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# [54] PHOTOGRAPHIC MATERIALS CURVE SHAPE STABILIZED WITH CARBOXY SUBSTITUTED 4-THIOURACILS

[75] Inventor: **Thomas Irving Abbott**, Rochester, N.Y.

[73] Assignee: **Eastman Kodak Company**, Rochester, N.Y.

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[21] Appl. No.: **303,295**

**Related U.S. Application Data**

[63] Continuation-in-part of Ser. No. 37,323, May 14, 1970.

[52] **U.S. Cl.** ........................... **96/74,** 96/45.1, 96/82, 96/84 UV, 96/100, 96/109
[51] **Int. Cl.** ........................... **G03c 1/84,** G03c 7/32
[58] **Field of Search** ............ 96/74, 109, 45.1, 94 R, 96/82, 84

[56] **References Cited**

UNITED STATES PATENTS

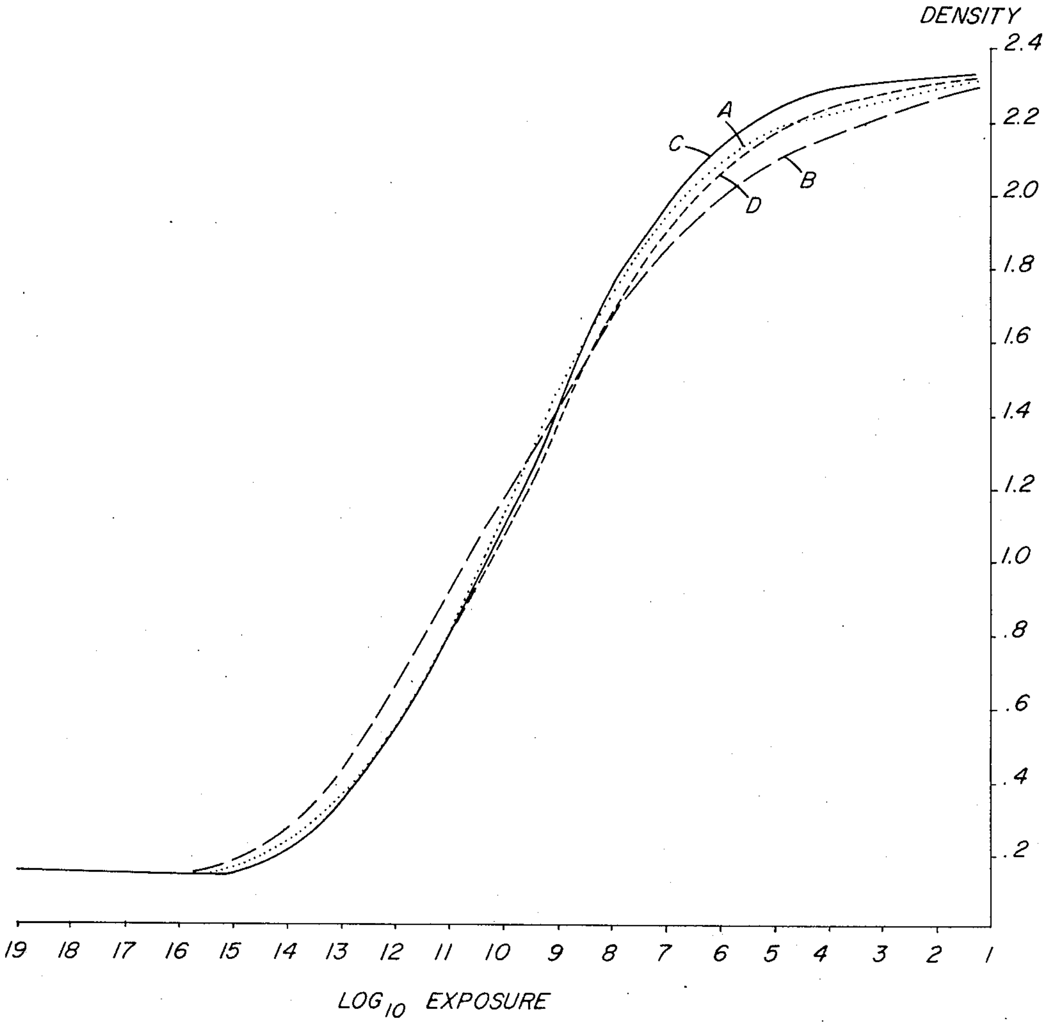
| | | | |
|---|---|---|---|
| 2,319,090 | 5/1943 | Sheppard et al. | 96/109 |
| 2,592,250 | 4/1942 | Davey et al. | 96/94 R |
| 3,226,233 | 12/1965 | Agruss | 96/82 |

*Primary Examiner*—David Klein
*Assistant Examiner*—Alfonso T. Suro Pico
*Attorney, Agent, or Firm*—C. O. Thomas

## [57] ABSTRACT

Photographic layers, emulsions and elements comprising them are stabilized against color balance distortion by addition of carboxy substituted 4-thiouracils. Specific examples of stabilizers include 1-carboxyalkyl 5(-H)-4-thio-cyclopenta-(d)-uracil.

