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3,730,724

SILVER HALIDE COLOR PHOTOGRAPHIC ELEMENT CONTAINING A MAGENTA COLOR COUPLER AND A CARBOXY SUBSTITUTED THIAZOLINE COMPOUND

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No Drawing. Continuation-in-part of abandoned application Ser. No. 21,468, Mar. 20, 1970. This application June 3, 1971, Ser. No. 149,815

Int. Cl. G03c 1/28, 1/76, 1/34

U.S. Cl. 96-74

10 Claims

ABSTRACT OF THE DISCLOSURE

Light sensitive photographic elements comprising surface sensitized converted-halide silver halide grains are contained in emulsions which are particularly and effectively stabilized by addenda which resist pre-processing deterioration, post-processing dye stability and unwanted shifting in color balance. Preferred such addenda are carboxy substituted thiazolinethione and carboxy substituted thiazolidines.

This is a continuation-in-part of applicant's copending application Ser. No. 21,468 filed Mar. 20, 1970, now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to photographic materials, their preparation and use. In one aspect, this invention relates to a photographic element comprising converted-halide silver halide grains whose optical density curve shape is stabilized by the addition of a carboxy-substituted compound. In another aspect, this invention relates to multilayer, multicolor photographic elements to which is added stabilizing addenda in order to provide true color balance.

DESCRIPTION OF THE PRIOR ART

Photographic elements comprising light sensitive silver halide grains are subject to a wide variety of factors which can adversely affect their ability to faithfully reproduce an image after exposure and processing. For example, fog, the more or less intense blackening of silver halide, can be caused by prolonged development, aerial oxidation, ageing and other physical factors including light reflection on lens surfaces. Speed losses or decreases in the sensitivity of the silver halide grain can be caused by a variety of factors including the addition of addenda which adversely affect the sensitometric characteristics of the grain and the element. When the sensitivity of halide grains is thus adversely affected, the density in the toe of the characteristic curve shape is changed. In color-containing elements this change substantially disrupts the color balance and leads to untrue colors in the reproduced image. In photographic elements and particularly multilayer color elements, the variation of light intensity or exposure time not only changes effective film speed and contrast but usually results in a shift in color balance due to the differences in reciprocity effect in each of the color-containing layers.

Differences of toe softness or sharpness of the characteristic curve are of great importance. A sharper toe tends to produce whiter whites, and brighter highlights, while a softer toe tends to distort and shift color balance. For example, a soft magenta toe produces unnatural and displeasing red or pink rather than white objects, such as clouds. As little as a 0.02 change in the toe density areas is far more critical than a 0.10 change in density in the

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maximum density areas. While the human eye can see slight changes in low density areas much easier than in areas of high color saturation, shifts in green maximum saturation can be perceived by the eye more readily than red or blue shifts, since the eye is most sensitive to green.

In the past, attempts to improve the appearance of the printed photographic image have included adding optical brightening agents or fluorescent agents to enhance the white or highlighted areas, such as set forth in U.S. Pat. 3,416,923 of VanCampen et al. issued Dec. 17, 1968.

Converted-halide silver halide grains have been found particularly effective in providing certain improved light sensitive silver halide-containing elements and emulsions, such as taught by Davey and Knott in U.S. Pat. 2,592,250 issued Apr. 8, 1952, but nowhere have such emulsions overcome the problems solved by the present invention including preprocess keeping and post process dye stability.

The incorporation into developer solutions of certain thiazoles in developing coarse grain silver halide radiographic emulsions is known from U.S. Pat. 3,306,746 issued Feb. 28, 1967 to Schwartz et al. Further, various compounds such as triazoles, imidazoles, benzimidazoles, triazines and the like are described as satisfactory anti-foggants for photographic elements in U.S. Pat. 2,819,965 issued Jan. 14, 1958 to Murray et al.

However, nowhere heretofore has there been any teaching that by incorporating the carboxy-substituted compounds disclosed herein in the photographic elements described, highly desirable and previously unattainable results are achieved. For even where known compounds such as the antifoggants described above have been successfully used in stabilizing the emulsion against fog, there appears to have been little or no effect upon improving either the curve shape of said emulsion, the preprocess keeping or the post process-dye stability.

It is, therefore, evident that the art would be enhanced by photographic elements and improved silver halide grains and emulsion systems which not only exhibit reduced fog but also possess increased speed, increased stability on keeping, better reciprocity characteristics and high level of color reproduction integrity after processing.

Accordingly, it is an object of this invention to provide photographic materials which exhibit improved combinations of sensitometric properties.

Another object of this invention is to provide photographic elements and layers, and particularly multilayers such as color-forming layers, which exhibit increased contrast and decreased shifting or color balance.

Still another object of this invention is to provide improved photographic elements comprising surface-sensitized converted-halide silver halide grains in combination with a carboxy-substituted thiazolinethione or thiazolidine whereby deviations in the characteristic sensitometric curve shape are controlled, i.e. effected in a desirable manner within tolerable limits.

Still other objects will become apparent to those skilled in the art from a consideration of the following examples, specification and claims.

SUMMARY OF THE INVENTION

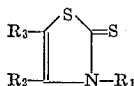
In accordance with this invention, there is now provided a photographic element comprising a support, surface sensitized converted-halide silver halide grains and a carboxy-substituted thiazolinethione or thiazolidine. In a preferred embodiment the carboxy-substituted thiazolinethione or thiazolidine is present in the element in a concentration sufficient to control the characteristic, i.e. the optical density curve shape of said silver halide grains such as to maintain the color balance, preprocess keeping and post process dye stability. The element can suitably

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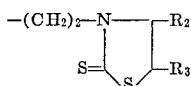
comprise a hydrophilic colloid layer, such as one containing amine-containing natural or synthetic polymers such as gelatin, for example, and other gel-compatible colloids which can be used as partial gel-substitutes.

