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[54] **PHOTOGRAPHIC MATERIALS AND PROCESSES**
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 94, 84, 70, 22

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UNITED STATES PATENTS
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 2,322,027 6/1943 Jelley et al..... 96/97

ABSTRACT: Light-sensitive photographic silver halide emulsions and elements are provided which feature converted-halide silver halide grains in which the halide consists of at least 50 mole percent bromide and up to 10 mole percent iodide, any remaining halide being chloride; the surface of said grains being chemically sensitized; and, said silver halide grains having contiguous thereto a photographic color coupler. Processes for producing photographic color images are also provided wherein emulsions and elements of the type described above, after exposure, are reacted with an aromatic primary amino color developing agent to form a dye image.

PHOTOGRAPHIC MATERIALS AND PROCESSES

This invention relates to photographic materials and processes, and more particularly to photographic materials and processes for producing color images.

It is well known in the art to provide photographic elements which feature blue-, green- and red-sensitive silver halide emulsion layers which are adapted to form, respectively, yellow, magenta and cyan dye images. A typical photographic element of this type is described in VanCampen et al. U.S. Pat. No. 3,416,923 issued Dec. 17, 1968, column 2, lines 20-29. While such elements provide good multicolor photographic records, it would be desirable to provide improved photographic elements which exhibit increased storage stability, higher speed, lower fog, a more satisfactory sensitometric curve shape, increased developability and better resistance to pressure sensitivity.

Accordingly, it is one object of this invention to provide photographic emulsions and elements which contain a photographic color coupler, and which exhibit good storage stability.

Another object of this invention is to provide photographic emulsions and elements which contain a photographic color coupler, and which exhibit good photographic speed.

Still another object of this invention is to provide photographic emulsions and elements which contain a photographic color coupler, and which produce low fog.

A further object of this invention is to provide photographic emulsions and elements which contain a photographic color coupler, and which produce excellent sensitometric curve shapes.

Still another object of this invention is to provide photographic emulsions and elements which contain photographic color couplers, and which exhibit good developability.

Still another object of this invention is to provide photographic emulsions and elements which contain photographic color couplers, and which exhibit high gamma.

Another object of this invention is to provide photographic emulsions and elements which contain a photographic color coupler, and which have high resistance to pressure sensitivity.

Still another object of this invention is to provide processes for forming dye images in photographic emulsions and elements of the type described herein.

Other objects of this invention will be apparent from the disclosure herein and the appended claims.

In accordance with one embodiment of this invention, a light-sensitive photographic emulsion is provided comprising converted-halide silver halide grains, the halide of said grains containing at least 50 mole percent bromide and up to 10 mole percent iodide, any remaining halide being chloride; the surface of said grains being chemically sensitized; and, said emulsion containing a photographic color coupler.

In another embodiment of this invention, photographic elements are provided comprising a support having coated thereon at least one light-sensitive photographic emulsion layer comprising converted-halide silver halide grains; the surface of said grains being chemically sensitized; and, said emulsion layer having a photographic color coupler contiguous to said silver halide grains.

In another embodiment of this invention, photographic elements are provided comprising a support having coated thereon at least three superposed hydrophilic colloid layers containing light-sensitive silver halide grains, said layers being differentially sensitive to red, green and blue radiation, said layers having contiguous to the silver halide thereof, respectively, cyan, magenta and yellow dye-forming photographic color couplers; the silver halide grains in at least one of said silver halide emulsions being converted-halide silver halide grains; and, the surface of said converted-halide grains being chemically sensitized.

In a preferred embodiment of this invention, a photographic element is provided comprising a support having coated thereon at least three superposed hydrophilic colloid layers

containing light-sensitive silver halide grains, and layers being differentially sensitive to red, green and blue radiation, said layers having incorporated therein, respectively, cyan, magenta and yellow dye-forming photographic color couplers; the light-sensitive silver halide in each of said layers comprising converted-halide silver halide grains; and, the surface of said grains being chemically sensitized. Particularly good results are obtained when the green-sensitive silver halide emulsion layer is coated between the red- and blue-sensitive silver halide emulsion layers, and the blue-sensitive layer is coated adjacent the support. A hydrophilic colloid layer containing ultraviolet absorber is advantageously employed between the red-sensitive and green-sensitive silver halide emulsion layers.

In still another embodiment of this invention, color images are provided in the exposed photographic elements described herein by developing said exposed photographic element with an aromatic primary amino color developing agent which reacts with the photographic color coupler in the photographic element to form a dye. Silver halide and silver image is removed from the element in any convenient manner, such as by fixing and bleaching.

The photographic emulsions and elements in accordance with this invention feature excellent storage stability, good speed, low fog, excellent sensitometric curve shape, good developability and high resistance to pressure sensitivity. The chemically sensitized converted-halide silver halide grains employed herein generally are superior to corresponding chemically sensitized conventional negative silver halide emulsions with respect to storage stability, speed, fog, sensitometric curve shape, developability and resistance to pressure sensitivity.

The converted-halide silver halide grains employed in the practice of this invention have a halide content of at least 50 mole percent, and preferably at least 80 mole percent bromide, and contain up to 10 mole percent, and preferably less than 5 mole percent iodide, any remaining halide being chloride. Especially good results are obtained with silver halide grains containing about 90 mole percent bromide and about 10 mole percent chloride.

The term "converted-halide silver halide grains" is employed herein as a word of art and denotes silver halide grains prepared by forming an emulsion of silver salt grains consisting at least partly of a silver salt more soluble in water than silver bromide, and "converting" at least a portion of such grains to silver bromide or silver bromoiodide salts.

More specifically, such silver halide grains can be prepared by forming a silver salt which is (1) more soluble in water than silver bromide, and (2) has a solubility of less than about 0.02 grams, and preferably less than about 0.00002 grams per 100 milliliters of water at 20° C. Useful salts more soluble than silver bromide include silver chloride, silver thiocyanate and silver citrate. Such salts are conveniently formed by adding separate solutions of silver nitrate in water, and a suitable aqueous alkali metal salt solution, such as potassium chloride, potassium citrate or potassium thiocyanate, to an aqueous gelatin solution containing a small amount of the alkali metal salt. The first two solutions are preferably added slowly to the aqueous gelatin solution. The temperature of all the solutions is preferably maintained between about 20° and 50° C. After the formation of the silver salts more soluble than silver bromide, a suitable bromide salt can be added to convert at least part of the more soluble silver salt to silver bromide. If desired, a suitable iodide salt can also be added to form silver bromoiodide. Potassium bromide and potassium iodide are especially useful for this purpose. When silver chloride is used as the silver salt more soluble than silver bromide, it is not essential to convert all the chloride to bromide or bromoiodide, nor is it essential that the silver halide grains contain iodide. The useful silver halide grains thus include silver bromide; silver bromoiodide; silver chlorobromide; and, silver chlorobromoiodide. The method for preparing emulsions of the type employed in this invention is described by Davey and Knott U.S. Pat. No. 2,592,250 issued Apr. 8, 1952.