**14 Claims, 1 Drawing Figure**



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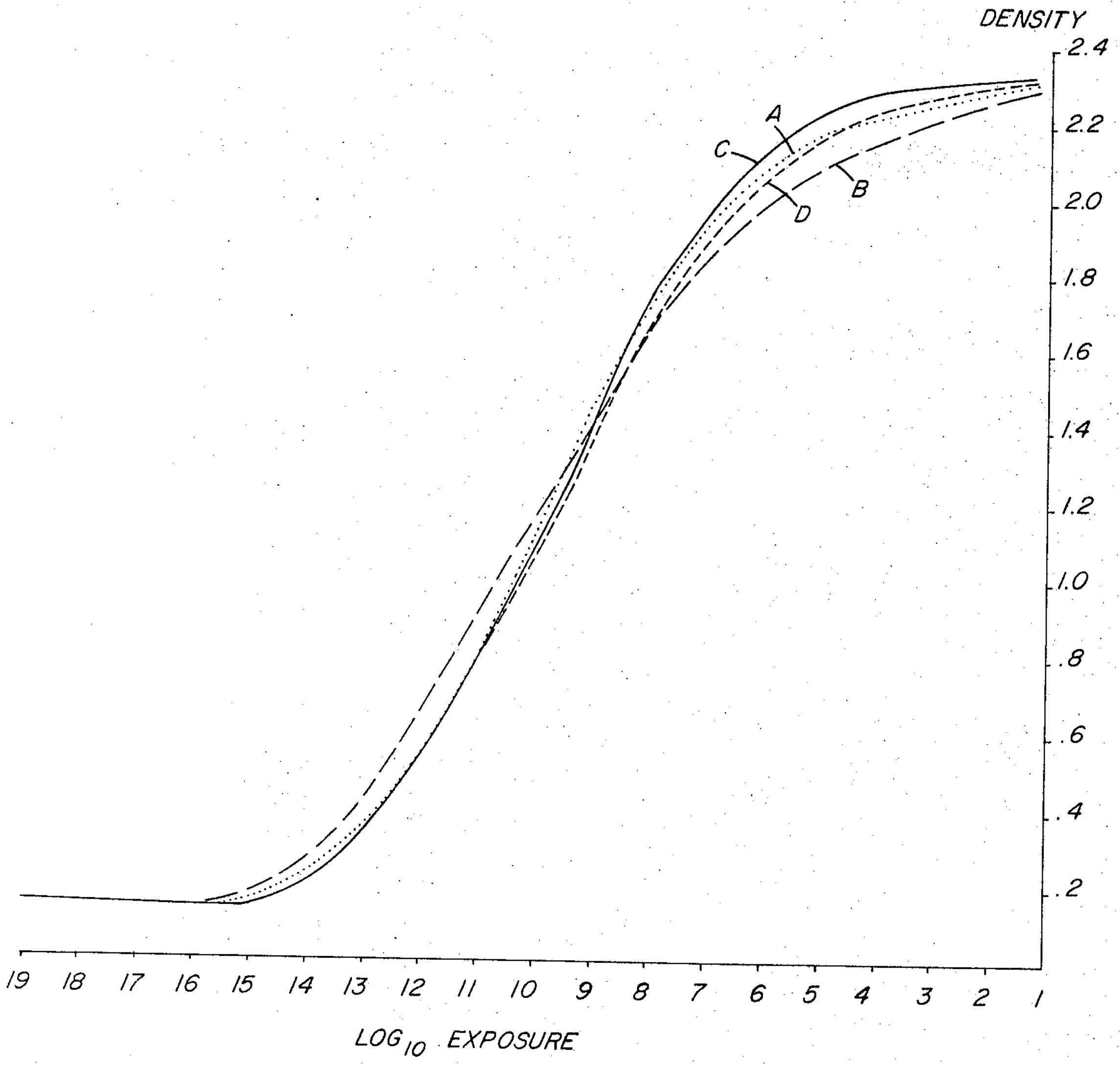


# PHOTOGRAPHIC MATERIALS CURVE SHAPE STABILIZED WITH CARBOXY SUBSTITUTED 4-THIOURACILS

## CROSS-REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of U.S. Pat. application Ser. No. 37,323 filed May 14, 1970, now Defensive Publication T882,019 published Jan. 26, 1971.

