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(54) Internally doped high chloride silver halide emulsions, processes for their preparation and photographic elements.

(57) This disclosure relates to high chloride, silver halide developing out emulsions, their method of preparation and photographic elements having coated thereon such silver halide emulsions. The silver halide emulsions are characterized as having silver halide grains which are internally doped with cadmium, lead, zinc, copper or mixtures thereof in speed increasing concentrations up to 7 X 10^{-5} mole/mole/mole of silver halide.

In the figure are shown the relative speeds for cadmium (A) lead (B), copper (C) and zinc (D) doped emulsions.

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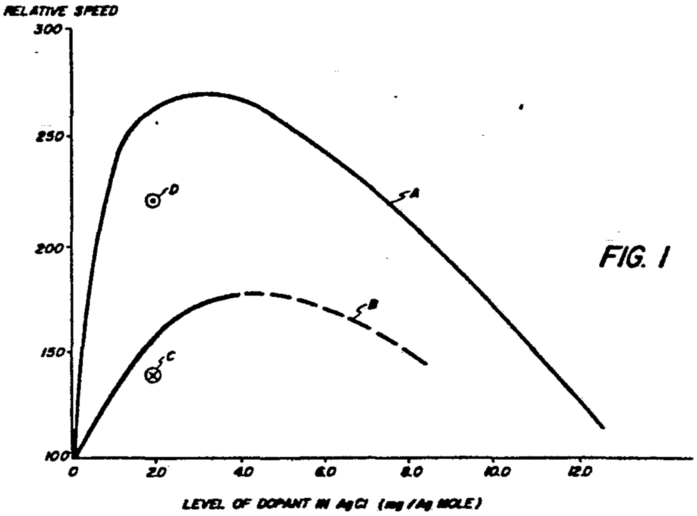

RELATIVE SPEED
300
250
200
150
100
0
2.0
4.0
6.0
8.0
10.0
12.0
LEVEL OF DOPANT IN AgCl (mg / Ag MOLE)
A
B
C
D

FIG. I

INTERNALLY DOPED HIGH CHLORIDE SILVER HALIDE EMULSIONS, PROCESSES FOR THEIR PREPARATION AND PHOTOGRAPHIC ELEMENTS

This invention is directed to improved photographic developing out high chloride silver halide emulsions, to methods of preparing such emulsions, and to photographic elements having coated thereon such emulsions.

There are many commercial photographic elements comprising radiation-sensitive silver halide emulsions of the developing out type. That is, the emulsions are rendered developable in areas where imagewise exposure to light occurs and are contacted with a developer solution to produce a visible image. Silver bromide and silver bromoiodide emulsions have been preferentially used for higher speed imaging applications.

As compared with silver bromide and silver bromoiodide, high chloride silver halide emulsions and photographic elements of the developing out type offer distinct advantages in a number of respects. For example, silver chloride possesses less native sensitivity in the visible region of the spectrum than silver bromide, thereby permitting yellow filter layers to be omitted from multicolor photographic elements. Further, high chloride silver halides are more soluble than silver bromide and silver bromoiodide, thereby permitting development to be achieved in shorter times. Unfortunately these advantages of high chloride silver halides have frequently not been realized in higher speed imaging applications, since the relatively higher speeds of silver bromide and silver bromoiodide have dictated their use.

There is thus a long standing problem in the art in providing high chloride silver halide emulsions of the developing out type of increased photographic speed.

In accordance with the invention, this problem is solved with silver halide emulsions of the developing out type comprised of silver halide grains which are at least 80 mole percent silver chloride and less than 5 mole percent silver iodide, based on total silver halide, characterized in that the silver halide grains are internally doped with cadmium, lead, copper, zinc or mixtures thereof in a speed increasing amount of up to 7 X 10^{-5} mole per mole of silver halide. More generally 2 X 10^{-6} to 7 X 10^{-5} mole per mole of silver halide of the metal dopant is utilized.

The emulsions of the invention can be prepared by reacting a water soluble silver salt with a water soluble halide salt in an aqueous medium containing a peptizer to form radiation-sensitive silver halide grains. The water soluble silver and halide salts are present in amounts so that silver halide grains are formed that are at least 80 mole percent silver chloride and less than 5 mole percent silver iodide. Water soluble salts of cadmium, lead, copper, zinc or mixtures thereof are introduced into the aqueous reaction medium during formation of silver halide grains in amounts up to 7 X 10^{-5} mole per mole of silver halide.

These novel emulsions can be coated on photographic supports in the usual manner to prepare photographic elements.

The high chloride silver halide emulsions of the invention containing low concentrations of divalent metal ion dopants as described above exhibit increased photographic speeds. Thus, such emulsions and photographic elements offer the art recognized advantages attributable to high chloride silver halide emulsions while achieving photographic speeds more commonly associated with silver bromide and silver bromoiodide photographic emulsions. The fact that the inclusion of low concentrations of divalent metal ions of the type identified above can increase photographic speeds of these emulsions and photographic elements is surprising in view of the teachings in the art that low concentration levels of divalent metal ion dopants have the effect of desensitizing silver halide emulsions of higher bromide concentration to visible light (e.g. U.S. Patent 2,950,972). By contrast, the sensitivity advantages of the emulsions and photographic elements of this invention can be realized under the exposure conditions of candid photography (that is, including low intensity and available light exposure conditions). Finally, the present improvement in sensitivity is a function of the halide content of the silver halide grains described herein.

The advantages and features of the present invention are further illustrated by reference to the following description directed to certain preferred embodiments considered in conjunction with the drawings, in which

Figure 1 is a plot of dopant level in mg per mole of silver versus relative speed and

Figures 2 and 3 are plots of percent increase in relative speed versus mole percent silver bromide and silver iodide, respectively.

The silver halide emulsions of the present invention are comprised of silver halide grains which are at least 80 mole percent silver chloride and less than 5 mole percent silver iodide, based on total silver halide. Preferably the silver halide grains consist essentially of silver chloride. Because the solubility product constant of silver chloride is orders of magnitude higher than that of silver bromide or silver iodide, it is recognized that formation, ripening or extended holding of silver chloride grains in the presence of bromide and/or iodide ions will result in the inclusion of silver bromide and/or silver iodide in the silver chloride grains. Desirably the silver halide grains are those which are at least 90 mole percent silver chloride. The remaining silver halide, if any, present in the silver halide grains can be silver bromide, silver iodide or some combination of the two. Silver bromide can be present in concentrations of up to 20 mole percent, preferably up to 15 mole percent, based on total silver halide. Silver iodide is preferably present in concentrations less than 2 mole percent, based on total silver halide. These silver halide grains are herein referred to as high chloride silver halide grains.

The high chloride silver halide grains contain a speed increasing amount of the metal dopant, cadmium, lead, copper, zinc or a combination of these elements in any proportion. While the metal dopants have the effect of increasing the sensitivity of surface chemically sensitized high chloride silver halide grains at concentrations up to 7×10^{-5} mole per mole of silver halide, if the concentration levels are extended upwardly, the effect is to desensitize the emulsions. Significant improvements in the sensitivity of surface chemically sensitized emulsions have been observed when the metal dopants are introduced in concentrations in the range of from 2×10^{-6} to 7×10^{-5} mole per mole of silver halide during formation of the high chloride silver halide grains.

While cadmium, lead, zinc and copper internal dopants produce qualitatively similar effects in increasing the speed of surface chemically sensitized high chloride to silver halide emulsions, these elements differ in the degree to which they are capable of sensitizing the emulsions. Cadmium produces emulsions of the highest attainable sensitivities followed in effectiveness by zinc, lead and copper in that order. To form emulsions of the highest attainable sensitivities it is preferred to employ cadmium, zinc or combinations of these elements in concentrations of from 3×10^{-6} to 6×10^{-5}, optimally 5×10^{-6} to 2.5×10^{-5}, mole per mole of silver halide during formation of the high chloride silver halide grains. For emulsion of the highest attainable sensitivities using lead, copper or combinations of these elements as dopants, it is preferred to provide concentrations in the range of from 3×10^{-6} to 5×10^{-5}, optimally from 8×10^{-6} to 2×10^{-5}, mole per mole of silver halide during formation of the high chloride silver halide grains.

Radiation-sensitive silver halide emulsions are conventionally formed by reacting a water soluble silver salt with one or more water soluble halide salts in an aqueous medium containing a peptizer. The choice and proportion of halide salts controls the halide content of the silver halide grains formed. The peptizer maintains the silver halide grains in dispersion. Where a metal dopant is intended to be introduced into the silver halide grains, it can be introduced in any convenient manner, typically separately or with one of the silver or halide salts or the peptizer, in the form of a salt which is water soluble in its contemplated concentration ranges. By regulating the compositions and rates of addition of halide and divalent metal salts, emulsions containing the internally doped high chloride silver halide grains of the invention can be produced by otherwise conventional techniques, such as the double and single jet precipitation techniques described in U.S. Patents 2,950,972 and 3,901,711, and in U.K. Patent 1,121,496.