The converted-halide silver halide emulsions described herein have also been referred to by those skilled in the art as "halide conversion emulsions" and "halide converted photographic emulsions".

The converted-halide silver halide grains employed in this invention can be chemically sensitized by any means suitable for this purpose, many methods having been previously described in the prior art. Chemical sensitization, as used herein, includes sensitization of the type described by Antoine Hautot and Henri Saubnier in "Science et Industries Photographiques," vol. XXVIII, Jan. 1057, pages 1-23 and Jan. 1957, pages 57-65. Such chemical sensitization includes four major classes, viz., noble metal or gold sensitization, sulfur sensitization, such as by a labile sulfur compound, selenium sensitization, such as by a labile selenium compound, 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, or tellurium sensitization. Sulfur and selenium sensitization are the preferred chemical sensitizers in the practice of this invention.

The converted-halide silver halide grains can be chemically sensitized by any of the accepted procedures. Emulsions containing such grains can be digested with naturally active gelatin, or sulfur compounds can be added, such as those described in Sheppard U.S. Pat. No. 1,547,944 issued Mar. 2, 1926, Sheppard et al. U.S. Pat. No. 1,623,499 issued Apr. 5, 1927 and Sheppard et al. U.S. Pat. No. 2,410,689 issued Nov. 5, 1946.

The converted-halide silver halide grains can also be treated with salts of the noble metals, such as ruthenium, rhodium, palladium, iridium, and platinum. Representative compounds are ammonium chloropalladate, potassium chloroplatinate, and sodium chloropalladate, 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 high 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 converted-halide silver halide grains can also be chemically sensitized with gold salts as described in Waller et al. U.S. Pat. No. 2,399,083 issued Apr. 23, 1946, and Damschroder et al. U.S. Pat. No. 2,642,361 issued 16, 1953. Suitable compounds are potassium chloraurite, potassium aurithiocyanate, potassium chloraurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

The converted-halide silver halide grains can also be reduction 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 and Jones U.S. Pat. No. 2,518,698 issued Aug. 15, 1950), polyamines, such as spermine (Lowe and Allen U.S. Pat. No. 2,521,925 issued Sept. 12, 1950), or bis(β -aminoethyl) sulfide and its water-soluble salts (Lowe and Jones U.S. Pat. No. 2,521,926 issued Sept. 12, 1950).

Labile selenium can be used to chemically sensitize the converted-halide silver halide grains used herein, as described in Sheppard U.S. Pat. No. 1,623,499 issued Apr. 5, 1927, as well as Sheppard U.S. Pat. Nos. 1,574,944 issued Mar. 2, 1926 and 1,602,592 issued Oct. 12, 1926.

Combinations of chemical sensitizers are also useful, such as a noble metal and labile selenium as described in Dunn U.S. Pat. No. 3,297,446 issued Jan. 10, 1967 and Dunn U.S. Pat. No. 3,442,653 issued May 6, 1969, or the combination of a noble metal, labile selenium and a sulfur compound as described in McVeigh U.S. Pat. No. 3,297,447 issued Jan. 10, 1967.

A mercuric salt can be present during the preparation of the converted-halide silver halide grains, such as during the formation of the silver salt which is more soluble than silver bromide. The mercuric salt increases the speed and reduces fog. Any mercuric salt can be used, including inorganic mercuric

salts such as mercuric sulfate, mercuric acetate, mercuric nitrate or a mercuric halide e.g., mercuric chloride; or, an organic mercuric salt, such as mercuric salts with amines, e.g., the mercuric amine salts described in Allen et al. U.S. Pat. No. 2,728,663 issued Dec. 27, 1955, the disclosure of which is incorporated herein by reference.

A wide variety of photographic color couplers can be employed in the practice of this invention. As used herein, the term "color coupler" includes any compound which reacts (or couples) with the oxidation products of primary aromatic amino developing agent or photographic development to form a dye. Typical useful color couplers include phenolic, 5-pyrazolone, heterocyclic and open-chain ketomethylene compounds. Specific cyan, magenta and yellow color couplers which can be used, respectively, in the cyan, magenta and yellow dye-forming units of the invention are described in Graham et al. U.S. Pat. No. 3,046,129 issued July 24, 1962, column 15, line 45 through column 18, line 51, which disclosure is incorporated herein by reference. Such color couplers can be dispersed in the emulsion layers in any convenient manner, such as by using the solvents and the techniques described in U.S. Pat. Nos. 2,322,027 or 2,801,171. The useful couplers include Fischer-type incorporated couplers such as those disclosed in Fischer U.S. Pat. No. 1,055,155, and particularly nondiffusible Fischer-type couplers containing branched carbon chains, e.g., those referred to in the references cited in Frohlich et al. U.S. Pat. No. 2,376,679, column 2, lines 50-60. These elements can be processed by one of the procedures described in Graham et al. U.S. Pat. No. 2,046,129, columns 23 and 24, or by the development process described by Edens et al. U.S. Pat. application Ser. No. 736,010 filed June 11, 1968, now U.S. Pat. No. 3,582,322 and corresponding German Pat. application 1,928,554 which features a color process in which the color development step is followed with a blix bath comprising silver halide solvent and an oxidizing agent for silver. The disclosure of the Edens et al. application is incorporated herein by reference.

The photographic color couplers employed in this invention can be positioned in photographic elements so that during processing in aqueous alkaline color developing solutions, color developing agent oxidized on developing silver halide in the photographic element reacts with the photographic color coupler. Accordingly, the photographic color couplers can be integral with and contiguous to the silver halide by being incorporated in the silver halide emulsion or in a separate layer contiguous thereto. Also, the photographic color couplers can be separated from silver halide emulsion layers by layers of a hydrophilic colloid such as gelatin or a related composition through which oxidized developing agents can really diffuse in the presence of an aqueous alkaline processing solution.

In color systems of the type useful in this invention, subtractive dye images can be generated by a color negative process, such as the process described by W. T. Hanson and W. I. Kesner in an article in the "Journal of the Society of Motion Picture and Television Engineers," Vol. 61 (1953) pages 667-701; or, by a color reversal process wherein reversal silver images are generated from a photographic color coupler, such as by using a direct positive emulsion or using a negative emulsion which is given an imagewise exposure, developed in a black-and-white developer to provide a negative silver image, and then at least one additional exposure (or other suitable fogging treatment) followed by additional development to generate the desired subtractively colored dye images.