## BACKGROUND OF THE INVENTION

### 1. 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 4-thiouracil. In another aspect, this invention relates to multilayer, multicolor photographic elements to which are added stabilizing addenda in order to provide true color balance.

### 2. 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 reproduce faithfully 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, aging 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 D log E 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 variations 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 difference in reciprocity effect in each of the color-containing layers.

Differences of toe softness or sharpness of the characteristic D log E 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 litte as a 0.02 change in the toe density area is far more critical than a 0.10 change in density in the 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 while or highlighted areas, such as set forth in U.S. Pat. No. 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. No. 2,592,250 issued Apr. 8, 1952.

A method of stabilizing photographic materials comprising a light sensitive gelatin silver halide emulsion is described in U.S. Pat. No. 2,232,707 issued Feb. 25, 1941 to Kendall employing 2-mercapto-4-hydroxy pyrimidines, their alkyl, aryl and aralkyl substitution derivatives, their tautomeric compounds and their alkali metal and ammonium salts. In particular, thiouracil and methyl thiouracil are disclosed.

U.S. Pat. No. 3,622,340 issued Nov. 23, 1971 to Lamon discloses 4-thiouracil compounds, including carboxy substituted 4-thiouracils, and their usefulness as photographic fog inhibitors.

## SUMMARY OF THE INVENTION

The present invention comprises a photographic element comprising a support, surface sensitized converted-halide silver halide grains in which the halide consists of at least about 50 mole percent bromide and up to about 10 mole percent iodide, the remaining halide being chloride and a member selected from carboxy substituted 4-thiouracils present in sufficient concentration to control the characteristic curve shape of said halide grains.

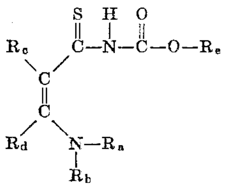
More particularly, the present invention comprises a photographic element comprising a support having coated thereon at least three superimposed hydrophilic colloid layers, one of said layers comprising a coupler capable of forming a cyan dye upon color development and surface sensitized converted-halide silver halide grains sensitive to red radiation; another of said layers comprising a coupler capable of forming a magenta dye upon color development and surface sensitized converted-halide silver halide grains sensitive to green radiation; and another of said layers comprising a coupler capable of forming a yellow dye upon color development, surface sensitized converted-halide silver halide grains sensitive to blue radiation and from about 50 to about 500 mg./mole of silver of at least one carboxy substituted 4-thiouracil; the halide in said converted-halide silver halide grains consisting of at least about 50 mole percent bromide, up to about 10 mole percent iodide and any remaining halide being chloride; whereby control of the characteristic D log E curve shape is improved and stability on keeping and $D_{max}$ are increased.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

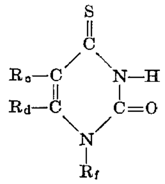
In accordance with this invention, there is now provided a photographic element comprising a support, surface sensitized converted-halide silver halide grains, and a carboxy substituted 4-thiouracil. The thiouracil is present in the element in a concentration sufficient to control the characteristic optical density curve shape so as to maintain the color balance, preprocess keeping and post-process dye stability. The element can suitably comprise a hydrophilic colloid layer, such as one containing aminecontaining synthetic or natural polymers, such as gelatin, for example. Other colloids which can be used as partial or complete gel-substitutes can also, of course, be employed.

It has now been found that these desirable properties of stability and color balance can be effectively obtained by utilizing aromatic heterocyclic compounds selected from the group consisting of carboxy substituted 4-thiouracils.

These thiouracils are prepared by techniques well known in the art. For example, a general method of preparation has been described by Lamon in U.S. Pat. No. 3,622,340 issued Nov. 23, 1971 wherein an amine is reacted with an adduct having the general formula

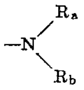


to form a 4-thiouracil having the formula

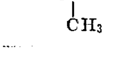


wherein $R_a$, $R_b$, $R_c$, $R_d$, $R_e$ and $R_f$ have the following meanings:

$R_a$ and $R_b$ each represent an alkyl group, such as methyl, ethyl, propyl, butyl, isopropyl, pentyl, hexyl, for example, especially a lower alkyl group of 1 to 6 carbon atoms and a benzene nucleus, and wherein



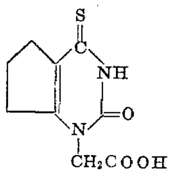
collectively represents a saturated 5 or 6 membered heterocyclic nucleus such as 1-pyrrolidinyl, piperidino, morpholino, 1-pyrazolidinyl and 3-oxazolidinyl, for example; $R_c$ represents hydrogen, lower alkyl, lower alkoxy, carb (lower alkoxy) and a benzene nucleus; $R_d$ is hydrogen or lower alkyl, and $R_c$ and $R_d$ collectively represent a polymethylene chain having at least two carbon atoms, such as ethylene ($-CH_2CH_2-$), trimethylene ($-CH_2CH_2CH_2-$), tetramethylene ($-CH_2CH_2CH_2CH_2-$), pentamethylene ($-CH_2CH_2CH_2CH_2CH_2-$), and hexamethylene ($-CH_2CH_2CH_2CH_2CH_2CH_2-$), for example, and thus together with the carbon atoms to which they are attached represent a cyclobutenylene nucleus, a cyclopentenylene nucleus, a cyclohexenylene nucleus, a cycloheptenylene nucleus and a cyclooctenylene nucleus, for example; $R_e$ represents an alkyl group, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, hexyl, octyl, decyl, etc., for example, especially a lower alkyl group; and $R_f$ represents carboxyl group-containing moiety such as, for example, $-COOH$, $-CH_2COOH$, $-CH_2CH_2COOH$, $-CH_2CH_2CH_2COOH$,



$$-CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCOOH$$

and the like.

Especially prefered as the carboxy substituted 4-thiouracil for use in the practice of this invention is 1-carboxymethyl-5H-4-thiocyclopenta(d)uracil having the formula:



The amine condensation reaction referred to above is effected in solution or suspension and preferably is conducted with agitation or stirring. The presence of an inert solvent is desirable but not required and suitable solvents include water, dimethyl formamide and alcohols, such as ethanol, n-propyl alcohol and isopropyl alcohol for example. The reaction takes place without the necessity of heat and can be carried out effectively at ambient temperatures. The reaction mixture is usually cooled just prior to filtering in order to insure maximum recovery of the precipitate. While cooling is common practice, it is not part of the reaction per se.

As will be understood by those skilled in the art, the presence of the characteristic D log E 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.

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. 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 being 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, such silver halide grains can be prepared by forming a silver salt which is (1) more soluble in water than silver bromide and (2) has a solubility of less than about 0.02 gram, 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, 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, potassium thiocyanate, and the like 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. The useful silver halide grains thus include silver bromide, silver bromoiodide, silver chlorobromide and silver chlorobromoiodide. One method for preparing emulsions of the general type employed in this invention is more fully described by Davey and Knott, U.S. Pat. No. 2,592,250 issued Apr. 8, 1952.

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

The 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, well known to those skilled in the art as the H and D curve or the D log E curve, 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 essential 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.

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 virtue of the present invention, the curve toe is maintained providing the desired improved color balance highlights.

The converted-halide silver halide grains employed in this invention are chemically sensitized at least on their surfaces by any means suitable for this purpose, many methods having been previously described in the prior art. Chemical sensitization, as used herein, includes sensitization of the type described by Antoine Hautot and Henri Saubenier in *Science et Industries Photographiques*, Vol. XXVIII, January, 1957, pp. 1–23 and January, 1957, pp. 57–65. Such chemical sensitization includes four major classes, viz., gold or noble metal sensitization, sulfur sensitization, such as by a labile sulfur compound, selenium sensitization such as by a labile selenium 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.

Emulsions containing the converted-halide silver halide grains can be digested with naturally active gelatin, or compounds of the sulfur group can be added, such as those described in Sheppard et al. U.S. Pat. Nos. 1,574,944 issued Mar. 2, 1926; 1,623,499 issued Apr. 5, 1927; and 2,410,589 issued Nov. 5, 1946. Particularly good results are obtained with sulfur, selenium or tellurium sensitizers.

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

The converted-halide silver halide grains can also be chemically sensitized with gold salts as described in Waller et al. U.S. Pat. No. 2,399,083 issued Apr. 23, 1946 and Damschroder et al. U.S. Pat. No. 2,642,361 issued 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. No. 2,487,850 issued Nov. 15, 1949), polyamines, such as diethylene triamine (Lowe and Jones U.S. Pat. No. 2,518,698 issued Aug. 15, 1950), polyamines, such as spermine (Lowe and Allen U.S. Pat. No. 2,521,925 issued Sept. 12, 1950), or bis ($\beta$-aminoethyl)sulfide and its water-soluble salts (Lowe and Jones U.S. Pat. No. 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-pyrazolone, heterocyclic and openchain ketomethylene compounds. Specific cyan, magenta and yellow color couplers which can be used, respectively, in the cyan, magenta, and yellow dye-forming units of the invention are described in Graham et al. U.S. Pat. No. 3,046,129 issued July 24, 1962, column 15, line 45 through column 18, line 51, which disclosure is incorporated herein by reference. Other suitable couplers are described in Salminen et al. U.S. Pat. No. 2,423,730 issued July 8, 1947; Loria et al. U.S. Pat. No. 2,600,788 issued June 17, 1952; DeMaria U.S. Pat. No. 2,875,051 issued Feb. 24, 1959; Bush et al. U.S. Pat. No. 2,908,573 issued Oct. 13, 1959; Weissberger et al. U.S. Pat. No. 3,265,506 issued Aug. 9, 1966; Greenhalgh et al. U.S. Pat. No. 3,127,269 issued Mar. 31, 1964; Loria U.S. Pat. No. 3,408,194 issued Oct. 29, 1968 and Lestina Belgian Pat. No. 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. No. 2,322,027 issued June 15, 1943 or Fierke and Chechak U.S. Pat. No. 2,801,171 issued July 30, 1957. The useful couplers include Fischer-type incorporated couplers such as those disclosed in Fischer U.S. Pat. No. 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. No.

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. No. 3,046,129 issued July 24, 1962, columns 23 and 24, or by the development process described by Edens et al. U.S. Pat. No. 3,582,322 issued June 1, 1971 which features a color process in which the color development step is followed with a bleach-fix bath comprising silver halide solvent and an oxidizing agent for silver. The disclosure of the Edens et al. patent 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 readily 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) pp. 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, such as a benzotriazole, e.g., 2-(2-hydroxy-3,5-di-tert-amylphenyl)benzotriazole. 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.

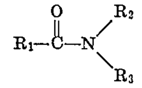
The multilayer color-producing elements of the invention preferably comprise blue-, green- and red-sensitive silver halide emulsion layers. As is well known, silver halide emulsions are typically sensitive to blue radiation, although additional sensitizing dyes absorbing in the blue region can also be 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. No. 2,526,632 issued Oct. 24, 1950; Sprague U.S. Pat. No. 2,503,776 issued Apr. 11, 1950; Brooker et al. U.S. Pat. No. 2,493,748 issued Jan. 10, 1950; and Taber et al. U.S. Pat. No. 3,384,486 issued May 21, 1968. Spectral sensitizers which can be used include the cyanines, merocyanines, complex (tri or tetranuclear) merocyanines, complex (tri or tetranuclear) cyanines, holopolar cyanines, styryls, hemicyanines (e.g. enamine hemicyanines), oxonols and hemioxonols. Dyes of the cyanine classes may contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenozoles and imidazoles. Such nuclei may contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl and enamine groups and may be fused to carbocyclic or heterocyclic ring sytems 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 substitutents on the methine or polymethine chain. The merocyanine dyes may contain the basic nuclei mentioned above as well as acid nuclei such as thiohydantoins, rhodanines, 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. No. 2,933,390 issued Apr. 19, 1960 and Jones et al. U.S. Pat. No. 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 in Belgian Pat. No. 729,204 of Aug. 28, 1969, and Schwan et al. U.S. Pat. No. 3,672,898 issued June 27, 1972.

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 in the form of a dispersion as described in Owens et al. British Pat. No. 1,154,781 of June 11, 1969. 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 layers are deposited by vacuum or laid-down in emulsion form, for example.

As will be more fully set forth by the examples which follow, a photographic element embodying a preferred aspect 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 colloidcontaining 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 4-thiouracil is contained in the blue-radiation-sensitive, i.e., yellow-forming, layer. 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, preferably from about 50 to about 250 mg/mole of silver.

A photographic element comprising the present invention can likewise contain water-insoluble, organic fluorescent agents dispersed in an amide solvent having the formula



$$R_1-\overset{O}{\overset{\|}{C}}-N\begin{matrix} R_2 \\ R_3 \end{matrix}$$

wherein $R_1$ is alkyl, aryl or aralkyl and $R_2$ and $R_3$ each are independently selected from the group consisting of hydrogen, alkyl, aryl and aralkyl, the sum of the carbon atoms in $R_1$, $R_2$ and $R_3$ being at least 6 and preferably 14. By "alkyl" is meant univalent radicals derived from alkanes, such as, for example, those of from one to 12 carbon atoms, such as methyl, ethyl, isopropyl, butyl, pentyl, decyl, dodecyl and the like. By "aryl" is meant those aromatic radicals corresponding to the aliphatic alkyl radicals above, such as methyl benzene, ethyl benzene, isopropyl benzene and the like. Likewise, the term "aralkyl" will be understood to describe an arylated alkyl moiety, such as alphyl for example. All of said described radicals being, in turn, capable of further substitution.

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 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 couplercontaining layers with 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. No. 2,886,437 issued May 12, 1959; Dann et al. U.S. Pat. No. 3,046,134 issued July 24, 1962; Carroll et al. U.S. Pat. No. 2,944,900 issued July 12, 1960; and Goffe U.S. Pat. No. 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. No. 2,131,038 issued Sept. 27, 1938 and Allen et al. U.S. Pat. No. 2,694,716 issued Nov. 16, 1954; the azaindenes described in Piper U.S. Pat. No. 2,886,437 issued May 12, 1959, and Heimbach et al. U.S. Pat. No. 2,444,605 issued July 6, 1948; the mercury salts as described in Allen et al. U.S. Pat. No. 2,728,663 issued Dec. 27, 1955; the urazoles described in Anderson et al. U.S. Pat. No. 3,287,135 issued Nov. 22, 1966; the sulfocatechols described in Kennard et al. U.S. Pat. No. 3,236,652 issued Feb. 22, 1966; the oximes described in Carroll et al. British Pat. No. 623,448; nitron; nitroindazoles; the mercaptotetrazoles described in Kendall et al. U.S. Pat. No. 2,403,927 issued July 16, 1946; Kennard et al. U.S. Pat. No. 3,266,897 issued Aug. 16, 1966 and Luckey et al. U.S. Pat. No. 3,397,987 issued Aug. 20, 1968; the polyvalent metal salts described in Jones U.S. Pat. No. 2,839,405 issued June 17, 1958; the thiuronium salts described in Herz et al. U.S. Pat. No. 3,220,839 issued Nov. 30, 1965; the palladium, platinum and gold salts described in Trivelli et al. U.S. Pat. No. 2,566,263 issued Aug. 28, 1951 and Yutzy et al. U.S. Pat. No. 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 phenylenediamines. 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. No. 2,592,368 issued Apr. 8, 1952 and Dunn et al. French Pat. No. 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. No. 3,142,568 issued July 28, 1964; White U.S. Pat. No. 3,193,386 issued July 6, 1965; Houch et al. U.S. Pat. No. 3,062,674 issued Nov. 6, 1962; Houck et al. U.S. Pat. No. 3,220,844 issued Nov. 30, 1965; Ream et al. U.S. Pat. No. 3,287,289 issued Nov. 22, 1966; and Dykstra U.S. Pat. No. 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. No. 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. No. 2,861,056 issued Nov.

18, 1958 and Sterman et al. U.S. Pat. No. 3,206,312 issued Sept. 14, 1965 or insoluble inorganic salts such as those described in Trevoy U.S. Pat. No. 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 on one or both sides with baryta and/or an alpha-olefin polymer, particularly a polymer of an alpha-olefin containing two to 10 carbon atoms such as polyethylene, polypropylene, ethylenebutene copolymers and the like.

The 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. No. 2,960,404 issued Nov. 1. 1966; fatty acids or esters such as those described in Robijns U.S. Pat. No. 2,588,765 issued Mar. 11, 1952 and Duane U.S. Pat. No. 3,121,060 issued Feb. 11, 1964; and silicone resins such as those described in DuPont British Pat. No. 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. No. 2,600,831 issued June 17, 1962; amphoteric compounds such as those described in Ben-Ezra U.S. Pat. No. 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. No. 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. No. 2,992,101 issued July 11, 1961 and Lynn U.S. Pat. No. 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. No. 972,067 and McFall et al. U.S. Pat. No. 2,933,390 issued Apr. 19, 1960 or dispersions of brighteners may be used such as those described in Jansen German Pat. No. 1,150,274, Oetiker et al. U.S. Pat. No. 3,406,070 issued Oct. 15, 1968 and Heidke French Pat. No. 1,530,244 and VanCampen U.S. Pat. No. 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. No. 3,252,921 issued May 31, 1966; Gaspar U.S. Pat. No. 2,274,782 issued Mar. 3, 1942; Silberstein et al. U.S. Pat. No. 2,527,583 issued Oct. 31, 1950 and VanCampen U.S. Pat. No. 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. No. 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. No. 2,912,343 issued Nov. 10, 1959; McCrossen et al. U.S. Pat. No. 3,342,605 issued Sept. 19, 1967; Audran U.S. Pat. No. 2,996,287 issued Aug. 15, 1961 and Johnson et al. U.S. Pat. No. 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. No. 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. No. 2,761,791 issued Sept. 4, 1956 and Wynn British Pat. No. 837,095. This invention also can be used for silver halide layers coated by vacuum evaporation as described in British Pat. No. 968,453 and LuValle et al. U.S. Pat. No. 3,219,451 issued Nov. 23, 1965.

As fully disclosed above and in a preferred embodiment, this invention can be used with elements designed for color photography, for example, elements containing color-forming couplers such as those described in Frohlich et al. U.S. Pat. No. 2,376,679 issued May 22, 1945; Jelley et al. U.S. Pat. No. 2,322,027 issued June 15, 1943; Fierke et al. U.S. Pat. No. 2,801,171 issued July 30, 1957; Godowsky U.S. Pat. No. 2,698,794 issued Jan. 4, 1955; Barr et al. U.S. Pat. No. 3,227,554 issued Jan. 4, 1966; and Graham et al. U.S. Pat. No. 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. No. 2,252,718 issued Aug. 19, 1941; Carroll et al. U.S. Pat. No. 2,592,243 issued Apr. 18, 1952; and Schwan et al. U.S. Pat. No. 2,950,970 issued Aug. 30, 1966; and in false-sensitized color materials such as those described in Hanson U.S. Pat. No. 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, hydroazines, reductones and the like; web processing such as described in Tregillus et al. U.S. Pat. No. 3,179,517 issued Apr. 20, 1965; stabilization processing as described in Russell et al. "Stabilization Processing of Films and Papers," *PSA Journal*, Vol. 16B, August, 1950; monobath processing as described in Levy "Combined Development and Fixation of Photographic Images with Monobaths," *Phot. Sci. and Eng.*, Vol. 2, No. 3, October, 1958, and Barnes et al. U.S. Pat. 3,392,019 issued July 9, 1968. If desired, the photographic elements of this invention can be processed in hardening developers such as those described in Allen et al. U.S. Pat. No. 3,232,761 issued Feb. 1, 1966; in roller transport processors such as those described in Russell et al. U.S. Pat. No. 3,025,779 issued Mar. 20, 1962; or by surface application processing as described in Example 3 of Kitze U.S. Pat. No. 3,418,132 issued Dec. 24, 1968.

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

The improvements in color balance, preprocess 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 4-thiouracils described herein, are further illustrated by the following example which is included for further understanding of the invention.

## EXAMPLE 1 (Control)

A multi-layer, multi-color photographic paper is prepared having the following structure borne by a polyethylene coated paper support. Over the support, the first layer comprises a surface sensitized converted-halide silver chlorobromide emulsion at a coverage of 50 mg per square foot, gelatin at a coverage of 200 mg per square foot, a yellow dye forming coupler at a coverage of 150 mg per square foot and 85 mg per mole of silver of benzothiazole methiodide (Compound I). The silver chlorobromide emulsion is prepared according to Example 2 of U.S. Pat. No. 3,622,318 issued Nov. 23, 1971 to Evans. The ratio of chloride ions to bromide ions is 12:88. An interlayer of gelatin is coated at 100 mg per square foot over the yellow layer. The third layer comprises a surface sensitized converted halide silver chlorobromide emulsion at a coverage of 44 mg per square foot, gelatin having a coverage of 200 mg per square foot, 200 mg per silver mole of 4-carboxymethyl-4-thiazoline-2-thione as described in Belgian Pat. No. 764,572 issued May 14, 1971 and a magenta dye forming coupler having a coverage of 55 mg per square foot. This emulsion is prepared according to Example 1 of U.S. Pat. No. 3,622,318 and the chloride to bromide ratio is 15:85. An interlayer is coated next containing an ultraviolet absorber in a concentration of 67 mg per square foot and gelatin at a coverage of 200 mg per square foot. The fifth layer comprises a surface sensitized converted halide silver chlorobromide emulsion at a coverage of 35 mg per square foot, gelatin at a coverage of 157 mg per square foot and a cyan dye forming coupler at a coverage of 35 mg per square foot. The silver chlorobromide emulsion is prepared according to Example 1 of U.S. Pat. No. 3,622,318 and has a ratio of chloride to bromide of 15:85. Finally, an overcoat of gelatin is coated over the cyan layer in a coverage of 100 mg per square foot. The grains in the yellow layer are spectrally sensitized to blue light. The grains in the cyan and magenta layers are spectrally sensitized to red and green light, respectively.

## EXAMPLE 2

Example 1 is repeated except that 50 mg per silver mole of 1-carboxymethyl-5H-4-thiocyclopenta(d)-uracil (Compound II) is substituted for the 85 mg per silver mole of benzothiazole methiodide employed therein.

## EXAMPLE 3

Samples of the coatings prepared in Examples 1 and 2 are subjected to the following keeping tests. One sample of each coating is kept for 16 weeks at room temperature (25°C) and a relative humidity of 50 percent. A second sample of each coating is kept refrigerated (temperature 3°C and relative humidity 50 percent) for a 16-week period and are used as keeping checks.

Samples of these refrigerated and incubated coatings are exposed on an Eastman 1B sensitometer and processed in a 3 solution bleach-fix process in which the solutions are kept at a temperature of 29°C. The total time of development is 3½ minutes, bleach-fix time is 1½ minutes, washing is 2 minutes and stabilizing is 1 minute.

The figure is a comparison of the blue curves of the samples of this Example (both refrigerated and shelf-kept samples). Curve A represents the control sample from Example 1 held for 16 weeks at 3°C and 50 percent relative humidity. Curve B represents the control sample from Example 1 held for 16 weeks at 25°C and 50 percent relative humidity. Curve C represents the sample prepared in accordance with the present invention (Example 2 ) held for 16 weeks at 3°C and 50 percent relative humidity. Curve D represents the sample prepared according to the present invention (Example 2) held for 16 weeks at 25°C and 50 percent relative humidity. It can be observed that the control coating containing Compound I in its yellow layer increases in blue speed and loses density in the shoulder upon keeping, both undesirable characteristics. The coating prepared according to the present invention containing Compound II in its yellow layer, upon keeping, has not gained nor lost any blue speed; and, although it loses density in the shoulder, it does not lose as much density as does the coating containing Compound I. Therefore, it has been demonstrated that Compound II succeeds in stabilizing the yellow layer upon keeping.

## EXAMPLE 4

Example 2 is repeated except that 50 mg per mole of silver of 1-carboxyethyl-5H-4-thiocyclopenta(d)uracil is substituted for the 1-carboxymethyl-5H-4-thiacyclopenta(d)uracil uracil employed therein. Upon being subjected to the tests set forth in Example 3 above, results equivalent to those of the carboxymethyl compound are obtained.

## EXAMPLE 5

Example 2 is repeated except that 50 mg. per mole of silver of 1-carboxypropyl-5H-4-thiocyclopenta(d)-uracil is substituted for the carboxymethyl compound employed therein. Again, upon subjection to the tests set forth in Example 3 above, results equivalent to those obtained with the carboxymethyl compound are obtained.

It will be understood by those skilled in the art that other carboxy substituted 4-thiouracils produced could result in controlling curve shapes such as those particular compounds set forth above.

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

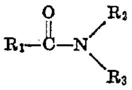
What is claimed is:

**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 cyan dye upon color development and surface sensitized converted-halide silver halide grains sensitive to red radiation; another of said layers comprising a coupler capable of forming a magenta dye upon color development and surface sensitized converted-halide silver halide grains sensitive to green radiation; and another of said layers comprising a coupler capable of forming a yellow dye upon color development, surface sensitized converted-halide silver halide grains sensitive to blue radiation and from about 50 to about 500 mg/mole of silver of at least one carboxy substituted 4-thiouracil; the halide in said converted-halide silver halide grains consisting of at least about 50 mole percent bromide, up to about 10 mole percent iodide and any remaining halide being chloride; whereby control of the characteristic D log E curve shape is improved and stability on keeping and $D_{max}$ are increased.

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

**3.** The element of claim **1** wherein the carboxy substituted 4-thiouracil is 1-carboxymethyl-5H-4-thiocyclopenta-(d)uracil.

**4.** The element of claim **1** wherein at least one hydrophilic colloid layer comprises a dispersion of a water-insoluble organic fluorescent agent in a solvent having the following formula:



wherein $R_1$ is selected from the group consisting of alkyl, aryl and aralkyl, and each of $R_2$ and $R_3$ is hydrogen, alkyl, aryl or aralkyl, the sum of the carbon atoms in $R_1$, $R_2$ and $R_3$ being at least 6.

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

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

**7.** The element of claim **6** wherein the red-sensitive layer containing the cyan-forming coupler is the outermost light sensitive layer.

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

**9.** The element of claim **7** wherein the blue-sensitive layer is disposed adjacent the support.

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

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

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

**13.** A photographic element comprising a support having coated thereon at least three superimposed hydrophilic colloid layers, the layer adjacent the support comprising a coupler capable of forming a yellow dye upon color development, surface sensitized converted-halide silver halide grains sensitive to blue radiation and from about 50 to about 500 mg/mole of silver of at least one carboxy substituted 4-thiouracil; an outermost light sensitive layer 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 layer comprising a coupler capable of forming a magenta dye upon color development and surface sensitized converted-halide silver halide grains sensitive to green radiation; the halide in said converted-halide silver halide grains consisting of at least about 50 mole percent bromide, up to 10 mole percent iodide and any remaining halide being chloride; whereby control of the characteristic D log E curve shape is improved and stability on keeping and $D_{max}$ are increased.

**14.** A photographic element comprising a white reflecting support having coated thereon at least three super-imposed gelatin layers, the layer adjacent the white reflecting support comprising a coupler capable of forming a yellow dye upon color development, sulfur, selenium or tellurium surface sensitized converted-halide silver halide grains sensitive to blue radiation and from about 50 to about 500 mg/mole of silver of 1-carboxymethyl-5H-4-thiocyclopenta(d)uracil; 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; 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 control of the characteristic D log E curve shape is improved and stability on keeping and $D_{max}$ are increased.

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