In a preferred embodiment emulsions containing the internally doped high chloride silver halide grains of the invention can be formed by a double jet precipitation technique using accelerated flow rates to produce relatively monodispersed, cubic grains. As used herein, the term "monodispersed" indicates that at least 95 percent, by weight or by number, of the silver halide grains are within 40 percent of their mean effective diameter. In a specifically preferred form at least 95 percent, by weight or by number, of the silver halide grains are within 25 percent of the mean effective diameter, optimally within 10 percent of the mean effective diameter. The term "effective diameter" is herein employed as the diameter of the circle corresponding in area to the area subtended by a silver halide grain as viewed through a microscope or in a photomicrograph. The measurement of silver halide grain sizes is discussed further in Mees and James, The Theory of the Photographic Process, 3rd Ed., Macmillan, 1966, pp. 36-43.

In double jet precipitations a silver salt, such as silver nitrate, and a chloride salt, optionally employed in combination with a bromide and/or iodide salt, such as one or more chloride or other halide salts of an alkali or alkaline earth metal (e.g., sodium, potassium, magnesium or calcium), each in the form of an aqueous salt solution, are concurrently and separately introduced into the reaction vessel. An aqueous dispersing medium is present in the reaction vessel prior to the introduction of the aqueous halide and silver salt solutions. The presence of the dispersing medium along with agitation, in most instances, facilitates uniform blending of the aqueous halide and silver salt solutions while avoiding localized concentration gradients. Typically a dispersing medium volume is initially present in the reaction vessel which is from about 10 to 90 percent, preferably 20 to 80 percent, that of the silver halide emulsion to be formed. The dispersing medium is conventionally water or a dispersion of peptizer in water, optionally containing other ingredients, such as one or more silver halide ripening agents, more specifically described below. Preferably peptizer in a concentration of at least 10 percent, most preferably 20 percent, of the total weight of the vehicle present in the finished emulsion is initially present in the dispersing medium within the reaction vessel. Where the peptizer is not initially entirely present in the dispersing medium, the balance of the peptizer is preferably added during addition of the silver and halide salts. A minor portion of one of the silver or halide salt solutions, typically less than about 10 percent, is also initially present in the reaction vessel to adjust the pAg (log reciprocal silver ion concentration) of the reaction vessel contents at the outset of silver halide precipitation.

During the initial introduction of the aqueous silver and halide salt solutions into the reaction vessel the dissolved silver salt reacts with dissolved halide salt to form silver halide crystals. This initial phase of silver halide emulsion formation in which new silver halide crystals are being formed is referred to as nucleation. During subsequent addition of silver and halide salts, additional silver halide formed as a reaction product can be precipitated onto these nuclei, causing the mean size of the silver halide to increase and ultimately resulting in silver halide grains of the desired mean effective diameter.

Although additional silver halide grain formation can occur after the initial formation of silver halide nuclei, by controlling the rate of addition of silver and halide salts continued silver halide precipitation onto the originally formed silver halide nuclei can be achieved. This has the effect of producing a population of silver halide grains of similar size--i.e., monodispersed silver halide emulsions. Techniques are known in the art which achieve shortened silver halide precipitation times by permitting accelerated rates of addition of silver and halide salts. Such techniques are disclosed, for example, in German OLS 2,107,118 and U.S. Patent 3,672,900.

Single jet silver halide grain precipitation is specifically contemplated as an alternative to double jet precipitation. In single jet precipitation substantially the entire halide salt solution is present in the reaction vessel prior to introduction of the silver salt solution. The silver halide grains which are formed are polydispersed--this is, they vary significantly in size and do not satisfy the grain size distribution requirements set forth above for monodispersed silver halide emulsions. Except for these differences, the preferred aspects of double jet silver halide precipitation techniques described above are also applicable to single jet precipitation techniques.

In both the single jet and double jet precipitation techniques the metal dopant salts, typically metal halides, can be introduced into the reaction vessel after silver halide grain nuclei have been formed and before introduction of at least 85 percent, most preferably 75 percent, of the silver salt solution has been completed. The divalent metal salts are preferably dissolved in water or other suitable solvent prior to addition to the reaction vessel. The solution containing the divalent metal salt typically comprises from about 1 to 10 percent by weight of the dispersing medium of the emulsion, the proportions being merely a matter of choice and convenience.

The individual reactants can be added to the reaction vessel through surface or sub-surface delivery tubes by gravity feed or by delivery apparatus for maintaining control of the rate of delivery and the pH and/or pAg of the reaction vessel contents, as illustrated by U.S. Patents 3,821,002 and 3,031,304, and Claes et al, Photographische Korrespondenz, 102 Band, Number 10, 1967, p. 162. In order to obtain rapid distribution of the reactants within the reaction vessel, specially contructed mixing devices can be employed, as illustrated by U.S. Patents 2,996,287; 3,342,605; 3,415,650 and 3,785,777; German OLS 2,556,885 and German OLS 2,555,364. An enclosed reaction vessel can be employed to receive the mix reactants upstream of the main reaction vessel, as illustrated by U.S. Patents 3,897,935 and 3,790,386.

The initially formed silver halide grains (i.e., silver halide nuclei) are sufficiently small that they can be dispersed by water alone. Thus, it is unnecessary to have any peptizer initially in the reaction vessel, although it is frequently convenient to have the peptizer at least partially present in the reaction vessel prior to initiating introduction of the silver and halide salts. Peptizer can be added to the reaction vessel with the halide salt, the silver salt or both and/or independently of both. While peptizer concentrations from 0.2 to about 10 percent by weight, based on the total liquid or emulsion weight in the reaction vessel, can be employed, it is preferred to keep the concentration of the peptizer in the reaction vessel prior to and during silver halide formation below about 6 percent by weight, based on the total weight. It is common practice to maintain the concentration of the peptizer in the reaction vessel in the range of from about 2 to 6 percent, based on the total weight, prior to and during silver halide formation and to adjust the emulsion vehicle concentration upwardly for optimum coating characteristics by delayed, supplemental vehicle additions. It is contemplated that the emulsion as initially formed will contain from about 5 to 50 grams of peptizer per mole of silver halide, preferably about 10 to 30 grams of peptizer per mole of silver halide. Additional vehicle can be added later to bring the concentration up to as high as 300 grams per mole of silver halide. Preferably the concentration of vehicle in the finished emulsion is below 50 grams per mole of silver halide. When coated and dried in forming a photographic element the vehicle preferably forms about 30 to 70 percent by weight of the emulsion layer.

Vehicles (which include both binders and peptizers) can be chosen from among those conventionally employed in silver halide emulsions. Preferred peptizers are hydrophilic colloids, which can be employed alone or in combination with hydrophobic materials. Suitable hydrophilic materials include both naturally occurring substances such as proteins, protein derivatives, cellulose derivatives--e.g., cellulose esters, gelatin --e.g., alkali-treated gelatin (cattle bone or hide gelatin) or acid-treated gelatin (pigskin gelatin), gelatin derivatives--e.g., acetylated gelatin, phthalated gelatin and the like, polysaccharides such as dextran, gum arabic, zein, casein, pectin, collagen derivatives, collodion, agar-agar, arrowroot, albumin and the like.

Other materials commonly employed in combination with hydrophilic colloid peptizers as vehicles including vehicle extenders--e.g., materials in the form of latices include synthetic polymeric peptizers, carriers and/or binders such as poly(vinyl lactams), acrylamide polymers, polyvinyl alcohol and its derivatives, polyvinyl acetals, polymers of alkyl and sulfoalkyl acrylates and methacrylates, hydrolyzed polyvinyl acetates, polyamides, polyvinyl pyridine, acrylic acid polymers, maleic anhydride copolymers, polyalkylene oxides, methacrylamide copolymers, polyvinyl oxazolidinones, maleic acid copolymers, vinylamine copolymers, methacrylic acid copolymers, acryloyloxyalkylsulfonic acid copolymers, sulfoalkylacrylamide copolymers, polyalkyleneimine copolymers, polyamines, N,N-dialkylaminoalkyl acrylates, vinyl imidazole copolymers, vinyl sulfide copolymers, halogenated styrene polymers, amine-acrylamide polymers, polypeptides and the like. These additional materials need not be present in the reaction vessel during silver halide precipitation, but rather are conventionally added to the emulsion prior to coating. The vehicle materials, including particularly the hydrophilic colloids, as well as the hydrophobic materials useful in combination therewith can be employed not only in the emulsion layers of the photographic elements of this invention, but also in other layers, such as overcoat layers, interlayers and layers positioned beneath the emulsion layers.

It is preferred that a silver halide ripening agent be present within the reaction vessel during silver halide formation. The ripening agent can be entirely contained within the dispersing medium in the reaction vessel before silver and halide salt addition, or it can be introduced into the reaction vessel along with one or more of the halide salt, silver salt or peptizer. The ripening agent can also be introduced independently during halide and silver salt additions.

Sulfur containing ripening agents are generally preferred. Conventional thioether ripening agents, such as those disclosed in U.S. Patent 3,271,157, can be employed. Sufficient thioether ripening agent is employed to provide concentrations of from 0.05 to 50 grams, preferably about 0.1 to 20 grams, per mole of silver halide, based on the weight of silver.