In preferred embodiments of the invention, the photographic element includes a hydrophilic colloid layer which contains a suitable ultraviolet absorber, U.S. as a benzotriazole, e.g., the phenyl-type compounds described in Sawdey U.S. Pat. No. 3,253,921 issued May 31, 1966 and the thiazolidines of the type described in a number of patents including Sawdey U.S. Pat. Nos. 2,739,971 issued Mar. 27, 1956, 2,739,888 issued Mar. 27, 1956 and 3,250,617 issued May 10, 1966. This layer can be an overcoat or can be posi-

tioned between the red- and green-sensitive emulsion layers in elements having a support coated, in the order given, with blue-, green- and red-sensitive emulsion layers.

The multilayer color-producing elements of the invention preferably comprise blue-, green- and red-sensitive silver halide emulsion layers. As is well known, silver halide emulsions are typically sensitive to blue radiation, although additional sensitizing dyes absorbing in the blue region can also be added to modify the sensitivity of the emulsion to blue radiation as desired. Green and red spectral sensitization can be conferred by any of the dyes suggested in the art for this purpose, including those described in Brooker et al. U.S. Pat. No. 2,526,632 issued Oct. 24, 1950; Sprague U.S. Pat. No. 2,503,776 issued Apr. 11, 1950; Brooker et al. U.S. Pat. No. 2,493,748 issued Jan. 10, 1950; and Taber et al. U.S. Pat. No. 3,384,486 issued May 21, 1968. Spectral sensitizers which can be used include the cyanines, merocyanines, complex (tri or tetranuclear) merocyanines, complex (tri or tetranuclear) cyanines, holopolar cyanines, styryls, hemicyanines (e.g., enamine hemicyanines), oxonols and hemioxonols. Dyes of the cyanine classes may contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, selenazoles and imidazoles. Such nuclei may contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl and enamine groups and may be fused to carbocyclic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, haloalkyl, cyano, or alkoxy groups. The dyes may be symmetrical or unsymmetrical and may contain alkyl, phenyl, enamine or heterocyclic substituents on the methine or polymethine chain. The merocyanine dyes may contain the basic nuclei mentioned above as well as acid nuclei such as thiohydantoins, rhodanines, oxazolinediones, thiazolinediones, barbituric acids, thiazolineones, and malononitrile. These acid nuclei may be substituted with alkyl, alkylene, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxyalkyl, alkylamino groups, or heterocyclic nuclei. Combinations of these dyes may be used, if desired. In addition, supersensitizing addenda which do not absorb visible light may be included, for instance, ascorbic acid derivatives, azaindenes, cadmium salts, and organic sulfonic acids as described in McFall et al. U.S. Pat. No. 2,933,390 and Jones et al. U.S. Pat. No. 2,937,089. The multilayer photographic elements of the invention can be spectrally sensitized, and can contain the filter layers described by Schwan et al. U.S. Pat. application Ser. No. 715,005 filed Mar. 21, 1968, now abandoned and corresponding Belgian Pat. 729,204 of Aug. 28, 1969, and Schwan et al. continuation-in-part application Ser. No. 864,275 filed Sept. 29, 1969.

Spectral sensitizing dyes can be added to the emulsions of any convenient manner, such as by treating the emulsion with a solution of a sensitizing dye in an organic solvent or the dye may be added in the form of a dispersion as described in Owens et al. British Pat. 1,154,781 of June 11, 1969. For optimum results, the dye may either be added to the emulsion as a final step or at some earlier stage.

The silver halide emulsions used in this invention can contain speed-increasing compounds such as polyalkylene glycols, cationic surface active agents and thioethers of combinations of these as described in Piper U.S. Pat. No. 2,886,437; Chechak U.S. Pat. No. 3,046,134; Carroll et al. U.S. Pat. No. 2,944,900; and Goffe U.S. Pat. No. 3,294,540.

The converted-halide silver halide emulsions used in this invention can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers, which can be used alone or in combination, include the thiazolium salts described in Staud U.S. Pat. No. 2,131,038 and Allen U.S. Pat. No. 2,694,716; the azaindenes described in Piper U.S. Pat. No. 2,886,437 and Heimbach U.S. Pat. No. 2,444,605; the mercury salts described in Allen U.S. Pat. No. 2,728,663; the urazoles described in Anderson U.S. Pat. No. 3,287,135; the sulfocatechols described in Kennard U.S. Pat. No. 3,236,652; the oximes described in Carroll et al. British Pat. 623,448;

nitron; nitroindazoles; the mercaptotetrazoles described in Kendall et al. U.S. Pat. No. 2,403,927; Kennard et al. U.S. Pat. No. 3,266,897 and Luckey et al. U.S. Pat. No. 3,397,987; the polyvalent metal salts described in Jones U.S. Pat. No. 2,839,405; the thiuronium salts described in Herz U.S. Pat. No. 3,220,839; and the palladium, platinum and gold salts described in Trivelli U.S. Pat. No. 2,566,263 and Damschroder U.S. Pat. No. 2,597,915.

Photographic elements including emulsions used in accordance with this invention can contain incorporated developing agents such as hydroquinones, catechols, aminophenols, 3-pyrazolidones, ascorbic acid and its derivatives, reductones and phenylenediamines, or combinations of developing agents. The developing agents can be in a silver halide emulsion and/or in another suitable location in the photographic element. The developing agents can be added from suitable solvents or in the form of dispersions as described in Yackel U.S. Pat. No. 2,592,368 and Dunn et al. French Pat. 1,505,778.

Silver halide emulsions useful in accordance with the invention can be dispersed in colloids that can be hardened by various organic or inorganic hardeners, alone or in combination, such as the aldehydes, and blocked aldehydes, ketones, carboxylic and carbonic acid derivatives, sulfonate esters sulfonyl halides and vinyl sulfones, active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, mixed function hardeners and polymeric hardeners such as oxidized polysaccharides, e.g., dialdehyde starch, oxyguargum, etc.

Photographic silver halide emulsions employed herein can contain various colloids alone or in combination as vehicles or binding agents. 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, e.g., poly(vinylpyrrolidone) acrylamide polymers or other synthetic polymeric compounds such as dispersed vinyl compounds 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 of Nottorf, issued July 28, 1964; 3,193,386 of White, issued July 6, 1965; 3,062,674 of Houck, Smith and Yudelson, issued Nov. 6, 1962; 3,220,844 of Houck, Smith and Yudelson, issued Nov. 30, 1965; Ream and Fowler 3,287,289 issued Nov. 22, 1966; and Dykstra U.S. Pat. No. 3,411,911; particularly effective are those water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, those which have cross-linking sites which facilitate hardening or curing and those having recurring sulfobetaine units as described in Canadian Pat. 774,054.

Photographic silver halide emulsions in accordance with this invention can be used in photographic elements which contain antistatic or conducting layers, such as layers that comprise soluble salts, e.g., chlorides, nitrates, etc., evaporated metal layers, ionic polymers such as those described in Minsk U.S. Pat. Nos. 2,861,056 and 3,206,312 or insoluble inorganic salts such as those described in Trevoxy U.S. Pat. No. 3,428,451.