It is now found that all of these desirable properties of stability and color balance can be effectively obtained by utilizing carboxy-substituted thiazolinethiones or thiazolidines and in particular those compounds selected from the group consisting of:

(I)

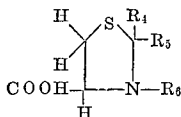


in which R_1 is hydrogen, carboxymethyl or



each R_2 is alkyl preferably lower alkyl of 1 to 5 carbon atoms such as methyl, ethyl, propyl, butyl, pentyl and the like, when R_1 is other than hydrogen or is carboxymethyl and each R_3 is hydrogen or carboxyl and wherein at least one of the radicals R_1 , R_2 and R_3 comprises a carboxyl group or a carboxymethyl group; or

(II)



in which R_6 is hydrogen or acyl such as formyl and the like, R_4 is hydrogen or methyl and R_5 is hydrogen, carboxyl, alkyl such as from 1 to 8 carbon atoms and preferably up to 6 carbon atoms such as methyl, ethyl, pentyl, hexyl, and the like.

These compounds are unexpectedly useful in achieving the purposes set forth herein and are prepared by techniques well known in the art. For example, general methods of preparation of compounds in Groups (I) or (II) have been previously reported and the methods for preparing said compounds are well known. In particular, 4-thiazoline-2-thiones, their intermediates and derivatives are prepared conveniently by the methods disclosed in J. Org. Chem. vol. 29, pp. 2146-2150 Humphlett and Lamon (1964) which respectively employs the reaction of ammonium dithiocarbamate and α -halo aldehydes or ketones and the reaction of ammonium dithiocarbamate and 1-alkylsulfonyl-3-bromo-2-propanones.

The compounds represented by structural Formula II can be conveniently prepared by the methods disclosed in preparing thiazolidines by aqueous calcium hydroxide decomposition of lanthionine as set forth fully in J. Am. Chem. Soc. 79, 1644 (1957) Dann et al. Exemplary of such compounds include

4-thiazolidine carboxylic acid

2-hexyl-4-thiazolidine carboxylic acid

2-methyl-2,4-thiazolidine dicarboxylic acid and

3-formyl-2,2-dimethyl-4-thiazolidine carboxylic acid.

By the practice of the present invention, an unexpected, highly desirable and significant stabilization of photographic elements is now achieved whereby pre-process keeping, post process dye stability and density curve shape control are improved. These improvements are made possible by combining with said grains an heterocyclic carboxy-substituted compound, such as for example, a carboxy-substituted thiazolinethione or thiazolidine and in a preferred embodiment a compound such as 4-carboxymethyl-4-thiazoline-2-thione.

As will be understood by those skilled in the art, the presence of said characteristic curve-shape control addenda can be effected in a number of ways, such as by the direct incorporation of any of the above class of compounds or by their immediate or mediate precursors.

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For example, it has been found to be particularly useful to utilize [5,4 - (1,2-D-gluco)-thiazolyl]-disulfide which when cleaved, functions as 2-thiones and is only one example of 4-thiazoline-2-thione precursor.

The light sensitive photographic silver halide emulsions, layers and elements disclosed in utilizing the present invention feature converted-halide silver halide grains in which the halide comprises at least about 50 mole percent bromide and up to about 10 mole percent iodide, any remaining halide being chloride. Preferentially some chloride should be present and it can vary within the limits disclosed that is an upper limit of about 50 mole percent down to a lesser amount present and preferably 12 to 15 percent chloride. The surface of said grains are chemically sensitized by a variety of sensitizers well known in the art such as is set forth more fully hereafter.

In accordance with one embodiment of this invention the grains thus described are present in a photographic layer containing a color forming coupler. Particularly 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" as employed herein is well known to those skilled in the art and denotes silver halide grains which are prepared in a variety of ways, one such way is by first forming an emulsion or dispersion of silver salt grains consisting at least in part of a silver salt more soluble in water than silver bromide, and then "converting" at least a portion of said salt grains to silver bromide or bromoiodide salts.

More specifically in one preferred method said 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 gram per 100 milliliters of water at 20° C. Useful silver salts more soluble than silver bromide include silver chloride, silver thiocyanate and silver citrate and the like. Such salts are conveniently formed, for example, 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 and the like respectively to an aqueous gelatin-containing solution containing a small amount of the alkali metal salt. The first two solutions are preferably added slowly to the aqueous gelatin-containing solution while maintaining the temperature of all the solutions 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 necessary to convert all the chloride to bromide or bromoiodide, nor is it necessary that the silver halide grains contain iodide. One method for preparing emulsions of the general type employed in this invention is more fully described by Davey and Knott, U.S. Pat. 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 characteristic curve shape of a photographic silver halide emulsion is generally S-shaped with a straight part between the two regions of underexposure and overexposure. This curve is well known to those skilled in the art as the H and D curve or the $D \log E$ curve. It results from the particular properties of the various grains and photographic reproduction of the image becomes more exact when the toe of the curve is sharpened to the benefit of the central straight part. Thus, where the true color balance of the red, blue and green curves is essen-

tial as in color photography, these three characteristic curves must be substantially superimposable at all points. An increase or decrease in contrast such as those which result in softening the toe, also results in unacceptable color balance.