Certain of the preferred organic thioether silver halide solvents can be represented by the formulas:

$$Q\text{-}[(CH_2)_r\text{-}CH_2\text{-}S\text{-}(CH_2)_2\text{-}X\text{-}(R)_p\text{-}(CH_2)_2\text{-}(R')_q\text{-}S\text{-}CH_2(CH_2)_m\text{-}Z]_n$$

and

$$Q\text{-}(CH_2)_m\text{-}(CH_2\text{-}S\text{-}(CH_2)_n\text{-}S\text{-}CH_2(CH_2)_r\text{-}Z$$

wherein: r and m are integers of 0 to 4; n is an integer of 1 to 4; p and q are integers of 0 to 3; X is an oxygen atom (-o-), a sulfur atom (-S-), a carbamyl radical $(\text{-}\overset{O}{\overset{\|}{C}}NH\text{-})$, a carbonyl radical $(\text{-}\overset{O}{\overset{\|}{C}}\text{-})$ or a carboxyl radical $(\text{-}\overset{O}{\overset{\|}{C}}OH)$; R and R' are ethylene oxide radicals $(\text{-}O\text{-}CH_2CH_2\text{-})$; Q and Z are hydroxy radicals (-OH), carboxy radicals, or alkoxy radicals (-O-alkyl) wherein the alkyl group has 1 to 5 carbon atoms; and Q and Z can also be substituents described for X linked to form a cyclic compound.

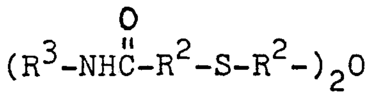
Preferred organic thioether silver halide ripening agents suitable for forming the emulsions of the invention include compounds represented by the formulas:

$HO(\text{-}R^2\text{-}S\text{-})_rR^2OH,$

$(HO\text{-}R^2\text{-}S\text{-}R^2\text{-}O\text{-}R^4)_2,$

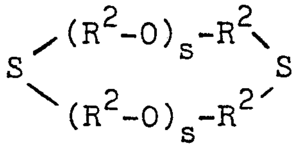
$R^3\text{-}O\text{-}R^2\text{-}S\text{-}R^2\text{-}CNH\text{-}R^4\text{-})_2,$

$(R^3\text{-}O\text{-}R^2\text{-}S\text{-}R^2\text{-})_2S,$



$$(R^3\text{-NH}\overset{O}{\overset{\|}{C}}\text{-}R^2\text{-S-}R^2\text{-})_2O$$

and



wherein: r is an integer of 1 to 3; s is an integer of 1 to 2; R^2 is an alkylene radical having 1 to 5 carbon atoms and is preferably ethylene (CH_2CH_2-); R^3 is an alkyl radical having 1 to 5 carbon atoms and is preferably ethyl; and R^4 is an alkylene radical having 1 to 5 carbon atoms and is preferably methylene (-CH_2-).

As an alternative to thioether ripening agents, thiocyanate salts can be used, such as alkali metal, most commonly potassium, and ammonium thiocyanate salts. While any conventional quantity of the thiocyanate salts can be introduced, preferred concentrations are generally from about 0.1 to 20 grams of thiocyanate salt per mole of silver halide, based on the weight of silver.

The emulsions of the invention containing high chloride silver halide grains are preferably washed or otherwise processed to remove soluble salts. The soluble salts can be removed by chill setting and leaching, by coagulation washing, by centrifugation and decantation of a coagulated emulsion, by employing hydrocyclones alone or in combination with centrifuges, by diafiltration with a semipermeable membrane, or by employing an ion exchange resin.

In order to achieve the optimum sensitivity of this invention it is preferred that the internally doped high chloride silver halide grains be surface chemically sensitized. The high chloride silver halide grains can be surface chemically sensitized with active gelatin, as illustrated by T. H. James, The Theory of the Photographic Process, 4th Ed., Macmillan, 1977, pp. 67-76, or with sulfur, selenium, tellurium, platinum, palladium, iridium, osmium, rhenium or phosphorus sensitizers or combinations of these sensitizers, such as at pAg levels of from 5 to 10, pH levels of from 5 to 8 and temperatures of from 30 to 80°C, as illustrated by Research Disclosure, Vol. 120, April 1974, Item 12008, Research Disclosure, Vol. 134, June 1975, Item 13452, U.S. Patents 1,623,499; 2,399,083; 2,642,361; 3,297,447; 3,297,446; 1,315,755; 3,772,031; 3,761,267; 3,857,711; 3,565,633; 3,901,714 and 3,904,415. The emulsions can also be reduction sensitized--e.g., with hydrogen, as illustrated by U.S. Patents 3,891,446 and 3,984,249, by low pAg (e.g., less than 5) high pH (e.g., greater than 8) treatment or through the use of reducing agents, such as stannous chloride, thiourea dioxide, polyamines and amineboranes, as illustrated by U.S. Patent 2,983,609, Research Disclosure, Vol. 136, August 1975, Item 13654, U.S. Patents 2,518,698; 2,743,182; 3,026,203 and 3,361,564.

In a preferred form of the invention the internally doped high chloride silver halide grains are surface chemically sensitized with gold sensitizers employed alone or in combination with other conventional chemical sensitizers. The internally doped high chloride silver halide grains can be surface gold sensitized with one or a combination of conventional gold sensitizers. Illustrative gold sensitizers include gold hydroxide, gold chloride, potassium aurate, potassium auriaurite, potassium auricyanide, potassium aurithiocyanate, gold sulfide, gold selenide, gold silver sulfide, gold iodide, potassium chloroaurate, ethylenediamine-bis-gold chloride and various organic gold sensitizers, as more fully described by U.S. Patents 2,642,361 and 3,297,447.

Depending upon the photographic application, emulsions containing the high chloride silver halide grains can contain other components of a conventional nature. For example, it is specifically contemplated to blend the high chloride silver halide emulsions of the invention with other silver halide emulsions. Blending of silver halide emulsions is commonly undertaken to optimize characteristic curve shapes--e.g., adjust contrast, extended exposure latitude, increase maximum density and to achieve other, similar curve modifications. Blends of surface-sensitive emulsions and internally fogged, internal image-forming emulsions can be employed, as illustrated by U.S. Patents 2,996,382; 3,397,987; 3,705,858 and 3,694,881, Research Disclosure, Vol. 134, June 1975, Item 13452, U.S. Patent Office Defensive Publication T-904017, April 21, 1972 and Research Disclosure, Vol. 122, June 1974, Item 12233. In a specifically preferred form the major portion, preferably essentially all, of the silver halide grains present in a silver halide emulsion or silver halide emulsion layer are internally doped high chloride silver halide grains substantially as described above.

The silver halide emulsion of the invention can be spectrally sensitized with dyes from a variety of classes, including the polymethine dye class, which includes the cyanines, merocyanines, complex cyanines and merocyanines (i.e., tri-,tetra- and poly-nuclear cyanines and merocyanines), oxonols, hemioxonols, styryls, merostyryls and streptocyanines.

The cyanine spectral sensitizing dyes include, joined by a methine linkage, two basic heterocyclic nuclei, such as those derived from quinolinium, pyridinium, isoquinolinium, 3H-indolium, benz[e]-indolium, oxazolium, thiazolium, selenazolinium, imidazolium, benzothiazolium, benzoselenazolium, benzimidazolium, naphthoxazolium, naphthothiazolium, naphthoselenazolium, thiazolinium dihydronaphthothiazolium, pyrylium and imidazopyrazinium quaternary salts.

The merocyanine spectral sensitizing dyes include, joined by a methine linkage, a basic heterocyclic nucleus of the cyanine dye type and an acidic nucleus, such as can be derived from barbituric acid, 2-thiobarbituric acid, rhodanine, hydantoin, 2-thiohydantoin, 4-thiohyantoin, 2-pyrazolin-5-one, 2-isoxazolin-5-one, indan-1,3-dione, cyclohexan-1,3-dione, 1,3-dioxan-4,6-dione, pyrazolin-3,5-dione, pentan-2,4-dione, alkylsulfonyl acetonitrile, malononitrile, isoquinolin-4-one, and chroman-2,4-dione.

One or more spectral sensitizing dyes can be used. Dyes with sensitizing maxima at wavelengths throughout the visible spectrum and with a great variety of spectral sensitivity curve shapes are known. The choice and relative proportions of dyes depends upon the region of the spectrum to which sensitivity is desired and upon the shape of the spectral sensitivity curve desired. Dyes with overlapping spectral sensitivity curves will often yield in combination a curve in which the sensitivity at each wavelength in the area of overlap is approximately equal to the sum of the sensitivities of the individual dyes. Thus, it is possible to use combinations of dyes with different maxima to achieve a spectral sensitivity curve with a maximum intermediate to the sensitizing maxima of the individual dyes.