Photographic silver halide emulsions used in the invention 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.

Photographic silver halide emulsions of the invention can contain plasticizers and lubricants such as polyalcohols, e.g.,

glycerin and diols of the type described in Milton U.S. Pat. No. 2,960,404; fatty acids or esters such as those described in Robijns U.S. Pat. No. 2,588,765 and Duane U.S. Pat. No. 3,121,060; and silicone resins such as those described in Dupont British Pat. 955,061.

The converted-halide photographic emulsions useful herein can contain surfactants such as saponin, anionic compounds such as the alkyl aryl sulfonates described in Baldsiefen U.S. Pat. No. 2,600,831 and amphoteric compounds such as those described in Ben-Ezra U.S. Pat. No. 3,133,816.

Photographic elements containing emulsion layers as described herein can contain matting agents such as starch, titanium dioxide, zinc oxide, silica polymeric beads including beads of the type described in Jelley et al. U.S. Pat. No. 2,992,101 and Lynn U.S. Pat. No. 2,701,245.

Silver halide emulsions described herein can be utilized in photographic elements which contain brightening agents including stilbene, triazine, oxazole and coumarin brightening agents. Water-soluble brightening agents can be used such as those described in Albers et al. German Pat. 972,067 and McFall et al. U.S. Pat. No. 2,933,390 or dispersions of brighteners can be used such as those described in Jansen German Pat. 1,150,274 and Oetiker et al. U.S. Pat. No. 3,406,070.

Light-sensitive photographic emulsion layers hereof can be used in photographic elements which contain light-absorbing materials and filter dyes such as those described in Sawdey U.S. Pat. No. 3,252,921; Gaspar U.S. Pat. No. 2,274,782; Carroll et al. U.S. Pat. No. 2,527,583 and VanCompen U.S. Pat. No. 2,956,879. If desired, the dyes can be mordanted, for example, as described in Milton and Jones U.S. Pat. No. 3,282,699.

The sensitizing dyes (and other emulsion addenda) can be added to the photographic emulsion from water solutions or suitable organic solvent solutions, for example with the procedure described in Collins et al. U.S. Pat. No. 3,342,605; 2,912,343; Owens et al. U.S. Pat. No. 3,342,605; Audran U.S. Pat. No. 2,996,287 or Johnson et al. U.S. Pat. No. 3,425,835. The dyes can be dissolved separately or together, and the separate or combined solutions can be added to a silver halide emulsion, or a silver halide emulsion layer can be bathed in the solution of dye or dyes.

Photographic emulsions of this invention can be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in Beguin U.S. Pat. No. 2,681,294. If desired, two or more layers may be coated simultaneously by the procedures described in Russell U.S. Pat. No. 2,761,791 and Wynn British Pat. 837,095.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

A light-sensitive silver chlorobromide gelatin emulsion is prepared which contains about 10 mole percent chloride and about 90 mole percent bromide per mole of silver halide, using a technique similar to that described in example 1 of Davey et al. U.S. Pat. No. 2,592,250 issued Apr. 8, 1952, except no iodide salt is added. The coagulation washing procedure, which is used to remove unwanted salts, is described in example 1 of Yutzy et al. U.S. Pat. No. 2,614,928 issued Oct. 21, 1952. When the washing procedure has been completed, additional gelatin and water are added to adjust the gelatin concentration and the final weight. The resulting light-sensitive silver chlorobromide emulsion is treated with sodium thiosulfate pentahydrate at a concentration of 20 mg. per silver mole for the purpose of creating electron traps at the surface of the silver halide grain. The sodium salt of 4-hydroxy-6-methyl-1,3,3a, 7-tetrazaindene, whose function is to slow the ripening process and prevent further grain growth, is also added at a concentration of 133 mg. per mole of silver. The emulsion is then ripened for 18 minutes at a temperature of

65° C. The resulting surface sensitized silver halide grains have higher surface sensitivity to light than do the unsensitized silver halide grains, which have a high internal native sensitivity.

EXAMPLE 2

A light-sensitive silver chlorobromide gelatin emulsion is prepared using the technique described in Davey et al. U.S. Pat. No. 2,592,250, except no iodide salt is added. The following variations are made. To a potassium chloride aqueous gelatin solution is added, at a controlled rate of addition, silver nitrate which has been dissolved in distilled water. When all the silver nitrate solution has been added, potassium bromide, dissolved in distilled water, is added while controlling the rate of addition. The resulting silver chlorobromide gelatin colloid is coagulation washed as described in example 1. The silver chlorobromide gelatin coagulum is adjusted to a desired gelatin concentration and weight by the addition of an aqueous gelatin solution. The halide concentration of the resulting silver chlorobromide photographic emulsion is about 10 mole percent chloride and about 90 mole percent bromide per mole of silver halide. This internally light-sensitive emulsion is then treated with an aqueous solution of sodium thiosulfate pentahydrate (chemical sensitizer). An amount of solution is added in sufficient quantity to give a total dry concentration of sodium thiosulfate pentahydrate of 9 mg. per mole of silver halide. An additional compound, the sodium salt of 4-hydroxy-6-methyl-1,3,3a, 7-tetrazaindene, whose function is described in example 1, is added at a silver halide molar concentration of 133 mg. This emulsion is then heated to 65° C. and held for a period of 20 minutes and then rapidly cooled. The addition of the above chemical sensitizer to this silver chlorobromide light-sensitive emulsion has changed its light-sensitive characteristics from high internal sensitivity to a high surface sensitivity.

EXAMPLE 3

Samples of 2 layer light-sensitive materials (coatings *d*, *e* and *f*) are prepared. Layer 1, which is coated on a paper support coated on both sides with polyethylene, comprises the silver chlorobromide gelatin emulsion of example 1 which has been spectrally sensitized to red light and coated at about 35 mg. of silver per square foot, about 155 mg. of gelatin per square foot and about 35 mg. of the cyan dye-forming color coupler 2-[α -(2,4-di-tert-amylophenoxy)butyramido]-4,6-dichloro-5-methylphenol per square foot. A second layer, a gelatin protective layer, is coated over layer 1 at a coverage of about 100 mg. of gelatin per square foot. Coatings *d*, *e* and *f*, which contain chemically sensitized converted-halide emulsions used in this invention, are compared to control sample coatings *a*, *b* and *c* which are of the same structure as coatings *d*, *e* and *f*, with the exception that coatings *a*, *b* and *c* employ conventional negative silver chlorobromide gelatin emulsions of the type described by Trivelli and Smith *Phot. J.*, Vol. LXX-IX, pp. 330-338, May, 1939. The halide composition of the control light-sensitive emulsions are about 10 percent chloride and about 90 percent bromide per mole of silver halide. The control emulsions are chemically sensitized with 20 mg. per mole of silver of sodium thiosulfate pentahydrate. Coatings *a*, *b*, *c*, *d*, *e* and *f* are each exposed to red light on an Eastman 1B Sensitometer and the latent images converted into visible images using color process described in Hanna U.S. Pat. No. 3,480,434 issued Nov. 25, 1969, example 1, columns 4 and 5, in which the solutions are kept at a temperature of about 30° C. Samples of the coatings are developed for a duration of 2, 4 and 6 minutes. Table 1 compares the relative speed, fog, and maximum density values for the development times noted.