As dramatically shown by the data in the following tables where the toe of the curve is soft, and particularly in the green curve, the color balance of highlight areas is shifted so that an undesirable general reddish-pink color is observed. By practicing this invention, the curve toe is unexpectedly maintained providing heretofore unattainable color balanced highlights.

In still another preferred embodiment, the halide of the silver halide grains present in the photographic element of this invention comprise at least about 50 mole percent bromide and up to about 10 mole percent iodide, any remaining halide being chloride and the surface of said grains being chemically sensitized and the like.

The converted-halide silver halide grains employed in this invention are chemically sensitized by any means suitable for this purpose, many methods having been previously described in the prior art. Chemical sensitization is a surface phenomenon and as used herein, includes sensitization of the type described by Antoine Hautot and Henri Sauvenier in "Science et Industries Photographiques," vol. XXVIII, January 1957, pages 1-23 and January 1957, pages 57-65. This chemical, i.e. surface sensitization includes three major classes, viz., gold or noble metal sensitization, sulfur sensitization, such as by a labile sulfur compound, and reduction sensitization, i.e., treatment of the silver halide with a strong reducing agent which does not fog appreciably the silver halide but introduces small specks of metallic silver into the silver halide crystal or grain.

The converted-halide silver halide grains can likewise be chemically sensitized by any of the accepted procedures. Emulsions containing such grains can be digested with naturally active gelatin, or compounds of the sulfur group can be added, such as those described in Sheppard U.S. Pat. 1,574,944 issued Mar. 2, 1926, Sheppard et al. U.S. Pat. 1,623,499 issued Apr. 5, 1927, and Sheppard et al. U.S. Pat. 2,410,689 issued Nov. 5, 1946. Particularly good results are obtained with sulfur, selenium, tellurium sensitizers and the like.

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 chloropalladite, which are used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in Smith and Trivelli U.S. Pat. 2,448,060 issued Aug. 31, 1948, and as antifoggants in high amounts, as described in Trivelli and Smith U.S. Pat. 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. 2,399,083 issued Apr. 23, 1946 and Damschroder et al., U.S. Pat. 2,642,361 issued June 16, 1953. Suitable compounds are potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, 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. 2,487,850 issued Nov. 15, 1949), polyamines, such as diethylene triamine (Lowe and Jones U.S. Pat. 2,518,698 issued Aug. 15, 1950), polyamines, such as spermine (Lowe and Allen U.S. Pat. 2,521,925 issued Sept. 12, 1950), or bis(β -aminoethyl) sulfide and its water-soluble salts (Lowe and Jones U.S. Pat. 2,521,926, issued Sept. 12, 1950).

A wide variety of photographic color couplers can be employed in the practice of this invention. As used herein, the term "color coupler" or color-forming dye couplers includes any compound which reacts (or couples) with

the oxidation products of primary aromatic amino developing agent on photographic development to form a dye. Typical useful color couplers include phenolic, 5-pyrazolon, 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. 3,046,129 issued July 24, 1962, column 15, line 45 through column 18, line 51, which disclosure is incorporated herein by reference. Other suitable couplers are described in Salminen et al. U.S. Pat. 2,423,730 issued July 8, 1947; Loria et al. U.S. Pat. 2,600,788 issued June 17, 1952; De Maria U.S. Pat. 2,875,051 issued Feb. 24, 1959; Bush et al. U.S. Pat. 2,908,573 issued Oct. 13, 1959; Weissberger et al. U.S. Pat. 3,265,506 issued Aug. 9, 1966; Greenhalgh et al. U.S. Pat. 3,127,269 issued Mar. 31, 1964; Loria U.S. Pat. 3,408,194 issued Oct. 29, 1968 and Lestina Belgian Pat. 698,354. Such color forming couplers can be dispersed in the emulsion layers in any convenient manner, such as by using the solvents and the techniques described in Jelley and Vittum U.S. Pat. 2,322,027 issued June 15, 1943 or Fierke and Chechak U.S. Pat. 2,801,171 issued July 30, 1957. The useful couplers include Fischer-type incorporated couplers such as those disclosed in Fischer U.S. Pat. 1,055,155 issued Mar. 4, 1913, and particularly non-diffusible Fischer-type couplers containing branched carbon chains, e.g., those referred to in the references cited in Frohlich et al. U.S. Pat. 2,376,679, issued May 22, 1945, column 2, lines 50-60. These elements can be processed by one of the procedures described in Graham et al. U.S. Pat. 3,046,129 issued July 24, 1962, columns 23 and 24, or by the development process described by Edens et al. U.S. patent application Ser. No. 736,010 filed June 11, 1968 and corresponding German patent 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 forming 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, many of which are well known to those skilled in the art, for example, those including the benzotriazoles and more particularly the phenyl-type compounds described in Sawdey U.S.