Combinations of spectral sensitizing dyes can be used which result in supersensitization--that is, spectral sensitization that is greater in some spectral region than that from any concentration of one of the dyes alone or that which would result from the additive effect of the dyes. Supersensitization can be achieved with selected combinations of spectra sensitizing dyes and other addenda, such as stabilizers and antifoggants, development accelerators or inhibitors, coating aids, brighteners and antistatic agents. Any one of several mechanisms as well as compounds which can be responsible for supersensitization are discussed by Gilman, Photographic Science and Engineering, Vol. 18, 1974, pp. 418-430.

Spectral sensitizing dyes also affect the emulsions in other ways. For example, many spectral sensitizing dyes either reduce (desensitize) or increase photographic speed within the spectral region of inherent sensitivity. Spectral sensitizing dyes can also function as antifoggants or stabilizers, development accelerators or inhibitors, reducing or nucleating agents, and halogen acceptors or electron acceptors, as disclosed in U.S. Patents 2,131,038; 3,501,310; 3,630,749; 3,718,470 and 3,930,860.

Sensitizing action can be correlated to the position of molecular energy levels of a dye with respect to ground state and conduction band energy levels of the silver halide crystals. These energy levels can in turn be correlated to polarographic oxidation and reduction potentials, as discussed in Photographic Science and Engineering, Vol. 18, 1974, pp. 49-53 (Sturmer et al), pp. 175-178 (Leubner) and pp. 475-485 (Gilman). Oxidation and reduction potentials can be measured as described by R. J. Cox, Photographic Sensitivity, Academic Press, 1973, Chapter 15.

The chemistry of cyanine and related dyes is illustrated by Weissberger and Taylor, Special Topics of Heterocyclic Chemistry, John Wiley and Sons, New York, 1977, Chapter VIII; Venkataraman, The Chemistry of Synthetic Dyes, Academic Press, New York, 1971, Chapter V; James, The Theory of the Photographic Process, 4th Ed., Macmillan, 1977, Chapter 8, and F. M. Hamer, Cyanine Dyes and Related Compounds, John Wiley and Sons, 1964.

Among useful spectral sensitizing dyes for sensitizing silver halide emulsions are those found in U.K. Patent 742,112; U.S. Patents 1,846,300; 1,846,300-4; 2,089,729, 2,165,338; 2,213,238; 2,493,747; 2,493,748; 2,526,632; 2,739,964, (Reissue 24,292); 2,778,823; 2,917,516; 3,352,857; 3,411,916; 3,431,111; 2,503,776; 3,282,933; 3,660,102; 3,660,103; 3,335,010; 3,352,680; 3,384;486; 3,397,981; 3,482,978; 3,623,881; 3,718,470 and 4,025,349. Examples of useful supersensitizing dye combinations, of non-light absorbing addenda which function as supersensitizers or of useful dye combinations are found in U.S. Patents 2,933,390; 2,937,089; 3,506,443 and 3,672,898.

Instability which increases minimum density in negative type emulsion coatings (i.e., fog) can be protected against by incorporation of stabilizers, antifoggants, antikinking agents, latent image stabilizers and similar addenda in the emulsion and contiguous layers prior to coating. Most of the antifoggants which are effective in emulsions can also be used in developers and can be classified under a few general headings, as illustrated by C.E.K. Mees, The Theory of the Photographic Process, 2nd Ed., Macmillan, 1954, pp. 677-680.

The photographic elements prepared with the emulsions of the invention can be color photographic elements which form dye images through the selective destruction, formation or physical removal of dyes.

The photographic elements can produce dye images through the selective destruction of dyes or dye precursors, such as silver-dye-bleach processes.

The photographic elements can produce dye images through the selective formation of dyes, such as by reacting aromatic amine in its oxidized form with a dye-forming coupler. The dye-forming couplers can be incorporated in the photographic elements.

In one form the dye-forming couplers are chosen to form subtractive primary (i.e., yellow, magenta and cyan) image dyes and are nondiffusible, colorless couplers, such as two and four equivalent couplers of the open chain ketomethylene, pyrazolone, pyrazolotriazole, pyrazolobenzimidazole, phenol and naphthol type hydrophobically ballasted for incorporation in high-boiling organic (coupler) solvents.

The dye-forming couplers upon coupling can release photographically useful fragments, such as development inhibitors or accelerators, bleach accelerators, developing agents, silver halide solvents, toners, hardeners, fogging agents, antifoggants, competing couplers, chemical or spectral sensitizers and desensitizers.

The sensitizing dyes and other addenda incorporated into the layers of the photographic elements can be dissolved and added prior to coating either from water or organic solvent solutions, depending upon the solubility of the addenda. Ultrasound can be employed to dissolve addenda. Semipermeable and ion exchange membranes can be used to introduce addenda, such as water soluble ions (e.g., chemical sensitizers). Hydrophobic addenda, particularly those which need not be absorbed to the silver halide grain surfaces to be effective, such as couplers, redox dye-releasers and the like, can be mechanically dispersed directly, or in high boiling (coupler) solvents, or the hydrophobic addenda can be loaded into latices and dispersed, as illustrated by Chen <u>Research Disclosure</u>, Vol. 159, July 1977, Item 15930.

In forming photographic elements the layers can be applied to photographic supports by various procedures, including immersion or dip coating, roller coating, reverse roll coating, air knife coating, doctor blade coating, gravure coating, spray coating, extrusion coating, bead coating, stretch-flow coating and curtain coating.

The layers of the photographic elements can be coated on a variety of conventional photographic supports. Typical photographic supports include polymeric film such as cellulose acetate and poly(ethylene terephthalate), wood fiber--e.g., paper, polyolefin-coated paper, metallic sheet and foil, glass and ceramic supporting elements provided with one or more subbing layers to enhance the adhesive, antistatic, dimensional, abrasive, hardness, frictional, antihalation and/or other properties of the support surface.

Photographic elements containing silver halide emulsions of this invention show particularly advantageous sensitivities when exposed to light. The photographic elements are specifically contemplated for imagewise exposure under ordinary lighting conditions--that is, less than high intensity lighting conditions. Exposures can be monochromatic, orthochormatic or panchromatic. Imagewise exposures at ambient, elevated or reduced temperatures and/or pressures, continuous or intermittent exposures, exposure times ranging from minutes to relatively short durations in the millisecond to microsecond range and solarizing exposures, can be employed within the useful response ranges determined by conventional sensitometric techniques, as illustrated by T. H. James, The Theory of the Photographic Process, 4th Ed., Macmillan, 1977, Chapters 4, 6, 17, 18 and 23.

Upon imagewise exposure the high chloride silver halide grains form latent image sites at or near their surface, both in their primitive state and after surface chemical sensitization, unless the emulsions as described above are otherwise modified. Accordingly the emulsions can be processed in all conventional silver halide developers--including those containing sufficient silver halide solvent to reveal internal latent image sites, referred to in the art as surface and sub-surface developers, and those containing higher levels of silver halide solvents, referred to in the art as internal developers. It is accordingly apparent that the emulsions of the invention are useful for photographic applications requiring negative-working silver halide emulsions and photographic elements.

The light-sensitive silver halide contained in the photographic elements can be processed following exposure to form a visible image by associating the silver halide with an aqueous alkaline medium in the presence of a developing agent contained in the medium or the element. Processing formulations and techniques are described in L. F. Mason, Photographic Processing Chemistry, Focal Press, London, 1966; Processing Chemicals and Formulas, Publication J-1, Eastman Kodak Company, 1973; Photo-Lab Index, Morgan and Morgan, Inc., Dobbs Ferry, New York, 1977, and Neblette's Handbook of Photography and Reprography - Materials, Processes and Systems, VanNostrand Reinhold Company, 7th Ed., 1977.

The photographic elements can be processed to form dye images which correspond to or are reversals of the silver halide rendered selectively developable by imagewise exposure.

Multicolor reversal dye images can be formed in photographic elements having differentially spectrally sensitized silver halide layers by black-and-white development followed by i) where the elements lack incorporated dye image formers, sequential reversal color development with developers containing dye image formers, such as color couplers, as illustrated by U.S. Patents 2,252,718; 2,950,970 and 3,547,650; ii) where the elements contain incorporated dye image formers, such as color couplers, a single color development step, as illustrated by the Kodak Ektachrome E4 and E6 and Agfa processes described in British Journal of Photography Annual, 1977, pp. 194-197, and British Journal of Photography, August 2, 1974, pp. 668-669; and iii) where the photographic elements contain bleachable dyes, silver-dye-bleach processing, as illustrated by the Cibachrome P-10 and P-18 processes described in the British Journal of Photography Annual, 1977, pp. 209-212.

The photographic elements can be adapted for direct color reversal processing (i.e., production of reversal color images without prior black-and-white development), as illustrated by U.S. Patents 3,243,294, 3,647,452; 3,457,077 and 3,467,520; U.K. Patents 1,075,385 and 1,132,736; German Patents 1,259,700; and 1,257,570; 1,259,701 and German OLS 2,005,091.

Multicolor dye images which correspond to the silver halide rendered selectively developable by imagewise exposure, typically negative dye images, can be produced by processing, as illustrated by the Kodacolor C-22, the Kodak Flexicolor C-41 and the Agfacolor processes described in British Journal of Photography Annual, 1977, pp. 201-205. The photographic elements can also be processed by the Kodak Ektaprint-3 and-300 processes as described in Kodak Color Dataguide, 5th Ed., 1975, pp. 18-19, and the Agfa color process as described in British Journal of Photography Annual, 1977, pp. 205-206, such process being particularly suited to processing color print materials, such as resin-coated photographic papers, to form positive dye images.

The photographic elements can be processed in the presence of reducible species, such as transition metal ion complexes (e.g. cobalt(III) and ruthenium (III) complexes containing amine and/or amine ligands) and peroxy compounds (e.g. hydrogen peroxide and alkali metal perborates and percarbonates).

Dye images can be formed or amplified by processes which employ in combination with a dye-image-generating reducing agent an inert transition metal ion complex oxidizing agent, as illustrated by U.S. Patents 3,748,138; 3,826,652; 3,862,842; 3,989,526 and 3,765,891; and/or a peroxide oxidizing agent, as illustrated by U.S. Patent 3,674,490, Research Disclosure, Vol. 116, December 1973, Item 11660, and Research Disclosure, Vol. 148, August 1976, Items 14836, 14846 and 14847. The photographic elements can be particularly adapted to form dye images by such processes, as illustrated by U.S. Patents 3,822,129; 3,834,907; 3,902,905; 3,847,619 and 3,904,413.

The presence of transition metal ion complexes can accelerate silver halide development, as illustrated by U.S. Patents 3,748,138; 3,901,712 and 3,964,912; can bleach silver images, as illustratedby U.S. Patent 3,923,511; and can be employed to form tanned colloid images, as illustrated by U.S. Patents 3,856,524 and 3,862,855.

The peroxide oxidizing agents can be employed to form vesicular images, as illustrated by U.S. Patents 3,615,491; 3,765,890; and 3,776,730; U.K. Patents 1,329,444 and 1,332,693, Liebe et al and German OLS 2,420,521.

The emulsion and photographic elements of this invention can form a part of an otherwise conventional image transfer system. Image transfer systems include colloid transfer systems, as illustrated by U.S. Patents 2,596,756 and 2,716,059; silver salt diffusion transfer systems, as illustrated by U.S. Patents 2,352,014; 2,543,181; 3,020,155 and 2,861,885; imbibition transfer systems, as illustrated by U.S. Patent 2,882,156, and color image transfer systems, as illustrated by Research Disclosure, Vol. 151, November 1976, Item 15162, and Vol. 123, July 1974, Item 12331.

Color image transfer systems (including emulsion layers, receiving layers, timing layers, acid layers, processing compositions, supports and cover sheets) and the images they produce can be varied by choosing among a variety of features, combinations of which can be used together as desired.

Film units can be chosen which are either integrally laminated or separated during exposure, processing and/or viewing, as illustrated by Canadian Patent 674,082; U.S. Patents 2,983,606; 3,445,228; 3,309,201; 2,543,181; 3,053,659; 3,415,644; 3,415,645 and 3,415,646; and U.K. Patent 1,330,524.

Positive-working chemistry can be chosen utilizing initially mobile dyes which are immobilized by development, as illustrated by U.S. Patents 2,983,606; 2,756,142; 3,880,658; 3,854,945 and 3,839,035, or initially immobile dyes which are rendered mobile by development, as illustrated by U.K. Patent 1,464,104 and U.S. Patent 3,980,479; or negative-working imaging chemistry can be chosen utilizing the release of diffusible dyes from an immobile image dye-forming compound (e.g., a redox dye-releaser) as a function of development, as illustrated by Belgian Patent 838,062, Canadian Patent 602,607 and U.S. Patents 3,227,550;

3,443,940; 3,628,952; 3,844,785; 3,698,897; 3,725,062; 3,728,113; 4,053,312 and 4,076,529; U.K. Patent 1,489,695; German OLS 2,729,820 and Research Disclosure, Vol. 151, November 1976, Item 15157.

An image to be viewed can be transferred from the image-forming layers. A retained image can be formed for viewing as a concurrently formed complement of the transferred image. Positive transferred images and useful negative retained images can be formed when one of the imaging chemistry and the emulsion is negative-working and the other positive-working; and negative transferred images and positive retained images can be formed when both the imaging chemistry and the emulsion(s) are negative-working or positive-working. Images retained in and transferred from the image-forming layers are illustrated by U.K. Patent 1,456,413; U.S. Patents 2,543,691; 3,443,940; 3,923,510 and 4,076,529.

In addition to the silver halide emulsion and photographic element features indicated above, it is appreciated that other conventional features requiring no detailed description can also be present. For example, the photographic elements can contain brighteners, absorbing and scattering materials, hardeners, coating aids, plasticizers and lubricants, antistatic layers, matting agents, developing agents and development modifiers as described in Paragraphs V, VIII, X, Xl, XII, XIII, XVI, XX and XXI, of Research Disclosure, Vol. 176, December 1978, Item 17643. Still other conventional photographic features and applications not inconsistent with this invention will be readily apparent to those skilled in the art.

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In a specific preferred form the photographic elements of this invention are intended to produce multicolor images which can be viewed in the elements or in a receiver when the elements form a part of a multicolor image transfer system. For multicolor imaging at least three superimposed color-forming layer units are coated on a support. Each of the layer units is comprised of at least one silver halide emulsion layer. At least one of the silver halide emulsion layers, preferably at least one of the silver halide emulsion layers in each color forming layer unit and most preferably each of the silver halide emulsion layers, contain an emulsion according to this invention as described herein. The emulsion layers of one of the layer units are primarily responsive to the blue region of the spectrum, the emulsion layers of a second of the layer units are primarily responsive to the green region of the spectrum, and the emulsion layers of a third of the layer units are primarily responsive to the red region of the spectrum. Since the high chloride silver halide emulsion exhibit only limited native sensitivity to the visible portion of the spectrum, the use of yellow filter dyes between adjacent layer units can be omitted in many instances and the layer units can be coated in any desired order. The layer units each contain in the emulsion layers or in adjacent hydrophilic colloid layers at least one image dye providing compound. Incorporated dye-forming couplers and redox dye-releasers constitute exemplary preferred image dye providing means. The blue, green and red responsive layer units preferably contain yellow, magenta and cyan image dye providing means, respectively.

The invention is further illustrated by the following examples.

Example 1

1A. A polydisperse silver chloride emulsion, mean grain size about 0.45 μm, was prepared in the following manner:

Two solutions were prepared as follows:

Solution 1

(Placed in the Reaction Vessel)

Gelatin	100 g
Distilled Water	7000 ml
Sodium Chloride	425 g

Dissolve at 40°C

Adjust pH to 3.0 with HNO_3

Solution 2

Silver Nitrate	850 g
Distilled Water to total volume	2900 ml

Dissolve at 40°C

Adjust pH to 3.0 with HNO_3

To solution 1 were added 1.7 mg of a fog inhibiting agent of the type described in U.S. Patent 2,728,663. Solution 2 was then added to the reaction vessel, at a constant flow rate, over a 40 minute period, with continuous agitation. Following precipitation the pH was adjusted to 4.5, a pH coaguable gelatin derivative was added to the emulsion, and the emulsion, was washed using the procedure described in Example 3 of U.S. Patent 2,614,929.

1B. A cadmium doped polydisperse silver chloride emulsion, mean grain size about 0.45 μm, was prepared as described above, except that 10 mg of cadmium chloride (1.1×10^{-5} mole/Ag mole) were added to the reaction vessel 5 minutes after the start of the precipitation.

The polydisperse silver chloride emulsions prepared as described above were coated, unsensitized and optimally gold sensitized, on a cellulose acetate film support at coverages of 6.90 g gelatin and 4.65 g Ag/m^2. The coated elements were then exposed through a graduated density step wedge, developed for 5 minutes in Kodak Developer DK-50, fixed, washed and dried. The sensitometric results are set forth below in Table II.

TABLE II

Cadmium Internal Dopant	Gold Sensitized	Relative Speed
No	No	100
Yes	No	132
No	Yes	355
Yes	Yes	501

From Table II it can be seen that the inclusion of cadmium as a dopant in a polydisperse silver chloride emulsion unexpectedly results in an increase in speed of the emulsion compared to an emulsion similarly prepared but lacking a cadmium dopant.

Example 2

2A. A monodisperse silver chloride emulsion (1.5 µm) was prepared in the following manner:

Three solutions were prepared as follows:

Solution 1

(Placed in the Reaction Vessel)

Gelatin	100 g
Distilled water	7000 ml

Dissolve at 40°C

Adjust pH to 2.0

Solution 2

Sodium Chloride	425 g
Distilled Water to total volume	2900 ml

Dissolve at 40°C

Solution 3

Silver Nitrate	850 g
Distilled Water to total volume	2900 ml

Dissolve at 40°C

To solution 1 were added 2.5 g of a silver halide ripening agent of the type described in U.S. Patent 3,271,157. The pAg of solution 1 was then adjusted to 8.0 using solution 2. Solutions 2 and 3 were them simultaneously run into solution 1 over a 40 minute period using an accelerated flow technique, maintaining the pAg at 8.0. Following precipitation the pH was raised to 5.5, a pH coaguable gelatin derivative was added to the emulsion, and the emulsion was washed using the procedure described in Example 3 of U.S. Patent 2,614,929.