TABLE I

Coating	Time of Development	Relative Speed	Fog	Dmax
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a (control)	2'	100	0.10	2.02
b (control)	4'	132	0.10	2.22
c (control)	6'	159	0.12	2.20
d (invention)	2'	145	0.10	2.28
e (invention)	4'	191	0.12	2.29
f (invention)	6'	214	0.14	2.28

Table I shows that the elements of the invention have greater developability, higher maximum density, lower fog at the 4 and 6 minute development times, and are faster than the control coating. The greater developability of the elements of the invention is further illustrated by the fact that the control element must be developed for 6 minutes to provide a sensitometric curve shape similar to the sensitometric curve of an element of the invention which is developed for 2 minutes. Results essentially similar to those of example 3 are obtained when the converted-halide emulsion of example 2 is replaced with a similar emulsion which is chemically sensitized with a noble metal sensitizer, such as potassium chloroaurate; a labile selenium sensitizer such as diethylselenide; a reduction sensitizer such as a stannous salt; a polyamine such as diethylene triamine or, a combination of sensitizers such as a noble metal together with a labile selenium compound and/or a sulfur compound, such as the combination of potassium chloroaurate, sodium thiosulfate pentahydrate and N,N-dimethylselenourea.

EXAMPLE 4

Two samples of a multilayer, multicolor light-sensitive photographic paper, coatings *c* and *d*, are prepared having the following composition:

Layer 6—gelatin

Layer 5—red-sensitive silver halide emulsion and a phenolic cyan coupler

Layer 4—gelatin

Layer 3—green-sensitive silver halide emulsion containing a pyrazolone magenta coupler

Layer 2—gelatin

Layer 1—blue-sensitive silver halide emulsion containing an acyl acetanilide yellow coupler

Paper support (both sides polyethylene coated) Layer 1, the yellow dye-forming layer, contains the chemically-sensitized converted-halide silver chlorobromide gelatin photographic emulsion described in example 2. Two other samples of a multilayer, multicolor light-sensitive photographic paper, control coatings *a* and *b*, are prepared just like coatings *c* and *d*, except that a silver chlorobromide photographic gelatin emulsion of a type similar to that described by Glafkides, *Photographic Chemistry*, Vol. 1, pp. 301-304, is substituted for the converted-halide silver halide emulsion. The halide composition of the photographic emulsion of coatings *a* and *b* is about 10 percent chloride, and 90 percent bromide. This emulsion is chemically sensitized by treatment with an aqueous sodium thiosulfate pentahydrate solution in a quantity sufficient to give a dry weight concentration of 9 mg. sodium thiosulfate pentahydrate per mole of silver halide. Samples of these coatings are exposed to blue light on an Eastman 1B Sensitometer and then processed as described in example 3. Coatings *a* and *c* are developed for 3 minutes and coatings *b* and *d* are developed for 6 minutes. Table II compares the relative speed, fog and maximum density of these coatings.

TABLE II

Coating	Time of Development	Relative Speed	Fog	Dmax
a (control)	3'	100	0.17	1.83
b (control)	6'	145	0.16	2.31
c (invention)	3'	126	0.14	2.30
d (invention)	6'	174	0.15	2.54

It should be noted that the coating *c*, containing an emulsion of this invention, when developed for 3 minutes, exhibits greater speed and higher maximum density than control coating *a* produces in the same 3 minute development. Coating *c* also exhibits higher gamma than the control coating *a*. Coating *c* of the invention, when developed for 3 minutes, produces a curve of the same gamma and slightly lower maximum density than coating *d* of the invention, which is developed for 6 minutes. Elements containing the silver chlorobromide emulsions of this invention exhibit greater developability than the control elements having conventional chemically sensitized silver chlorobromide emulsions.

EXAMPLE 5

A light-sensitive silver chlorobromide gelatin emulsion is prepared using the technique described in Davey et al. U.S. Pat. No. 2,592,250. The following steps are employed. To a potassium chloride aqueous gelatin solution is added, at a controlled rate of addition, silver nitrate which has been dissolved in distilled water. When all the silver nitrate has been added, potassium bromide and potassium iodide, dissolved in distilled water, are added while controlling the rate of addition. When all the potassium bromide solution has been added, another potassium bromide solution is added, again controlling the rate of addition. The resulting silver chlorobromide emulsion is coagulation washed as in example 1, and the gelatin concentration and final weight is adjusted, and the emulsion is chemically sensitized as described in example 2. The halide concentration of the resulting silver chlorobromide photographic emulsion is about 12 mole percent chloride, about 87 mole percent bromide and about 1 mole percent iodide per mole of silver halide. This emulsion is substituted for the emulsion of the yellow dye-forming layer of coating *c* in example 4. This coating, and a sample of control coating *a* of example 4, are perforated and then developed for 3 minutes as in example 4. Coating *a* of example 4, containing a conventional negative type emulsion, produces a yellow stain around the punch marks. The sample coating of this example, containing a converted-halide emulsion, produces no stain and remains white in the areas of the punches. A similar test is conducted on coating *c* of example 4, and no stain is observed; the coating remains white in the areas of the punch marks. The photographic elements of this invention thus exhibit greater resistance to pressure sensitivity than color-producing photographic elements employing conventional negative silver halide emulsions. Similar resistance to pressure sensitivity is observed when the emulsion of coating *c* of example 4 is replaced with a converted-halide silver halide emulsion chemically sensitized with a noble metal sensitizer, such as potassium chloroaurate; a labile selenium sensitizer such as diethylselenide; a reduction sensitizer such as a stannous salt; a polyamine such as diethylene triamine or, a combination of sensitizers such as a noble metal together with a labile selenium compound and/or a sulfur compound, such as the combination of potassium chloroaurate, sodium thiosulfate pentahydrate and N,N-dimethylselenourea.