Pat. 3,253,921 issued May 31, 1966 and the thiazolidines of the type described in a number of Sawdey U.S. Pats. 2,739,971 issued Mar. 27, 1956, 2,739,888 issued Mar. 27, 1956 and 3,250,617 issued May 10, 1966 and others. This layer can be an overcoat or can be positioned 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. 2,526,632 issued Oct. 24, 1950; Sprague U.S. Pat. 2,503,776 issued Apr. 11, 1950; Brooker et al. U.S. Pat. 2,493,748 issued Jan. 10, 1950; and Taber et al. U.S. Pat. 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, thiazoles, selenazoles and imidazoles. Such nuclei may contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxy-alkyl, 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 thiohydantoin, rhodanines, oxazolidenediones, thiazolidenediones, 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. 2,933,390 issued Apr. 19, 1960 and Jones et al. U.S. Pat. 2,937,089 issued May 17, 1960. The multilayer photographic elements of the invention can be spectrally sensitized, and contain the filter layers described by Schwan et al. U.S. Pat. application Ser. No. 715,005 filed Mar. 21, 1968 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 in 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.

These silver halide grains can be present in the element in any convenient fashion such as in one or more layers which are themselves deposited by vacuum or laid-down in emulsion form for example.

As will be more fully set forth by examples which follow, a preferred photographic element of this invention can provide a multicolor image and in such elements, the curve-shape-controlling addenda are most effectively contained in at least one hydrophilic colloid-containing layer, such as a gelatin layer. Where the supported element has coated thereon at least three superimposed hydrophilic

colloid layers containing color-forming dye couplers sensitive to red, green and blue radiation; particularly good and unexpected results are obtained when the carboxy-substituted thiazolinethione or thiazolidine is contained in the layer having the green radiation sensitive color forming dye coupler. In such cases, the effective concentration varies from about 50 to about 500 mg./mole of silver based upon the total converted-halide silver halide grains.

Particularly good results are obtained where this invention is embodied in an element having a white reflecting support bearing layers comprising the converted-halide silver halide grains above described. These layers are separate and are radiation sensitive respectively to blue, green and red, said layers containing color-forming dye couplers capable of forming respectively, yellow, magenta, and cyan dyes upon color development. The red-sensitive layer containing the cyan-forming coupler is preferably the outermost light sensitive layer and can contain in a preferred aspect the above described fluorescent agent in the solvent. In another preferred embodiment of this invention, the blue-sensitive layer can be effectively disposed adjacent the reflecting support. It is understood that various subbing, binding or other intermediate layers can be placed between, over and under these coupler-containing layers with equally good results.

The halide conversion silver halide grains used with this invention may be combined with speed increasing compounds such as polyalkylene glycols, cationic surface active agents and thioethers or combinations of these as described in Piper U.S. Pat. 2,886,437 issued May 12, 1959; Dann et al. U.S. Pat. 3,046,134 issued July 24, 1962; Carroll et al., U.S. Pat. 2,944,900 issued July 12, 1960; and Goffe U.S. Pat. 3,294,540 issued Dec. 27, 1966.

The halide conversion silver halide grains used in the practice of this invention can be protected against the production of fog and can be further stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers each used alone or in combination include thiazolium salts described in Brooker et al., U.S. Pat. 2,131,038 issued Sept. 27, 1938 and Allen et al., U.S. Pat. 2,694,716 issued Nov. 16, 1954; the azaindenes described in Piper U.S. Pat. 2,886,437 issued May 12, 1959, and Heimbach et al., U.S. Pat. 2,444,605 issued July 6, 1948; the mercury salts as described in Allen et al. U.S. Pat. 2,728,663 issued Dec. 27, 1955; the urazoles described in Anderson et al., U.S. Pat. 3,287,135 issued Nov. 22, 1966; the sulfocatechols described in Kennard et al. U.S. Pat. 3,236,652 issued Feb. 22, 1966; the oximes described in Carroll et al. British Pat. 623,448; nitron; nitroindazoles; the mercaptotetrazoles described in Kendal et al., U.S. Pat. 2,403,927 issued July 16, 1946; Kennard et al., U.S. Pat. 3,266,897 issued Aug. 16, 1966 and Luckey et al., U.S. Pat. 3,397,987 issued Aug. 20, 1966; the polyvalent metal salts described in Jones U.S. Pat. 2,839,405 issued June 17, 1958; the thiuronium salts described in Herz et al., U.S. Pat. 3,220,839 issued Nov. 30, 1965; the palladium, platinum and gold salts described in Trivelli et al., U.S. Pat. 2,566,263 issued Aug. 28, 1951 and Yutzy et al., U.S. Pat. 2,597,915 issued May 27, 1952.

The photographic elements of this invention can contain incorporated developing agents such as hydroquinones, catechols, aminophenols 3-pyrazolidones, ascorbic acid and its derivatives, reductones and phenylene diamines. Combinations of developing agents can be employed in the practice of the invention. 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. 2,592,368 issued Apr. 8, 1952 and Dunn et al., French Pat. 1,505,778.

The photographic and other hardenable layers used in the practice of this invention 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 sulfonyl ethers, active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, mixed function hardeners and polymeric hardeners such as oxidized polysaccharides like dialdehyde starch and oxyguar gum and the like.

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

The described photographic emulsion layers and other layers of a photographic element employed in the practice of this invention can also contain alone or in combination with hydrophilic, water permeable colloids, other synthetic polymeric compounds such as dispersed vinyl compounds such as in latex form and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described, for example, in Nottorf U.S. Pat. 3,142,568, issued July 28, 1964; White U.S. Pat. 3,193,386, issued July 6, 1965; Houck et al., U.S. Pat. 3,062,674, issued Nov. 6, 1962; Houck et al., U.S. Pat. 3,220,844 issued Nov. 30, 1965; Ream et al., U.S. Pat. 3,287,289 issued Nov. 22, 1966; and Dykstra U.S. Pat. 3,411,911 issued Nov. 19, 1968; 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, those having recurring sulfobetaine units as described in Dykstra Canadian Pat. 774,054.