2B. A cadmium doped monodisperse silver chloride emulsion (1.5 µm) was prepared as described above (A), except that 10 mg of cadmium chloride (1.1×10^{-5} mole/Ag mole) were added to the reaction vessel prior to the start of the precipitation.

The monodisperse silver chloride emulsions prepared as described above (A and B) were optimally gold sensitized and coated and tested as described in Example 1. The sensitometric results are set forth below in Table III.

TABLE III

Cadmium Internal Dopant	Relative Speed
No	100
Yes	162

From Table III it can be seen that the inclusion of cadmium as a dopant in a monodisperse silver chloride emulsion unexpectedly results in an increase in speed of the emulsion compared to an emulsion similarly prepared but lacking a cadmium dopant.

Example 3

A series of monodisperse silver chloride emulsions of approximately equal grain size (1.4-1.5 µm) were prepared by a method similar to that utilized in Example 2, except that varying amounts of cadmium chloride were added to the reaction vessel 5 minutes after the start of precipitation. The resulting emulsions were then optimally gold sensitized, coated and processed as described in Example 1. Table IV shows the concentrations of cadmium chloride utilized in the various emulsions. Relative speeds for these emulsions are shown in Curve A in Figure 1.

TABLE IV

Cadmium Chloride		Emulsion
mg/Ag mole	Mole/Ag mole	Grain Size (µm)
No cadmium chloride added		1.5
0.5	2.75×10^{-6}	1.4
1.0	5.5×10^{-6}	1.5
2.0	1.1×10^{-5}	1.5
4.0	2.2×10^{-5}	1.5
8.0	4.4×10^{-5}	1.5
12.0	6.6×10^{-5}	1.5

Example 4

A series of monodisperse silver chloride emulsions were prepared by a method similar to that described in Example 2, except that varying amounts of lead chloride were added 5 minutes after the start of the precipitation. The resulting emulsions were then optimally gold chemically sensitized and processed as described in Example 1. Table V shows the concentrations of lead chloride utilized. Relative speeds are shown in Curve B in Figure 1.

TABLE V

Lead Chloride mg/Ag mole	Lead Chloride Mole/Ag mole	Emulsion Grain Size (μm)
No lead chloride added		1.5
1.0	3.6×10^{-6}	1.4
2.0	7.2×10^{-6}	1.5
4.0	1.4×10^{-5}	1.5

Example 5

A series of monodisperse silver chloride emulsions were prepared by a method similar to that described in Example 2, except that the doped emulsions were prepared by adding 10 mg of either copper chloride or zinc chloride to the reaction vessel 5 minutes after the start of the precipitation. The resulting emulsions were then optimally gold chemically sensitized, coated and processed as described in Example 1. Table VI below shows the concentration of the dopants utilized and the relative speeds are shown for the copper and zinc doped emulsions at points C and D, respectively, in Figure 1.

TABLE VI

Metal Dopant	mg/Ag Mole	Moles/Ag Mole	Emulsion Grain Size (μm)
None	---	---	1.5
$CuCl_2$	2.0	1.5×10^{-5}	1.6
$ZnCl_2$	2.0	1.47×10^{-5}	1.5

Example 6

A. A silver chlorobromide emulsion (20 mole percent bromide) lacking an internal metal dopant was prepared in the following manner:

Three solutions were prepared as follows:

Solution 1

(Placed in the Reaction Vessel)

Gelatin	100 g
Distilled water	7000 ml
Dissolve at 40°C,	
Adjust pH to 2.0	

Solution 2

Sodium chloride	367 g
Potassium bromide	119 g
Distilled water to total volume at 40°C	2900 ml

Solution 3

Silver nitrate	850 g
Distilled water to total volume	2900 ml
Dissolve at 40°C	

To solution 1 were added 2.5 g of a silver halide ripening agent of the type disclosed in U.S. Patent 3,271,157. The pAg of solution was then adjusted to 7.94 with solution 2. Solutions 2 and 3 were then simultaneously run into solution 4 over a 40 minute period using an accelerated flow technique, maintaining the pAg at 7.94. Following precipitation a pH coagulable gelatin derivative was added to the emulsion, and the emulsion was washed using the procedure described in Example 3 of U.S. Patent 2,614,929.

B. A cadmium doped silver chlorobromide emulsion (20 mole percent bromide), was prepared as described in paragraph A above except that 10 mg of cadmium chloride (1.1×10^{-5} mole/Ag mole) were added to the reaction vessel 5 minutes after the start of the precipitation.

C. A silver chlorobromide emulsion (50 mole percent bromide) was prepared as in Paragraph A, except that the amounts of sodium chloride and potassium bromide utilized in the preparation of solution 2 were 279 g and 298 g, respectively.

D. A cadmium doped silver chlorobromide emulsion (50 mole percent bromide) was prepared as described in Paragraph C, except that the 10 mg of cadmium chloride (1.1 X 10^{-5} mole/Ag mole) were added to the reaction vessel 5 minutes after the start of precipitation.

E. The silver chlorobromide emulsions prepared in Paragraphs A-D were optimally gold chemically sensitized, coated and processed as described in Example 1. Table VII shows the fog levels.

TABLE VII

AgClBr (mole % Br)	Cadmium Dopant mg/Ag Mole	Cadmium Dopant Mole/Ag Mole	Emulsion Grain Size (μm)
20	None	None	1.0
20	2.0	1.1 X 10^{-5}	1.0
50	None	None	0.8
50	2.0	1.1 X 10^{-5}	0.8

In Figure 2 a plot is provided of the increase in relative speed versus the halide content. The increase in relative speed is obtained by taking the relative speed of a photographic element formed with an undoped, surface chemically sensitized emulsion as 100 and plotting as an ordinate the additional speed of an otherwise identical element formed with an emulsion differing by containing a dopant, as described above. The abscissa is plotted in terms of mole percent, the mole percent chloride in the silver halide emulsion being the numerator and the mole percent bromide in the silver halide emulsion being the denominator.

Example 7

A series of six monodisperse silver chloroiodide emulsions (0.7 μm), were prepared in a manner similar to Example 2 except that a constant flow technique was utilized rather than an accelerated flow and the precipitation was carried out at a temperature of 60°C. The emulsion series contains two silver chloroiodide emulsions (undoped and doped with 2 mg/Ag mole of cadmium chloride) at each of three separate chloride/iodide ratios, 100/0, 98/2 and 96/4. The emulsions having these chloride/iodide ratios were prepared by adding either 0, 16.6 or 33.2 g of potassium iodide, respectively, to solution 2 prior to precipitation. The resulting emulsions were coated, exposed and processed by the method described in Example 1. In Figure 3 a plot is provided of the increase in relative speed achieved by doping versus the halide ratio.

Example 8

Two incorporated coupler color print materials were prepared in the same manner, except differing in the emulsions utilized in the blue-sensitive, yellow dye-forming layer. The multilayer coatings were prepared in the following manner:

Separate portions of the polyethylene coated paper support were coated with gelatin layers comprising the yellow dye-forming coupler α-[4-(4-benzyloxyphenylsulfonyl)-phenoxy]-α-pivalyl-2-chloro-5-[γ-butyramido]-acetanilide at a coverage of 1.07 g/m^2 and optimally gold chemically sensitized silver chloride emulsions prepared as described in Example 2 at a coverage of 0.33 g Ag/m^2. The silver chloride emulsions were both spectrally sensitized to the blue region of the visible spectrum using a blue spectral sensitizer. The rest of the multilayer coating for each of the above variations are common and are described as a gelatin interlayer comprising gelatin and an anti-stain agent; a magenta dye-forming layer comprising a green-sensitized silver chloride emulsion, a magenta dye-forming coupler and gelatin; an interlayer comprising gelatin, an antistain agent and a UV absorber; a cyan dye-forming layer comprising a red sensitized silver chloride emulsion, a cyan dye-forming coupler and gelatin and a protective overcoat layer comprising gelatin. The multilayer photosensitive elements were then exposed to a tungsten light source through a graduated density step wedge and processed in a 3-solution color process of the type described in U.S. Reissue Patent 28,112. The relative blue sensitivities of the two processed materials are shown in Table VIII.

TABLE VIII

Emulsion in Blue-Sensitive, Yellow Dye-Forming Layer	Cadmium Chloride Dopant	Relative Blue Sensitivity
AgCl	None	100
AgCl	2 mg/Ag Mole	182

Example 9

Two multicolor negative image-forming elements suitable for use in a color image transfer process, wherein color prints are obtained through the use of color negatives, were prepared. The elements were identical, except for the emulsions utilized in the blue sensitized, yellow dye-releasing unit. The elements were prepared as described below. The quantities of components are stated as grams/meter^2 in parenthesis. Silver halide quantities are given in terms of silver.