EXAMPLE 6

A multicolor photographic element, element A, containing the chemically sensitized converted-halide silver halide emulsions employed in the invention is prepared as follows:

ELEMENT A

Layer 6—gelatin overcoat coated at about 100 mg. gelatin per square foot

Layer 5—a chemically sensitized converted-halide silver halide gelatin emulsion of example 1, spectrally sensitized to red light, is coated at a silver coverage of about 35 mg. per square foot, about 155 mg. of gelatin per square foot and contains about 35 mg. per square foot of the cyan dye-forming coupler 2-[α -(2,4-di-tert-amyl-phenoxy)butyramido]-4,6-dichloro-5-methylphenol

Layer 4—a gelatin layer coated at about 200 mg. gelatin per square foot and containing about 65 mg. per square foot of the ultraviolet absorber 2-(2-hydroxy-3,5-di-tert-amylphenyl)benzotriazole

Layer 3—a chemically sensitized converted-halide silver halide gelatin emulsion of example 1, spectrally sensitized to green light, is coated at a coverage of about 45 mg. silver per square foot, about 200 mg. gelatin per square foot and about 55 mg. per square foot of the magenta dye-forming coupler 1-(2,4,6-trichlorophenyl)-3-[2-chloro-5 (α 4-hydroxy-3-tert.butylphenoxy tetradecanoamido)anilino]-5-pyrazolone

Layer 2—a gelatin interlayer coated at about 100 mg. gelatin per square foot

Layer 1—a chemically sensitized converted-halide silver halide gelatin emulsion of example 1, spectrally sensitive to blue light, coated at a silver coverage of about 50 mg. per square foot and about 200 mg. gelatin per square foot, and containing about 150 mg. per square foot of the yellow dye-forming coupler α-[4-(4-benzyloxyphenyl-sulfonyl)-phenoxy]-α-pivalyl-2-chloro-5-[γ-(2,4-di-tert-amylphenoxy)butyramido]-acetanilide

Support—coated on both sides with white TiO₂ pigmented polyethylene electron bombarded to promote adhesion between the support and the overlying hydrophilic colloid layers

A control photographic element, element B, is prepared exactly like element A except that the chemically sensitized converted-halide silver halide grains in each emulsion layer are replaced with conventional negative silver halide emulsions prepared as described by Trivelli and Smith *Photo. J.*, Vol. LXXIX, pp. 330-338, May, 1939, the halide of the silver halide consisting of about 10 mole percent chloride and about 90 mole percent bromide, and chemically sensitized with about 20 mg. per mole of silver of sodium thiosulfate pentahydrate. Samples of elements A and B are then exposed and developed, as described in example 3, for various development times. The relative speeds (calculated at a reflection density of 1.0) and the minimum density (Dmin) and the maximum density (Dmax) are shown in table III below:

TABLE III

Element	Development Time (min.)	Relative Speed	Blue	
			Dmin	Dmax
A (invention)	1		0.08	0.62
"	2	16.5	0.10	1.35
"	3	46	0.10	1.96
"	4	63	0.12	2.19
"	5	68	0.10	2.22
"	6	73	0.12	2.10
B (control)	2		0.09	0.92
"	4	60	0.11	1.84
"	6	100	0.12	2.36
"	8	112	0.13	2.46
"	10	123	0.13	2.56
"	12	123	0.14	2.54

Element	Development Time (min.)	Relative Speed	Green	
			Dmin	Dmax
A (invention)	1	31	0.10	1.96
"	2	55	0.14	2.06
"	3	55	0.10	2.15
"	4	74	0.12	2.19
"	5	89	0.10	2.22
"	6	97	0.12	2.26
B (control)	2	47	0.10	2.17
"	4	80	0.10	2.46
"	6	100	0.10	2.48
"	8	118	0.13	2.47
"	10	129	0.11	2.56

Element	Development Time (min.)	Relative Speed	Red	
			Dmin	Dmax
A (invention)	1	83	0.10	2.36
"	2	102	0.10	2.12
"	3	115	0.10	2.23
"	4	132	0.12	2.25
"	5	141	0.10	2.32
"	6	166	0.12	2.30
B (control)	2	45	0.07	2.42
"	4	76	0.10	2.51
"	6	100	0.10	2.50
"	8	120	0.12	2.53
"	10	148	0.13	2.56
"	12	159	0.13	2.54

20 Table III shows the greater developability, higher speed and increased maximum density of photographic elements containing the chemically sensitized converted-halide silver halide emulsions of this invention as compared with the control element having conventional chemically sensitized silver halide emulsions. Essentially similar results are obtained when the chemical sensitizer used in the emulsions of element A is a noble metal sensitizer, such as potassium chloroaurate; a labile selenium sensitizer such as diethylselenide; a reduction sensitizer such as a stannous salt; a polyamine such as diethylene triamine or, a combination of sensitizers such as a noble metal together with a labile selenium compound and/or a sulfur compound, such as the combination of potassium chloroaurate, sodium thiosulfate pentahydrate and N,N-dimethyl-selenourea, or when the halide of each emulsion contains about 75 mole percent bromide, 20 mole percent chloride and 5 mole percent iodide.

EXAMPLE 7

40 Samples of elements A and B of example 6 are incubated for up to 28 weeks at a temperature of 20° C. and a relative humidity of 50 percent. These coatings are then exposed and processed as described in example 6. Table IV compares the change of shoulder density of the incubated coatings relative to the fresh processed coatings.

TABLE IV

Keeping period	Element A (invention)			Element B (control)		
	ΔD _{max} cyan	ΔD _{max} magenta	ΔD _{max} yellow	ΔD _{max} cyan	ΔD _{max} magenta	ΔD _{max} yellow
Fresh	0.00	0.00	0.00	0.00	0.00	0.00
4 weeks	-0.03	0.00	-0.01	-0.04	+0.05	-0.01
8 weeks	0.00	+0.03	-0.01	-0.10	-0.10	-0.03
12 weeks	0.00	-0.04	+0.01	-0.07	+0.07	-0.02
16 weeks	0.00	-0.02	-0.02	-0.07	+0.09	-0.05
20 weeks	-0.04	+0.01	-0.09	-0.06	+0.13	-0.08
24 weeks	-0.05	-0.05	-0.09	-0.06	+0.13	-0.08
28 weeks	-0.05	-0.10	-0.12	-0.08	+0.14	-0.07

60 Table IV shows the high stability of element A of this invention through a period of 16 weeks before any major shifts become visible. The control coating, element B, has increased 0.10 in magenta density at the end of 8 weeks and any resulting photographic prints would have an overall pink tone. Table V compares the stain increase of the incubated coatings (at 20° C. and 50 percent relative humidity) when compared with the fresh. These data display the relative stability of both the cyan and magenta layers of both elements A and B.

70 The yellow emulsion of element B increases rapidly in stain and by the end of 12 weeks has reached the point where it is no longer usable. The yellow layer of element A of this invention remains relatively stable. The growth of stain tends to shift the white areas of the print toward the dominant color density change, in this case toward the yellow. It should be pointed

out that a 0.02 minimum density shift is far more critical than a 0.10 density change in the shoulder. The human eye is much more sensitive to density changes in the minimum density areas than it is in the areas of high color saturation; however, a change such as that seen in the magenta shoulder is perceptible and shifts the color balance toward the red.