The photographic elements used with this invention can contain antistatic or conducting layers, such layers can comprise soluble salts, e.g. chlorides, nitrates, etc., evaporated metal layers, ionic polymers such as those described in Minsk U.S. Pat. 2,861,056 issued Nov. 18, 1958 and Serman et al., U.S. Pat. 3,206,312 issued Sept. 14, 1965 or insoluble inorganic salts such as those described in Trevoy U.S. Pat. 3,428,451 issued Feb. 18, 1969.

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

The photographic layers employed in the practice of this invention can contain plasticizers and lubricants such as polyalcohols, e.g. glycerin and diols of the type described in Milton et al., U.S. Pat. 2,960,404 issued Nov. 1, 1966; fatty acids or esters such as those described in Robijns U.S. Pat. 2,588,765 issued Mar. 11, 1952 and Duane U.S. Pat. 3,121,060 issued Feb. 11, 1964; and silicone resins such as those described in Du Pont British Pat. 955,061.

It is also advantageous in the practice of this invention to provide the photographic layers with surfactants such as saponin; anionic compounds such as the alkyl aryl sulfonates described in Baldsiefen U.S. Pat. 2,600,831 issued June 17, 1962; amphoteric compounds such as those described in Ben-Ezra U.S. Pat. 3,133,816 issued

May 19, 1964; and water soluble adducts of glycidol and an alkyl phenol such as those described in Olin Mathieson British Pat. 1,022,878.

The photographic elements employed in the practice of this invention may 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. 2,992,101 issued July 11, 1961 and Lynn U.S. Pat. 2,701,245 issued Feb. 1, 1955.

The photographic elements used in this invention can contain brightening agents including stilbenes, triazines, oxazoles 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. 2,933,390 issued Apr. 19, 1960 or dispersions of brighteners may be used such as those described in Jansen German Pat. 1,150,274, Oetiker et al., U.S. Pat. 3,406,070 issued Oct. 15, 1968 and Heidke French Pat. 1,530,244 and VanCampen U.S. Pat. 3,416,923 issued Dec. 17, 1968.

The various layers, including the photographic layers, employed in the practice of this invention can contain light absorbing materials and filter dyes such as those described in Sawdey U.S. Pat. 3,252,921 issued May 31, 1966; Gaspar U.S. Pat. 2,274,782 issued Mar. 3, 1942; Silberstein et al., U.S. Pat. 2,527,583 issued Oct. 31, 1950 and VanCampen U.S. Pat. 2,956,879 issued Oct. 18, 1960. If desired, the dyes can be mordanted, for example, as described in Jones et al., U.S. Pat. 3,282,699 issued Nov. 1, 1966.

The sensitizing dyes and other addenda used in the practice of this invention may be added from water solutions or suitable organic solvent solutions can be used. The compounds can be added using various procedures including those described in Collins et al., U.S. Pat. 2,912,343 issued Nov. 10, 1959; McCrossen et al., U.S. Pat. 3,342,605 issued Sept. 19, 1967; Audran U.S. Pat. 2,996,287 issued Aug. 15, 1961 and Johnson et al., U.S. Pat. 3,425,835 issued Feb. 4, 1969.

The photographic layers used in the practice 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. 2,681,294 issued June 15, 1954. If desired, two or more layers can be coated simultaneously by the procedures described in Russell U.S. Pat. 2,761,791 issued Sept. 4, 1956 and Wynn British Pat. 837,095.

As fully disclosed above and in a preferred embodiment this invention can be used with elements designed for color photography, for example, elements containing colorforming couplers such as those described in Frohlich et al., U.S. Pat. 2,376,679 issued May 22, 1945; Jelley et al., U.S. Pat. 2,322,027 issued June 15, 1943; Fierke et al., U.S. Pat. 2,801,171 issued July 30, 1957; Godowsky U.S. Pat. 2,698,794 issued Jan. 4, 1955; Barr et al., U.S. Pat. 3,227,554 issued Jan. 4, 1966; and Graham et al., U.S. Pat. 3,046,129 issued July 24, 1962; or elements to be developed in solutions containing color-forming couplers such as those described in Mannes et al., U.S. Pat. 2,252,718 issued Aug. 19, 1941; Carroll et al., U.S. Pat. 2,592,243 issued Apr. 18, 1952; and Schwan et al., U.S. Pat. 2,950,970 issued Aug. 30, 1966; and in false-sensitized color materials such as those described in Hanson U.S. Pat. 2,763,549 issued Sept. 18, 1956.

In addition to the developing processes set forth in the examples, the halide conversion-silver halide grains and elements containing them according to this invention can be processed by various methods including processing in alkaline solutions containing conventional developing agents such as hydroquinones, catechols, aminophenols, 3-pyrazolidones, phenylenediamines, ascorbic acid derivatives, hydroxylamines, hydrazines, reductones and the like.

Similar good results are obtained in the practice of this invention when the photographic material is a multicolor paper and is processed in the five solution photo-

graphic development process commercially available by its trademarked name as Eastman Kodak Ektaprint C in addition to the three solution bleach and fix development process described herein.

The improvements in color balance, pre-process keeping, and post-process stability of photographic elements by controlling the characteristic density curve shape of the silver halide grains, by the addition of the carboxy-substituted thiazolines or thiazolidines described herein, is further illustrated by the following examples of certain preferred embodiments of my invention.