A poly(ethylene terephthalate) film support coated on one side with a carbon-pigmented gelatin layer was coated on the other side with the following layers:

(1) a cyan dye-providing layer comprising a dispersion of a cyan redox dye-releaser and gelatin;

(2) a light-sensitive layer comprising a red sensitized, chemically sensitized silver chloride emulsion;

(3) interlayer comprising gelatin and an antistain agent;

(4) a magenta dye-providing layer comprising a dispersion of a magenta redox dye-releaser and gelatin;

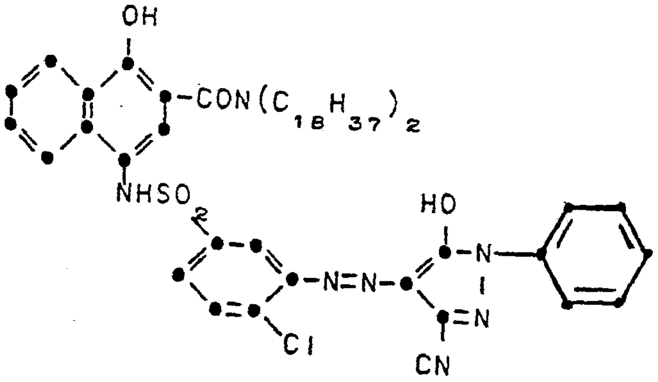
(5) a light-sensitive layer comprising a green sensitized, chemically sensitized silver chloride emulsion and gelatin;

(6) interlayer comprising gelatin and an antistain agent;

(7) a yellow dye-providing layer comprising a dispersion of Compound A* (a yellow redox dye-releaser) (0.49) and gelatin (1.07);

Separate samples of the above-described element were then overcoated with layers comprising gelatin (1.07) and chemically sensitized silver chloride (0.30) emulsions prepared either as described in Control 4 or as in Example 1. The silver chloride emulsions were both spectrally sensitized to the blue region of the visible spectrum using a blue spectral sensitizer. Each sample was provided with a gelatin overcoat layer.

*Compound A



Samples of each element were identically exposed to blue light through a graduated density test object and processed as follows:

The exposed elements were soaked for 10 seconds at 28°C in an activator solution comprising water to 1000 ml, benzyl alcohol (10 ml), 5-methylbenzotriazole (1 g), 11-aminoundecanoic acid (2 g) and 6-aminohexanoic acid, laminated to a receiving element (described below) for 2 1/2 minutes at 24°C, and then peeled apart. The transferred yellow dye images produced in the receiving element were evaluated and the results are shown below in Table IX.

TABLE IX

Emulsion in Blue-Sensitive Layer	Cadmium Chloride Dopant	Relative Blue Sensitivity
AgCl	None	100
AgCl	2 mg/Ag Mole	162

Receiving Element

The receiving element utilized comprised a paper support overcoated with a white-pigmented polyethylene layer, an acid layer comprising co-poly(styrene-maleic anhydride), a polymeric timing layer, a receiving layer comprising gelatin, 4-hydroxymethyl 4-methyl-1-phenyl-3-pyrazolidone, poly(N-vinylimidazole-co-3-hydroxyethyl-1-vinylimidazolium chloride) 90:10 weight ratio) and a gelatin overcoat layer.

CLAIMS:

1. A silver halide emulsion of the developing out type comprised of silver halide grains which are at least 80 mole percent silver chloride and less than 5 mole percent silver iodide, based on total silver halide, characterized in that said silver halide grains are internally doped with cadmium, lead, copper, zinc or mixtures thereof in a speed increasing amount of up to 7×10^{-5} mole per mole of silver halide.

2. A silver halide emulsion according to Claim 1 wherein said silver halide grains are formed in the presence of cadmium, lead, copper, zinc or mixtures thereof in a concentration of from 2×10^{-6} to 7×10^{-5} mole per mole of silver halide.

3. A silver halide emulsion according to Claim 1 or 2 in which said silver halide grains consist essentially of silver chloride.

4. A silver halide emulsion according to Claim 1, 2 or 3, in which said silver halide grains are substantially monodispersed.

5. A silver halide emulsion according to Claim 1, 2, 3 or 4 in which said silver halide grains are gold sensitized.

6. A silver halide emulsion according to Claim 1, 2, 3 or 4 in which said silver halide grains are sulfur and gold sensitized.

7. a photographic element comprised of a support having coated thereon a silver halide emulsion according to Claim 1.

8. A photographic element comprised of a support having coated thereon at least three superimposed color-forming layer units, one of said layer units containing a blue light responsive silver halide emulsion and a yellow image dye providing means, a second of said layer units containing a green light

responsive silver halide emulsion and a magenta image dye providing means and a third of said layer units containing a red light responsive silver halide emulsion and a cyan image dye providing means, characterized in that at least one of said silver halide emulsions is a silver halide emulsion according to Claim 1.

9. A process of forming a silver halide emulsion according to Claim 1 which comprises reacting a water soluble silver salt with a water soluble halide salt in an aqueous medium containing a peptizer to form radiation-sensitive silver halide grains, said grains containing at least 80 mole percent silver chloride and less than 5 mole percent silver iodide, characterized in that water soluble salts of cadmium, lead, copper, zinc or mixtures thereof are introduced into said aqueous medium during formation of said silver halide grains in a speed increasing amount up to 7×10^{-5} mole per mole of silver halide.

10. A process of forming a silver halide emulsion according to Claim 1 which comprises separately and concurrently introducing into a reaction vessel (1) a water soluble silver salt in an aqueous solution and (2) a water soluble halide salt in an aqueous solution, in the presence of gelatin or a gelatin derived peptizer, to form radiation-sensitive silver halide grains containing at least 80 mole percent silver chloride and less than 5 mole percent silver iodide, and surface chemically sensitizing said grains with a gold sensitizer, characterized in that there is introduced into the reaction vessel after silver halide grain nuclei have been formed, but prior to introduction of at least 85 percent of the solution of water soluble silver salt, water soluble salts of cadmium, lead, copper, zinc or mixtures thereof in

a speed increasing amount sufficient to comprise up to 7 X 10^{-5} moles per mole of silver halide of said grains.

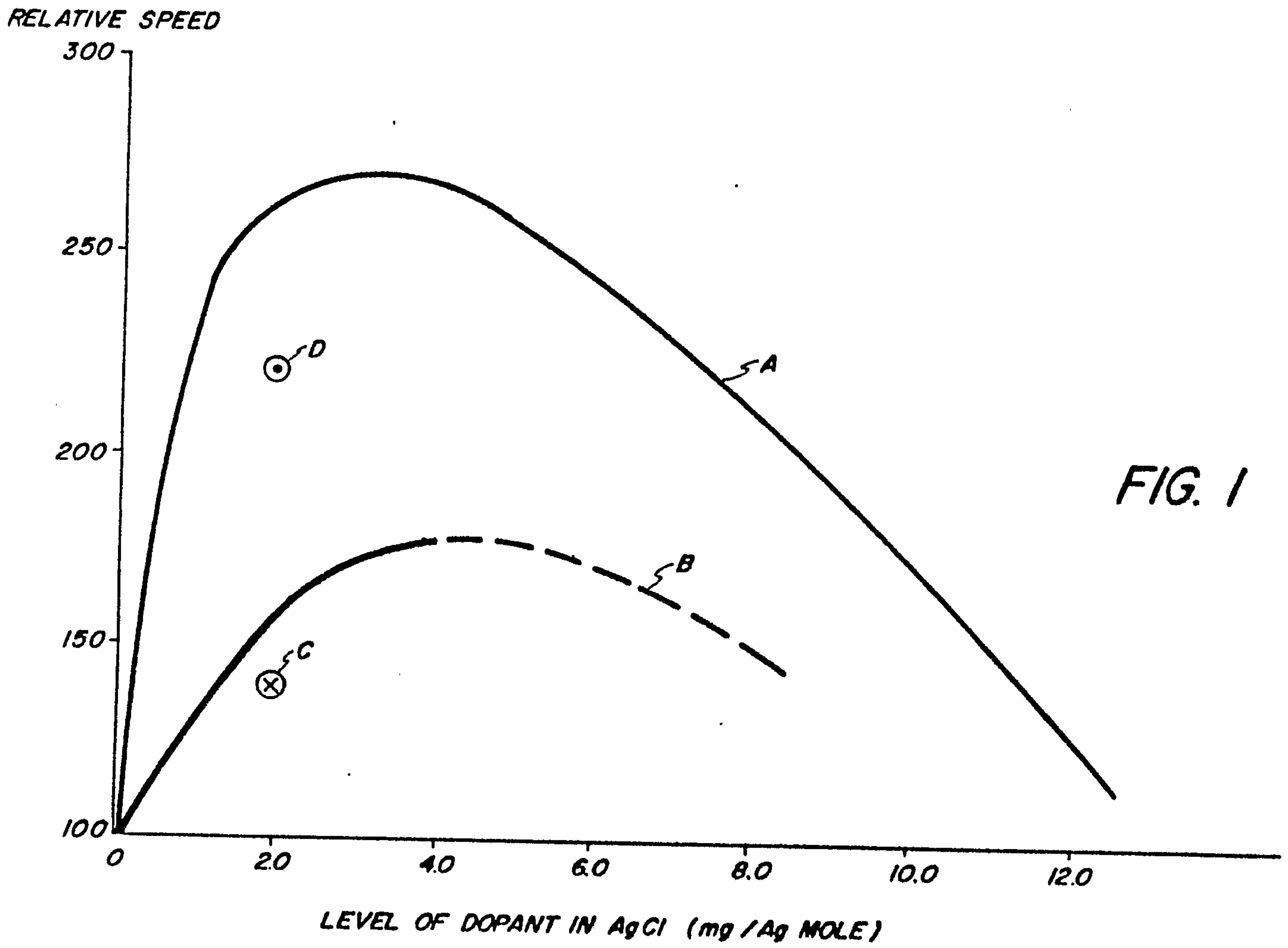

RELATIVE SPEED
300
250
200
150
100
0
2.0
4.0
6.0
8.0
10.0
12.0
LEVEL OF DOPANT IN AgCl (mg / Ag MOLE)
A
B
C
D

FIG. 1

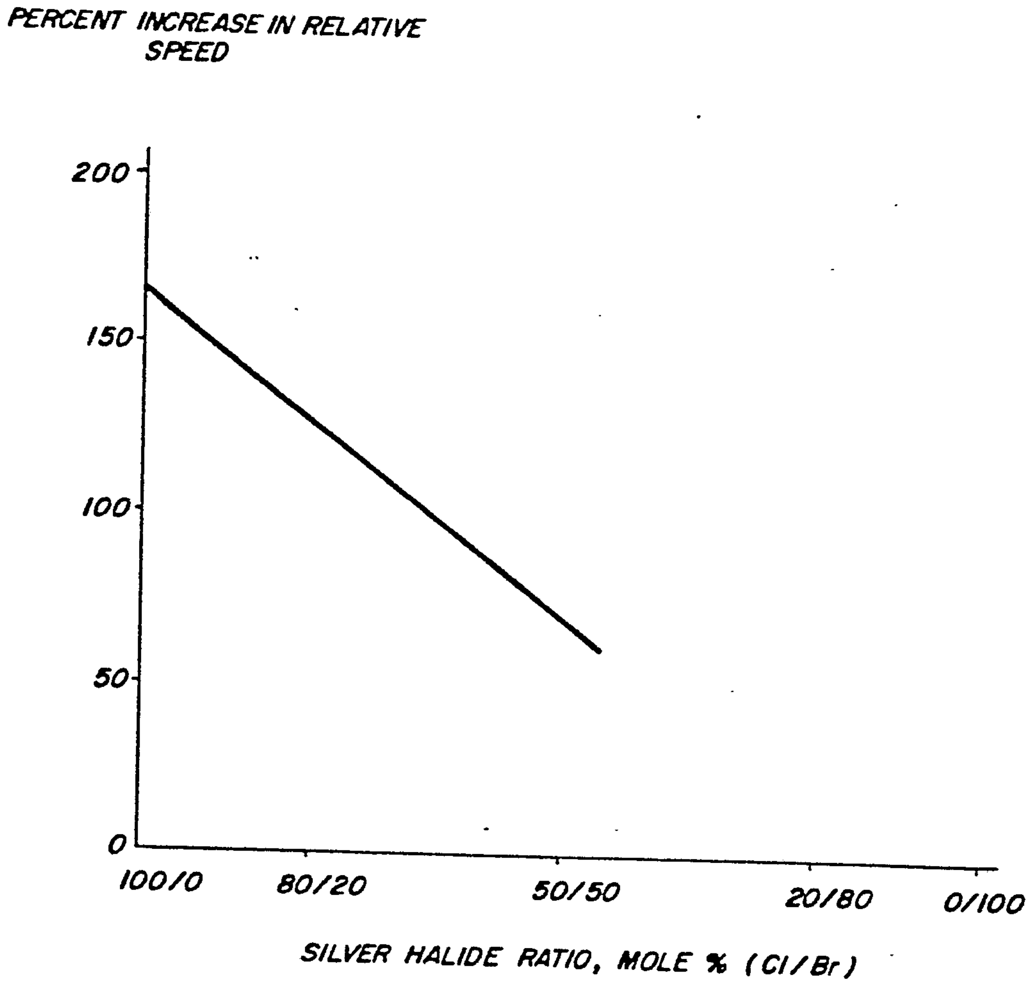

PERCENT INCREASE IN RELATIVE SPEED
200
150
100
50
0
100/0
80/20
50/50
20/80
0/100
SILVER HALIDE RATIO, MOLE % (Cl/Br)

FIG. 2

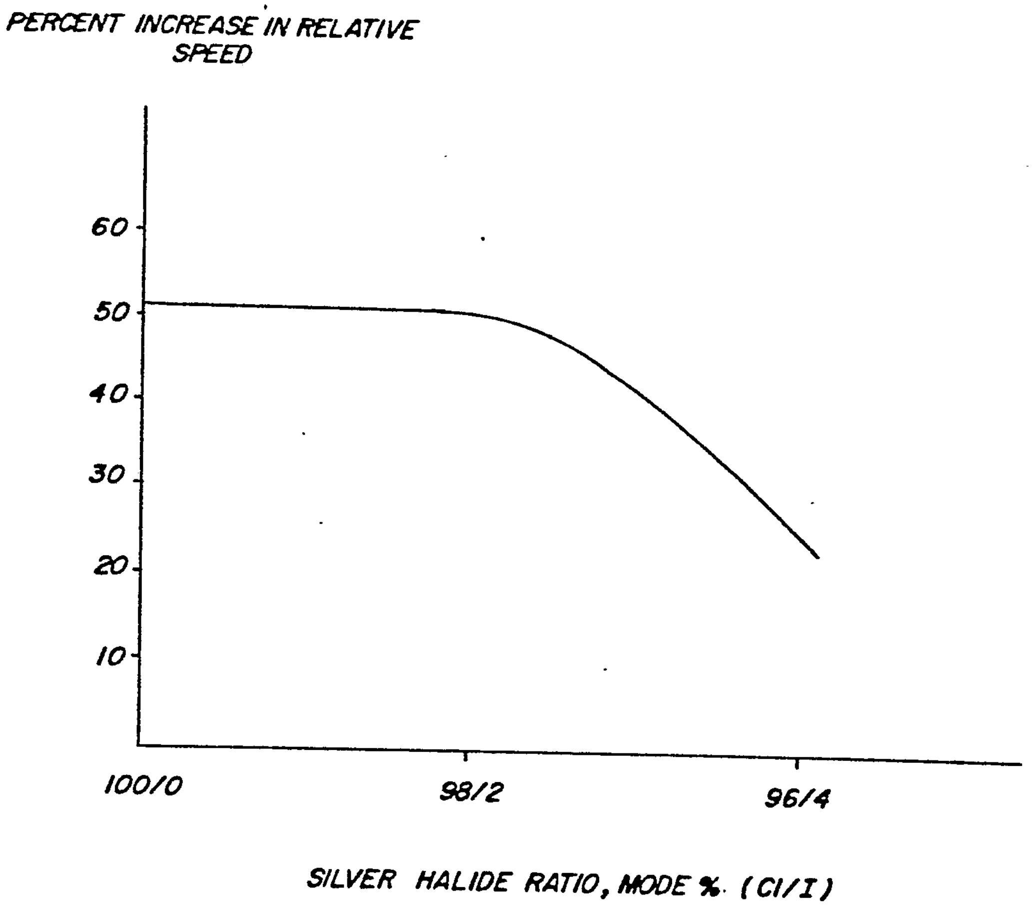

PERCENT INCREASE IN RELATIVE SPEED
60
50
40
30
20
10
100/0
98/2
96/4
SILVER HALIDE RATIO, MODE %. (Cl/I)

FIG. 3

0017148

European Patent
Office

EUROPEAN SEARCH REPORT

Application number
EP 80101580.1

Category	DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
	DE - A1 - 2 806 855 (KODAK) + Page 22, line 9 + --	1	G 03 C 1/06 G 03 C 7/26
	DE - A - 2 138 873 (KODAK) + Page 6, line 20 + --	1	
	FR - A - 2 209 126 (KODAK) + Page 1, lines 1-40; page 2, lines 1-3 + --	1	TECHNICAL FIELDS SEARCHED (Int.Cl. ³)
D	US - A - 2 950 972 (KODAK) + Column 1, lines 19-33 + --	1	G 03 C
D	GB - A - 1 21 496 (KODAK) + Page 1, lines 26-50 + --	1	
D	US - A - 3 901 711 (IWAOSA) + Claim 1 + ----	1,5	

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family,
corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	17-06-1980	SALTEN

EPO Form 1503.1 06.78