TABLE V

Keeping period	Element A (invention)			Element B (control)		
	$\Delta D_{\min.}$ cyan	$\Delta D_{\min.}$ magenta	$\Delta D_{\min.}$ yellow	$\Delta D_{\min.}$ cyan	$\Delta D_{\min.}$ magenta	$\Delta D_{\min.}$ yellow
Fresh.....	0.00	0.00	0.00	0.00	0.00	0.00
4 weeks.....	0.00	0.00	+0.02	0.00	0.00	+0.02
8 weeks.....	0.00	0.00	+0.02	0.00	0.00	+0.04
12 weeks.....	0.00	+0.01	+0.02	0.00	+0.02	+0.05
16 weeks.....	0.00	-0.03	+0.02	0.00	+0.02	+0.07
20 weeks.....	0.00	-0.03	+0.02	0.00	+0.02	+0.09
24 weeks.....	0.00	-0.04	-0.02	0.00	+0.02	+0.10
28 weeks.....	+0.04	0.00	+0.03	0.00	+0.02	+0.12

The invention has been described in detail with particular reference to preferred embodiments thereof, but, it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A light-sensitive photographic emulsion comprising converted-halide silver halide grains, the halide of said grains containing at least 50 mole percent bromide and up to 10 mole percent iodide, any remaining halide in said grains being chloride; the surface of said grains being chemically sensitized; and, said emulsion containing a photographic color coupler.

2. A light-sensitive photographic emulsion comprising converted-halide silver halide grains, the halide of said grains containing at least 80 mole percent bromide and up to 5 mole percent iodide, any remaining halide in said grains being chloride; the surface of said grains being chemically sensitized; and, said emulsion containing a photographic color coupler.

3. A light-sensitive photographic emulsion comprising converted-halide silver halide grains, the halide of said grains containing at least 80 mole percent bromide and up to 5 mole percent iodide, any remaining halide in said grains being chloride; the surface of said grains being chemically sensitized with at least one chemical sensitizer selected from the group consisting of a sulfur sensitizer, a noble metal sensitizer, a reduction sensitizer and a selenium sensitizer; and, said emulsion containing a photographic color coupler selected from the group consisting of an open-chain ketomethylene color coupler, a 5-pyrazolone color coupler, and a phenolic color coupler.

4. A light-sensitive photographic emulsion comprising converted-halide silver chlorobromide grains dispersed in gelatin, the halide of said grains consisting essentially of about 10 mole percent chloride and 90 mole percent bromide; the surface of said grains being chemically sensitized with about 20 milligrams sodium thiosulfate pentahydrate per mole of silver; and, said emulsion containing the phenolic color coupler 2-[α -(2,4-di-tert-amylphenoxy)butyramido]-4,6-dichloro-5-methylphenol.

5. A photographic element comprising a support having coated thereon at least one light-sensitive photographic emulsion layer comprising converted-halide silver halide grains, the halide of said grains containing at least 50 mole percent bromide and up to 10 mole percent iodide, any remaining halide being chloride; the surface of said grains being chemically sensitized; and, said emulsion layer having a photographic color coupler contiguous to said silver halide grains.

6. A photographic element comprising a support having coated thereon at least one light-sensitive photographic emulsion layer comprising converted-halide silver halide grains, the halide of said grains containing at least 80 mole percent bromide and up to 5 mole percent iodide, any remaining halide being chloride; the surface of said grains being chemically sensitized; and, said emulsion layer having a photographic color

sensitized; and, said emulsion layer having a photographic color coupler contiguous to said silver halide grains.

7. A photographic element comprising a support having coated thereon at least one light-sensitive photographic emulsion layer comprising converted-halide silver halide grains, the halide of said grains containing at least 80 mole percent bromide and up to 5 mole percent iodide, any remaining halide being chloride; the surface of said grains being chemically sensitized with at least one chemical sensitizer selected from the group consisting of a sulfur sensitizer, a noble metal sensitizer, a reduction sensitizer and a labile selenium sensitizer.

8. A photographic element comprising a support having coated thereon at least three superposed hydrophilic colloid layers containing light-sensitive silver halide grains, said layers being differentially sensitive to red, green and blue radiation, said layers having contiguous to the silver halide thereof, respectively, cyan, magenta and yellow dye-forming photographic color couplers; the silver halide grains in at least one of said silver halide emulsions comprising converted-halide silver halide grains, the halide of said grains containing at least 50 mole percent bromide and up to 10 mole percent iodide, any remaining halide being chloride, the surface of said converted-halide grains being chemically sensitized.

9. A photographic element comprising a support having coated thereon at least three superposed hydrophilic colloid layers containing light-sensitive silver halide grains, said layers being differentially sensitive to red, green and blue radiation, said layers having contiguous to the silver halide thereof, respectively, cyan, magenta and yellow dye-forming photographic color couplers; the silver halide grains in at least one of said silver halide emulsions comprising converted-halide silver halide grains, the halide of said grains containing at least 80 mole percent bromide and up to 5 mole percent iodide, any remaining halide being chloride, the surface of said converted-halide grains being chemically sensitized with a chemical sensitizer from the group consisting of a sulfur sensitizer, a noble metal sensitizer, a reduction sensitizer and a selenium sensitizer.

10. The photographic element as defined in claim 9 wherein said photographic color couplers are incorporated in the emulsion layers; said red-sensitive emulsion layer contains a phenolic cyan dye-forming photographic color coupler; said green-sensitive emulsion layer contains a 5-pyrazolone photographic color coupler; and, said blue-sensitive emulsion layer contains an open-chain ketomethylene photographic color coupler.

11. A photographic element comprising a support having coated thereon at least three superposed hydrophilic colloid layers containing light-sensitive silver halide grains, said layers being differentially sensitive to red, green and blue radiation, said layers having incorporated therein, respectively, cyan, magenta and yellow dye-forming photographic color couplers; the light-sensitive silver halide in each of said layers comprising converted-halide silver halide grains, the halide of said grains containing at least 50 mole percent bromide and up to 10 mole percent iodide, any remaining halide being chloride; and, the surface of said grains being chemically sensitized.

12. A photographic element comprising a support having coated thereon at least three superposed hydrophilic colloid layers containing light-sensitive silver halide grains, said layers being differentially sensitive to red, green and blue radiation, said layers having incorporated therein, respectively, cyan, magenta and yellow dye-forming photographic color couplers; the light-sensitive silver halide in each of said layers comprising converted-halide silver halide grains, the halide of said grains containing at least 80 mole percent bromide and up to 5 mole percent iodide, any remaining halide being chloride; and, the surface of said grains being chemically sensitized with at least one chemical sensitizer selected from the group consisting of a sulfur sensitizer, a noble metal sensitizer, a reduction sensitizer and a selenium sensitizer; said emulsion layers being arranged with the green-sensitive layer between the red- and blue-sensitive emulsion layers, and the blue-sensitive emulsion layer being closest to the support.

