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PHOTOGRAPHIC COLOR REVERSAL FILMS

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No Drawing. Continuation-in-part of application Ser. No. 301,964, Aug. 14, 1963. This application Aug. 7, 1964, Ser. No. 388,282
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Int. Cl. G03c 7/00

ABSTRACT OF THE DISCLOSURE

Multilayer color films comprising a film support bearing, in order, a red-sensitive silver halide layer containing a cyan color former, a green-sensitive silver halide layer containing a magenta color former, a yellow filter layer, a blue-sensitive silver halide layer containing a yellow color former, the color formers being nondiffusing, and an antiabrasion layer, there being present in one of the contiguous layers a bisulfite ion, salts thereof or complexes thereof with a water-soluble organic carbonyl compound and a water-soluble silver halide developing agent of the hydroxybenzene or organic amine type.

This application is a continuation-in-part of our prior application Ser. No. 301,964, filed Aug. 14, 1963, now abandoned.

This invention relates to color photography. More particularly this invention relates to color reversal films for color photography. Still more particularly, this invention relates to color reversal films having improved stability against latent image fading and latent image growth in the respective silver halide record layers.

Color reversal films for color photography are, of course, well known and comprise basically, a film support having coated thereon, in order, a red-sensitive gelatino-silver halide layer containing a cyan color coupler, a green-sensitive gelatino-silver halide layer containing a magenta color coupler, a yellow filter layer; and, finally, a blue-sensitive gelatino silver halide layer containing a yellow color coupler. Other auxiliary layers such as antihalation layers, separator layers and antiabrasion layers may also be present in the element. The art is replete with various types of chemical structures which have been found to be useful as color couplers in color photographic elements. One of the basic requirements of integral color couplers is that they be nondiffusible, that is, they should not be able to migrate from the layer in which they are incorporated to a contiguous layer. Diffusion or wandering is characteristic of many of the known color couplers in their simplest molecular configuration. Attempts to prevent diffusion have taken many forms. One is to attach weighting groups, e.g., large fatty acid groups to the color coupler or color-former molecule. Another method is to encapsulate the molecule in a polymer or similar material which is insoluble in the colloid carrier for the silver halide. Another method which has been found to have many advantages is to attach the color coupler molecule to the carbon chain of a synthetic polymer which is either compatible with or dispersible in the colloid carrier for the silver halide, e.g., gelatin. Representative polymeric color couplers of the compatible type disclosed in McQueen U.S. 2,513,190, dated June 27, 1950, and both hydrophilic and lipophilic types are disclosed in assignee's Firestine et al., U.S. application Ser. No. 21,959, filed Apr. 13, 1960 (U.S. Patent 3,163,625, Dec. 29, 1964). Polymeric color-formers or couplers have been used to make color reversal films such as described in Chu and

Umberger, U.S. Ser. No. 287,746, filed June 14, 1963, now U.S. Patent 3,342,592.

Color reversal films employing the polymeric color-formers of the McQueen and Firestine et al. references are generally so constructed that a substantial amount of the gelatin normally present in the gelatino-silver halide layers is replaced by the polymeric color-former, the polymer acting in the role of color-former and colloid carrier. There also may be present other noncolor-forming polymers which act as flexibilizers for the gelatin and also as colloid carriers. Color film structures embodying these gelatin-polymeric color-former mixtures are disclosed and claimed in Chu et al., U.S. Ser. No. 113,100, filed May 29, 1961, U.S. Patent 3,211,532, Oct. 12, 1965. This patent application discloses and claims color reversal film structures having very thin layers so that the integral emulsion thickness is not more than 12.5 microns. This structure allows one to obtain colored images of very high definition and resolution. The polymeric color-formers are compatible with or dispersible in gelatin and are color-forming vinyl addition polymers containing a plurality of color-former nuclei capable of forming a quinoneimine, azomethine or azo dye on color-coupling development of the silver salt image. The polymeric color-former is usually present in an amount of about 7 to 25 parts by weight per 10 to 30 parts by weight of gelatin. The color-former nuclei are extralinear, being linked to a carbon atom of a wholly carbon chain by various linkages including amide, ether and cyclic acetal linkages. In the case of the yellow layer, because of the low tinctorial strength of the yellow dye, it is desirable to replace a larger quantity of the gelatin with the polymeric color-former than is necessary in the case of the magenta and cyan layers to obtain a maximum density which is in balance with magenta and cyan maximum densities.

Photographic color films having the general structure described above are used to a large extent in 8 mm. cine and 35 mm. miniature cameras. The exposure of films such as described above quite often result in different frames being exposed at different times for any particular roll of film. For example, the user may expose a portion of a roll at one time and another portion or the remainder of the roll at another and later time. In other words, a roll of film may have a series of latent images, some or all of which have been exposed at different times. This is in addition to the fact that, quite frequently, a relatively long period of time may elapse between exposure of the film and development. It is obvious, therefore, that latent image stability is important, particularly in color reversal films where color balance of several emulsion layers depends in a large measure on this stability. Latent image stability means that the latent image neither fades nor intensifies or grows between the time of exposure and development. If there is a lack of latent image aging stability, a noticeable color shift in the processed colored image formed in the multilayer film is easily observed visually. For example, on a single roll of color reversal film there may be July 4th exposures and Christmas holiday exposures and any change in the latent image during the six-months' interim leads to undesirable changes in color balance.

It is known that gelatin acts to prevent latent image fading in silver halide systems. [E. E. Loening, "Latent Image Fading in a Silver Bromide Sol." Bristol Symposium, March 1950, Buttersworth, London (1951) p. 149.] It follows therefore, that removal of any substantial amount of gelatin from the system can greatly contribute to latent image fading. This latent image instability may be caused not only by the lower quantities of gelatin but also by the chemical nature of the various color-formers. Because each layer in the above described structures contains color-formers having different chemi-

cal characteristics, it is believed that these different characteristics contribute to the different aging behavior encountered in the various emulsions.

Regardless of the many possible theoretical interpretations, the fact remains that latent image fading is quite detrimental to good color balance, particularly in color reversal elements having thin layers for high definition where a substantial portion of the gelatin has been replaced by polymeric color-formers and by noncolor-forming polymers. In some layers, e.g., those yellow and cyan layers described above containing the ether and acetal type linkages between the polymer chain and the color-former nucleus, latent image fading is most apparent. In other layers, e.g., those magenta layers containing the 3-acrylamidopyrazolone linkage, latent image growth seems to be more frequent than with yellow and cyan color formers which more often tend to fade. In such films it can be appreciated that although fresh latent images may, on development, yield pictures having satisfactory color balance, aged latent images would yield developed images with an undesirable greenish cast or poor color.

It is an object of this invention to provide color reversal photographic films for color photography having improved latent image stability. A further object is to provide color reversal films which will produce images on processing which have good color balance. A still further object is to provide color reversal films having the above characteristics which are simple and easy to construct according to methods well known in the art.

The improved photographic film of this invention has a film support bearing in order on one surface:

(1) A red-sensitive gelatino-silver halide emulsion layer containing a nondiffusing, cyan color former nuclei,

(2) A green-sensitive gelatino-silver halide emulsion layer containing a nondiffusing magenta color former,

(3) A yellow filter layer,

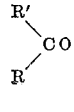
(4) A blue-sensitive gelatino-silver halide emulsion layer containing a nondiffusing yellow color former, and

(5) A water-permeable colloid antiabrasion layer, preferably gelatin.

Said photographic film being characterized in that at least one of the contiguous layers and preferably the antiabrasion layer contains (i) a member selected from the group consisting of a bisulfite ion (e.g., from alkali metal and alkaline earth metal sulfites, bisulfites and metabisulfites) and their complexes with an organic carbonyl compound in admixture or combination with (ii) a photographic silver halide develpoing or reducing agent, preferably an aromatic amino developing agent.