EXAMPLE I

Several multilayer, multicolor photographic papers are prepared having the following structure borne by a paper support, resin-coated on both sides. The resin is the α -poly-olefin, polyethylene. Over the support, the first layer, comprises silver chlorobromide at a coverage of 50 mg./ft.², gelatin at a coverage of 200 mg./ft.² and a yellow dye forming coupler in a concentration of 150 mg./ft.². The ratio of chloride ions to bromide ions is 12:88. An interlayer of gelatin is coated at 100 mg./ft.² over the yellow layer. The third layer is a magenta layer having a silver chlorobromide coverage of 44 mg./ft.², gelatin of 200 mg./ft.² and a magenta dye forming coupler of 55 mg./ft.². The chloride to bromide ratio is 15:85. An interlayer is coated next containing an ultraviolet absorber in a concentration of 67 mg./ft.² and gelatin at a coverage of 200 mg./ft.². Next a cyan layer is coated having a cyan dye forming coupler in a concentration of 35 mg./ft.², gelatin at a coverage of 157 mg./ft.² and silver chlorobromide coverage of 35 mg./ft.², the ratio of chloride to bromide being 15:85. An overcoat of gelatin is coated over the cyan layer in a coverage of 100 mg./ft.². These silver chlorobromide emulsions contain the converted-halide silver halide grains formed as described more fully in Davey and Knott U.S. Pat. 2,592,250 issued Apr. 8, 1952 and have a solubility less than about 0.02 grams (silver citrate) and preferably a solubility less than about 0.00002 gram (silver thiocyanate) per 100 ml. of water at 20° C. These grains in the yellow layer are only blue sensitive and more than 10 times the blue sensitivity of the red and green sensitive layers, i.e. the cyan and magenta layers.

One coating is made having the above composition and containing 170 mg./mole of silver of benzothiazole methiodide a known antifoggant and emulsion stabilizer shown as compound II. A second coating prepared from the above composition containing 200 mg./mole silver in the magenta layer of 4-carboxymethyl-4-thiazoline-2-thione, shown as compound I.

A third coating is identical to the second but contains no additional compounds in the magenta layer.

Samples of each coating are exposed on an Eastman 1B sensitometer and processed using an 85° F. three solution process described in U.S. patent application Ser. No. 736,010 filed June 11, 1968 by Edens and Van Campen in which the following times are employed: development 3½ minutes, bleach and fix 1 minute, wash 2 minutes and stabilize 1 minute.

The sensitometric results are as follows:

TABLE I

Coating with compound	Blue			Green			Red		
	Relative speed ¹	D _{min.}	D _{max.}	Relative speed ¹	D _{min.}	D _{max.}	Relative speed ¹	D _{min.}	D _{max.}
II.....	100	0.12	2.23	100	0.12	2.31	100	0.10	2.22
	100	0.12	2.25	110	0.12	2.32	105	0.12	2.20
I.....	100	0.11	2.25	102	0.11	2.32	102	0.12	2.22

¹ Compared at a reflection density of 1.0.

This Table I shows that no loss of relative speed occurs when using the curve-shape control addenda of this invention. Neither is there any adverse changes in density.

TABLE II

Coating and compound	$\Delta D_{0.3}$	$\Delta D_{0.5}$
II.....	0.00	0.00
I.....	-0.10	-0.04

Table II shows that there is no difference in toe shape of the curve of the coating containing compound II and the coating not containing any additional compound. The coating containing compound I, as shown by the negative measurements, has a sharper toe than either of the other coatings in its characteristic curve shape as represented by curve intersects of a 0.3 and 0.5 negative shift in log E.

The significance of the measurements of Table II is explained by noting that the green curve which resulted from the coating containing compound II in its magenta layer has a softer toe than does the green curve which results from the coating containing compound I in its magenta layer. The softer toe of the green curve of the comparison coating tends to shift the color balance of highlight areas (such as clouds and white backgrounds) toward a reddish pink, which is undesirable. Sharpening the toe, as accomplished by the addition of compound I to the magenta layer, results in whiter whites and more acceptable color balanced highlights.

EXAMPLE II

In order to demonstrate the unexpected stability of the magenta layer when the curve shape stabilizing addendum is added, tests are conducted on incubation and compared to the fresh coatings. These show (1) no toe softening, employing the addenda of this invention, (2) a shift in color balance accompanied by softening of the toe and shown by the positive values in the following table.

Samples of the coatings from Example I are subjected to the keeping conditions of 120° F. and a relative humidity of 50% for a period of 7 days. Additional samples are kept refrigerated at a temperature of 40° F. and 50% R.H. for the 7 day period.

Samples of these refrigerated and incubated coatings are exposed on an Eastman 1B Sensitometer and processed as in Example I in which the solutions are kept at a temperature of 85° F. The time of development is 6 minutes.

Table III shows the toe density differences of these coatings when compared at a negative log E shift of 0.3 and 0.5 using the technique described in Example I.

TABLE III

7 day keeping	Coating and compound	$\Delta D_{0.3}$	$\Delta D_{0.5}$
40° F./50% R.H.....	None.....		
120° F./50% R.H.....	do.....	+0.02	+0.03
40° F./50% R.H.....	II.....		
120° F./50% R.H.....	II.....	+0.07	+0.03
40° F./50% R.H.....	I.....		
120° F./50% R.H.....	I.....	-0.01	-0.01

¹ Shows softened toe.

² Stable.