13. A photographic element as defined in claim 12 having a hydrophilic colloid layer containing an ultraviolet absorber between the green- and red-sensitive emulsion layers.

14. A photographic element comprising a paper support having coated thereon, in the order given:

a blue sensitive silver halide emulsion coated at a silver coverage of about 35 milligrams silver per square foot and about 155 milligrams gelatin per square foot, said layer containing about 35 milligrams per square foot of the cyan dye-forming coupler α -[4-(4-benzyloxy-phenylsulfonyl)-phenoxy]- α -pivalyl-2-chloro-5-[γ -(2,4-di-tert-amylphenoxy)butyramido]-acetanilide;

a gelatin interlayer;

a green-sensitive silver halide emulsion coated at about 35 milligrams silver per square foot and about 155 milligrams gelatin per square foot, said layer containing about 35 milligrams per square foot of the magenta dye-forming coupler 1-(2,4,6-trichlorophenyl)-3-[2-chloro-5(α -{4-hydroxy-3-tert.butylphenoxy} tetradecanoamido)-anilino]-5-pyrazolone;

a galatin interlayer containing about 65 mg. per square foot of the ultraviolet absorber 2-(2-hydroxy-3,5-di-tert-amylphenyl)benzotriazole;

a red-sensitive gelatin silver halide emulsion coated at about 35 milligrams silver per square foot and about 155 milligrams gelatin per square foot, said layer containing about 35 milligrams per square foot of the cyan dye-forming coupler 2-[α -(2,4-di-tert-amylphenoxy)butyramido]-4,6-dichloro-5-methylphenol; and, a gelatin overcoating; each of said emulsion layers consisting essentially of converted-halide silver halide grains, the halide of said grains containing about 10 mole percent chloride and about 90 mole percent bromide.

15. A process for providing color images in an exposed photographic element comprising a support having coated thereon a light-sensitive photographic emulsion comprising converted-halide silver halide grains, the halide of said grains containing at least 50 mole percent bromide and up to 10 mole percent iodide, any remaining halide being chloride; the surface of said grains being chemically sensitized; and, said silver halide grains having contiguous thereto a photographic color coupler; which comprises: developing said exposed photographic element with an aromatic primary amino color developing agent which reacts with said color coupler to form a dye.

16. A process for providing color images in an exposed photographic element comprising a support having coated thereon a light-sensitive photographic emulsion comprising converted-halide silver halide grains, the halide of said grains containing at least 80 mole percent bromide and up to 5 mole percent iodide, any remaining halide being chloride; the surface of said grains being chemically sensitized with a chemical sensitizer selected from the group consisting of a sulfur sensitizer, a noble metal sensitizer, a reduction sensitizer and a selenium sensitizer; and, said silver halide grains having contiguous thereto a photographic color coupler selected from the group consisting of a 5-pyrazolone, a phenolic and an open-chain ketomethylene photographic color coupler; which comprises:

developing said exposed photographic element with a *p*-phenylenediamine color developing agent which reacts

with said color coupler to form a dye; and, removing silver halide and silver image from said element.

17. A process for providing color images in an exposed photographic element comprising a support having coated thereon at least three superposed hydrophilic colloid layers containing light-sensitive silver halide grains, said layers being differentially sensitive to red, green and blue radiation, said layers having incorporated therein, respectively, cyan, magenta and yellow dye-forming photographic color couplers; the light-sensitive silver halide in each of said layers comprising converted-halide silver halide grains, the halide of said grains containing at least 50 mole percent bromide and up to 10 mole percent iodide, any remaining halide being chloride; and, the surface of said grains being chemically sensitized; which comprises:

developing said exposed photographic element with an aromatic primary amino color developing agent which reacts with said color coupler to form a dye; and, removing silver halide and silver image by fixing and bleaching.

18. A process for providing color images in an exposed photographic element comprising a support having coated thereon at least three superposed hydrophilic colloid layers containing light-sensitive silver halide grains, said layers being differentially sensitive to red, green and blue radiation, said layers having incorporated therein, respectively, cyan, magenta and yellow dye-forming photographic color couplers; the light-sensitive silver halide in each of said layers comprising converted-halide silver halide grains, the halide of said grains containing at least 80 mole percent bromide and up to 5 mole percent iodide, any remaining halide being chloride; and, the surface of said grains being chemically sensitized with at least one chemical sensitizer; selected from the group consisting of a sulfur sensitizer, a noble metal sensitizer, a reduction sensitizer and a selenium sensitizer; said emulsion layers being arranged with the green-sensitive layer between the red- and blue-sensitive emulsion layers, and the blue-sensitive emulsion layer being closest to the support; which comprises:

developing said exposed photographic element with an aromatic primary amino color developing agent which reacts with said color coupler to form a dye; and, removing silver halide and silver image from said element by fixing and bleaching.

19. A light-sensitive photographic emulsion as defined in claim 3 wherein said chemical sensitizer is selected from a sulfur sensitizer and a selenium sensitizer.

20. A light-sensitive photographic element as defined in claim 7 wherein said chemical sensitizer is selected from a sulfur sensitizer and a selenium sensitizer.

21. A light-sensitive photographic element as defined in claim 9 wherein said chemical sensitizer is selected from a sulfur sensitizer and a selenium sensitizer.

22. A light-sensitive photographic element as defined in claim 12 wherein said chemical sensitizer is selected from a sulfur sensitizer and a selenium sensitizer.

23. A process for providing color images as defined in claim 16 wherein said chemical sensitizer is selected from a sulfur sensitizer and a selenium sensitizer.

24. A process for providing color images as defined in claim 18 wherein said chemical sensitizer is selected from a sulfur sensitizer and a selenium sensitizer.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,622,318 Dated November 23, 1971

Inventor(s) Francis J. Evans

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

Column 2, line 1, "and" should read -- said --;
line 51, after "Useful" insert -- silver --; column 3,
line 26, "1,547,944" should read -- 1,574,944 --; line
45, after "issued" insert -- June --; column 4, line 31,
"2,046,129" should read --3,046,129 --; column 7, line
37, cancel "3,342,605;"; column 8, line 30, "as" should
read -- is --; line 47, "tert" should read -- tert --;
column 10, line 74, "tert" should read -- tert --; column
11, line 23, "Support-coated" should read -- Support--paper
coated --; column 13, line 60 "tert" should read -- tert --.

Signed and sealed this 12th day of December 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents