rollers.

sodium hydroxide	40	g.
4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	4	g.
5-methylbenzyltriazole	2.4	g.
potassium iodide	0.01	g.
hydroxyethyl cellulose	25	g.
distilled water to	1000	ml.

After 4 min., the element is separated from the opaque sheet, subjected to a 1-min. acid rinse, fixed for 4 min., washed and dried. The following sensitometric results are obtained:

Maximum Density			Minimum Density		
Red	Green	Blue	Red	Green	Blue
2.01	2.08	1.64	0.20	0.22	0.24

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. In an image-transfer film unit which comprises an image-receiving layer, at least one layer of a photo-sensitive composition having associated therewith an image dye-providing material, a developing agent, and a processing composition which can be discharged to facilitate development of said photosensitive composition by passing said unit between a pair of juxtaposed pressure-applying members, the improvement comprising (1) said photosensitive composition in said film unit comprising unfogged silver halide grains having metal dopants occluded therein, which grains 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 said photosensitive composition 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 using undoped silver halide grains of the same grain size and halide composition when coated, exposed and developed in like manner, and (2) a fogging agent located in said film unit whereby it will be in contact with said photosensitive composition upon discharge of said processing composition.

2. A film unit according to claim **1** wherein said film unit includes a rupturable pod within which said fogging agent is located.

3. A film unit according to claim **1** wherein said fogging agent is located in at least one layer of said film unit in association with said layer containing said silver halide grains.

4. A film unit according to claim **1** wherein said film unit comprises at least three of said silver halide layers wherein the silver halide in one of said layers is spectrally sensitized to the red region of the visible light spectrum and the silver halide in another layer is spectrally sensitized to the green region of the visible light spectrum.

5. A film unit according to claim **1** wherein said metal dopants are polyvalent metal ions.

6. A film unit according to claim **1** wherein said metal dopant is comprised of sulfur and gold.

7. A film unit according to claim **1** wherein said fogging agent is a hydrazine compound.

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

9. A film unit according to claim **1** wherein said image-receiving layer is located in said unit between said photosensitive composition and the support for said photosensitive composition.

10. A film unit according to claim **1** wherein said image-receiving layer is coated on a support and is adapted to be superposed on a support carrying said photosensitive composition after exposure thereof.

11. A film unit according to claim 1 wherein said metal dopant is composed of sulfur and gold and said unfogged silver halide grains are chemically sensitized on the surface thereof with a sulfur compound to obtain said level of surface sensitization.

12. In a process of forming a transfer image, the improvement comprising:

I. imagewise-exposing a photosensitive element comprising a support having thereon at least one layer of a photosensitive composition having associated therewith an initially immobile image dye-providing material and silver halide grains having metal dopants occluded therein and wherein said halide is predominantly bromide, which grains have been chemically sensitized on the surface thereof (a) to a level which would produce a density of less than 0.4 after imagewise exposure when developed in Kodak Developer DK-50, provided 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 0.5 using undoped silver halide grains of the same grain size and halide composition when coated, exposed and developed in like manner;

II. treating said photosensitive element with an alkaline processing composition, which is a silver halide surface developer, in the presence of a fogging agent; and thereby

III. effecting development of each of said exposed silver halide emulsion layers, thus causing selective imagewise diffusion of image dye to an image-receiver layer.

13. A process according to claim 12 wherein said film unit comprises at least three separate layers, each containing said silver halide emulsion and each having associated therewith an initially immobile image dye-providing material.

14. A process according to claim 12 wherein said silver halide grains have been chemically sensitized on the surface thereof with sulfur-, gold-, or sulfur-and-gold-containing compounds.

15. In an image-transfer film unit which comprises an image-receiving layer, at least one layer containing a photosensitive composition having associated therewith an initially immobile image dye-providing material, a developing agent and a processing composition which can be discharged to facilitate development of said photosensitive composition by passing said unit between a pair of juxtaposed pressure-applying members, the improvement comprising (1) said photosensitive composition in said film unit being unfogged 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 photosensitive composition 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 using undoped silver halide grains of the same grain size and halide composition when coated, exposed and developed in like manner, and (2) a fogging agent located in said film unit whereby it will be in contact with said photosensitive composition upon discharge of said processing composition.

16. An image-transfer film unit according to claim 15 which comprises at least three separate layers containing said photosensitive composition wherein the silver halide of one of said layers is spectrally sensitized to the red region of the visible light spectrum and has associated therewith a cyan image dye-providing material, the silver halide of another layer is spectrally sensitized to the green region of the visible light spectrum and has associated therewith a magenta image dye-providing material, and the silver halide in another layer is sensitive to the blue region of the visible light spectrum and has associated therewith a yellow image dye-providing material.

17. An image-transfer process according to claim 16 wherein each of said image dye-providing materials is initially immobile and releases a preformed, diffusible image dye as a function of oxidation followed by hydrolysis.

18. An image-transfer film unit according to claim 15 wherein said image-receiving layer is coated on the same support as the layers containing said photosensitive composition.

19. An image-transfer film unit comprising:

1. a photographic element having thereon:
   a. a layer containing a blue-sensitive silver halide emulsion having associated therewith an immobile yellow image dye-providing material,
   b. a layer containing a green-sensitized halide emulsion having associated therewith an immobile magenta image dye-providing material, and
   c. a layer containing a red-sensitized silver halide emulsion having associated therewith an immobile cyan image dye-providing material,
2. an image-receiving layer,
3. means containing an alkaline processing composition for developing said silver halide emulsion layers adapted to discharge its contents within said film unit, and
4. a silver halide developing agent located within said film unit,

wherein each of said silver halide emulsions comprises unfogged silver halide grains having metal dopants occluded therein, which grains 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 said photosensitive composition is coated at a coverage of between about 300 to about 400 mg of silver/ft^2 and
   b. to at least a level which would provide a density of 0.5 using undoped silver halide grains of the same grain size and halide composition when coated, exposed and developed in like manner, and

5. a fogging agent located in said film unit whereby it will be in contact with said photosensitive composition upon discharge of said processing composition.

20. A film unit according to claim 19 wherein said fogging agent is located in each of said layers containing said silver halide emulsions.

21. A film unit according to claim 19 wherein each of said layers containing said silver halide emulsions has associated therewith a benzotriazole antifoggant.

22. A film unit according to claim 19 wherein said metal dopants are comprised of sulfur and gold and

said silver halide grains are sensitized on the surface thereof with a sulfur sensitizer.

23. A film unit according to claim **21** wherein each of said immobile image dye-providing materials contains a preformed dye moiety.

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