EXAMPLE III

In order to demonstrate post processing dye stability and pre-processing keeping, two coated samples are pre-

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pared having the same layer structure as in Example I. The magenta layer of one coating contains 170 mg. of compound II/mole silver while the second coating contains 150 mg./mole silver of the curve-shape stabilizing addenda used in the practice of this invention.

Samples of these two coatings are tested for keeping stability for a period of 24 weeks. One set, a control set, is kept refrigerated at a temperature of 40° F. and 50% R.H. The test set is kept at room temperature (78° F.) and a relative humidity of 50%.

Samples of these refrigerated and incubated coatings are exposed on an Eastman 1B Sensitometer and processed in the three solution process as described in Example I.

TABLE IV

Coating and compound	24 weeks keeping	Relative speed ¹		
		Blue	Green	Red
II.....	40° F./50% R.H.....	100	100	100
II.....	78° F./50% R.H.....	145	123	102
I.....	40° F./50% R.H.....	100	100	100
I.....	78° F./50% R.H.....	110	112	97

¹ Calculated at a reflection density of 1.0.

Stability is easily demonstrated in comparing the 45% speed increase in the blue and 23% increase in the green of compound II with the refrigerated control. In sharp contrast, the addenda used in practicing this invention exhibits only a 10% speed increase in the blue and a 12% speed increase in the green layers.

EXAMPLE IV

In order to demonstrate the unexpected results obtained by the carboxy-substituted thiazolinethione addition to converted-halide silver halide grains and to elements containing said grains, a substantial number of compounds of similar structure and those having known emulsion and grain stabilizing effects are combined in multilayer, green light-sensitive coatings. While some insignificant negative density differences at the log E shifts are noted, only the addition of compound I provides a desirable color balance.

While the range of effectiveness of this stabilizing addenda varies from about 50 to about 500 mg./mole of silver, a preferred range which produces outstanding results is from about 100 to about 300 mg./mole silver.

Several two-layer green, light-sensitive photographic coatings are prepared consisting of a magenta layer which is coated on a polyethylene resin coated paper support having a gelatin protective layer coated over the magenta layer.

Samples of these coatings are exposed on an Eastman 1B Sensitometer and processed by the method described in Example I. Toe density differences are compared at a negative log E shift ΔD of 0.3 and 0.5 using the technique described in Example I.

TABLE V

Compound	Level (g./mole)	D _{min.}	D _{max.}	$\Delta D_{0.3}$	$\Delta D_{0.5}$
4-carboxymethyl-4-thiazoline-2-thione.....	0.20	0.12	2.50	-0.07	-0.04
Benzothiazole methiodide.....	0.17	0.10	2.49
1,15-dibromo-3,5,11,13-tetraxo-6-oxa-4,10,12-triazopentadecane.....	5.00	0.12	2.50	-0.02	-0.02
6,7-dihydro-2-methyl-5H-cyclopenta-pyrimidine-4-(1H)-thione.....	0.20	0.11	2.50	0.00	-0.02
α -Bromo-N-butylcaproamide.....	3.00	0.12	2.48	-0.03	+0.03
4-bromo-N-octylbutyramide.....	3.00	0.11	2.46	-0.01	-0.02
3-(β -N,N'-dimethylcarboxamidoethylthio)-4-phenyl-1,2,4-thiazoline-5-thione.....	0.20	0.11	2.18	+0.03	+0.05
4-formyl-4-thiazoline-2-thione oxime.....	0.20	0.12	2.42	0.00	0.00
4-propionyloxymethyl-4-thiazoline-2-thione.....	0.20	0.12	2.50	+0.04	+0.06
3-(1-carboxy-3-methylthiopropyl)-4-methyl-4-thiazoline-2-thione.....	5.00	0.11	0.17	No curve
1-acetyl-5,5-dimethyl-2-thiohydantoin.....	0.20	0.12	2.50	+0.02	0.00
1-acetyl-5-ethyl-5-methyl-2-thiohydantoin.....	0.20	0.11	2.51	0.00	+0.02

EXAMPLE V

In order to demonstrate the effectiveness of certain other carboxy substituted thiazolinethione and thiazolidines set forth below a series of two layers, green, light sensitive photographic coatings supported on a resin-coated paper are prepared having a gel coverage of 200 mg./ft.², a magenta dye forming coupler in a concen-

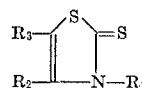
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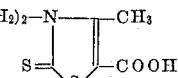
tration of 55 mg./ft.² and a converted-halide silver chlorobromide concentration of 50 mg./ft.² with a chloride:bromide ratio of 15:85. Over this is coated a gelatin overcoat of 100 mg./ft.².

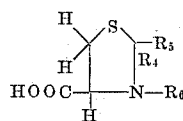
Samples of the coatings of this example are exposed to green light on an Eastman 1B sensitometer and processed by the method described in Example I. Table VI compares the maximum and minimum densities of the coatings containing a curve shape inhibiting compound with a coating not containing said inhibitor. Table VI, further compares toe density differences at a negative log E shift of 0.3 and 0.5 using the technique described in Example I.

TABLE VI

Coating and compound	D _{min.}	D _{max.}	$\Delta D_{0.3}$	$\Delta D_{0.5}$
None.....	0.13	2.41
I.....	0.10	2.38	-0.05	-0.02
XIII.....	0.11	2.44	-0.04	-0.02
XIV.....	0.15	2.45	-0.03	+0.02
XV.....	0.11	2.36	-0.16	-0.08
XVI.....	0.13	2.44	-0.03	-0.02
XVII.....	0.14	2.35	-0.14	-0.08
XVIII.....	0.13	2.42	-0.02	0.00



Compound	R ₁	R ₂	R ₃
I.....	H	-CH ₂ COOH	-H
XIII.....	-(CH ₂) ₂ -N-  -CH ₃	-CH ₃	-COOH
XIV.....	-CH ₂ COOH	-CH ₃	-COOH



Compound	R ₄	R ₃	R ₂
XV.....	-H	-H	-H
XVI.....	-H	-H	-(CH ₂) ₂ CH ₃
XVII.....	-H	-CH ₃	-COOH
XVIII.....	-CHO	-CH ₃	-CH ₃

The significance of the measurements of Table VI can be explained by noting that all the above listed compounds sharpened the toe (indicated by negative numbers) at a 0.3 negative log E shift when compared to the coating not containing a fog inhibiting compound.

EXAMPLE VI

Several multicolor, multilayer photographic materials are prepared according to the general structure described in Example I.

Separate coatings are prepared as described above containing their magenta layer 200 mg. of compound I per

silver mole; 200 mg. of compound XVII per mole of silver; and 200 mg. of compound XV per mole of silver.

Samples of these coatings are exposed on an Eastman 1B sensitometer and processed by the procedure described in Example I.

Table VII further compares the coatings of this example with a coating containing compound II in an amount of 170 milligrams per mole of silver in its magenta layer, the coating described in Example I not containing any additional compound in its magenta layer. The comparisons of Table VII record toe density differences at a negative log E shift of 0.3 and 0.5 using the technique described in Example I.

TABLE VII

Coating and compound	D _{min.}	D _{max.}	ΔD _{0.3}	ΔD _{0.5}
None	0.12	2.32	0.00	0.00
II	0.12	2.31	-0.04	-0.04
I	0.10	2.40	-0.09	-0.06
XVII	0.12	2.42	-0.09	-0.06
XV	0.12	2.50	-0.08	-0.05

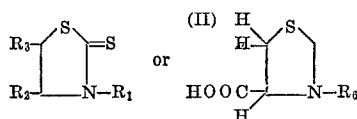
These results indicate that compounds I, XVII and XV sharpened the toe (indicated by the negative numbers) at both negative log E shifts of 0.3 and 0.5.

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.

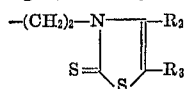
I claim:

1. A photographic element comprising a support having coated thereon at least three superimposed hydrophilic colloid layers, one of said layers comprising a coupler capable of forming a yellow dye upon color development and surface sensitized converted-halide silver halide grains sensitive to blue radiation; another of said layers comprising a coupler capable of forming a cyan dye upon color development and surface sensitized converted-halide silver halide grains sensitive to red radiation; and another of said layers comprising a coupler capable of forming a magenta dye upon color development, surface sensitized converted-halide silver halide grains sensitive to green radiation and from about 100 to about 300 mg./mole of silver of a carboxy substituted compound selected from the group consisting of

(I)



in which R₁ is hydrogen, carboxymethyl or



each R₂ is alkyl when R₁ is other than hydrogen or is carboxymethyl and each R₃ and R₆ are each hydrogen or acyl, R₄ is hydrogen or methyl and R₅ is hydrogen, carboxyl or lower alkyl, provided at least one of R₁ or R₂ is carboxymethyl; the halide in said converted-halide silver halide grains consisting of at least 50 mole percent

bromide, up to 10 mole percent iodide and any remaining halide being chloride; whereby sharpness is maintained in the toe area of the characteristic *D* log *E* curve.

2. The element of claim 1 wherein the hydrophilic colloid is gelatin.

3. The element of claim 1 wherein the carboxy substituted compound is 4-carboxymethyl-4-thiazoline-2-thione.

4. The element of claim 1 wherein the support is a white reflecting support.

5. The element of claim 1 wherein the red-sensitive layer containing the cyan-forming coupler is the outermost light sensitive layer.

6. The element of claim 1 wherein the blue-sensitive layer is disposed adjacent the support.

7. The element of claim 1 wherein the cyan color-forming coupler is a phenolic compound.

8. The element of claim 1 wherein the magenta color-forming coupler is a pyrazolone.

9. The element of claim 1 wherein the converted-halide silver halide grains are surface sensitized by a sensitizer selected from the group consisting of sulfur, selenium and tellurium.

10. A photographic element comprising a white reflecting support having coated thereon at least three superimposed gelatin layers, the layer adjacent the white reflecting support comprising a coupler capable of forming a yellow dye upon color development and sulfur, selenium or tellurium surface sensitized converted-halide silver halide grains sensitive to blue radiation; an outermost light sensitive layer comprising a phenolic coupler capable of forming a cyan dye upon color development and sulfur, selenium or tellurium surface sensitized converted-halide silver halide grains sensitive to red radiation; and another layer comprising a pyrazolone coupler capable of forming a magenta dye upon color development, sulfur, selenium or tellurium surface sensitized converted-halide silver halide grains sensitive to green radiation and from about 100 to about 300 mg./mole of silver of 4-carboxymethyl-4-thiazoline-2-thione; the halide in said converted-halide silver halide grains consisting of at least 50 mole percent bromide, up to 10 mole percent iodide and any remaining halide being chloride; whereby sharpness is maintained in the toe area of the characteristic *D* log *E* curve.

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U.S. Cl. X.R.

96-56, 67, 95, 100, 107, 109