The developing or reducing agent may be either of the hydroxy benzene type, e.g., o-dihydroxy-benzene (catechol); 2,5-dihydroxydiphenyl, hydroquinone, etc., or the aromatic amine type, e.g., monoalkylaminomonohydroxybenzenes, e.g., N-methyl-p-aminophenol (Metol), N-ethyl-p-aminophenol, p-diethylamino aniline, p-dimethylaminoaniline, p-aminoaniline, etc. The reducing compounds are beneficial in controlling the effectiveness of the sulfur compound and allow greater latitude in the quantities of the sulfur compound which may be added. The reducing compounds may be used in the form of the base or in the form of an addition salt, e.g., hydrochloride or sulfate. The salts are preferred because of their stability and solubility in water.

The water-soluble sulfur compound may be sodium or potassium sulfite, bisulfite or metabisulfite or the bisulfites of the alkaline earth metals. The carbonyl compounds which have been found to be useful in forming the above sulfur compound complexes can be represented by the formula

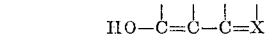


where R and R′ may be hydrogen or lower alkyl or substituted alkyl, e.g., acetone, methyl ethyl ketone, formaldehyde, acetaldehyde, etc. In general, the compounds may be used in quantities ranging from .1 to 1 part of reducing agent per part of sulfur compound; however, this is not critical and other relative quantities may be used.

Suitable color formers for the red-sensitive and green-sensitive silver halide layers include the addition copolymers described in assignee's Umberger application, U.S. Ser. No. 113,101, filed May 29, 1961 (abandoned), Firestine and Umberger, et al., U.S. Ser. No. 21,959, filed Apr. 13, 1960, and corresponding Belgian Patents Nos. 618,202 and 602,516. A class of preferred copolymers are those disclosed and claimed in said applications and patents made from 90–10 parts by weight of the addition polymerizable monomer containing the color former nuclei, and 10–90 parts by weight of one or more hydrophilic or lipophilic vinyl monomers, e.g., acids, esters and/or amides from acrylic, alkacrylic and chloroacrylic acids.

The addition of (i) the water-soluble sulfite or bisulfite compound and (ii) the photographic developing agent to the color film, e.g., to the antiabrasion layer from whence it can distribute throughout the film, gives unexpected results in the multicolor reversal films of the invention in that the addition of the admixture to the above color reversal film corrects either fading or growth of latent image in any of the layers to a commercially acceptable degree.

The particularly favored class of non-diffusing color formers referred to above as being present in the light-sensitive silver halide emulsion layers are macromolecular, that is, of high molecular weight, essentially colorless and contain as an active color-former or color-coupler nucleus, a structure of the formula:



where =X is =CH, =CCl, =CBr, =C—SO$_3$H, or =N

which is a general structure of the color-coupling nucleus in an enol form.

The foregoing nuclei are found in the reactive methylene dye intermediates and in aromatic hydroxyl compounds and include the reactive ethenol groups. These groups occur in phenols, napthols, acylacetamides, cyanoacetyls, betaketoesters, pyrazolones, homophthalimides, coumaranones, indoxyls, thioindoxyls, and indazolones. Useful color formers including those of this structure are described in the applications referred to above.

The above sulfur compounds or complexes may be added to any layer but it is usually most convenient to add it to one of the upper layers, e.g., the antiabrasion or yellow emulsion layers, in amounts of 0.01 to 2.5% based on the weight of the gelatin in the layer to which the mixture or complex is added, these quantities as used being insufficient to exhibit any developing action. The color reversal elements may also be bathed in a solution of the complex or mixture although this is not a preferred method. All of the above compounds, the reducing agents, the sulfur compounds and the carbonyl derivatives thereof may be added separately or as a mixture to the colloid composition to be coated. If the quantities of the sulfur compounds or carbonyl derivatives thereof are carefully controlled within the above limits, the reducing agent will ordinarily be present in amounts of 0.01 to 0.75 mg. per dm.^{2} in the layer. The admixture of a reducing agent is advantageous because of the synergistic effect.

As before mentioned, it is surprising to find that the above additives work to prevent latent image fading in layers which normally fade and to prevent latent image growth in those layers where it may occur, thus correcting the aforementioned green color shift.

The invention will now be illustrated in and by the following examples but it is not intended that the inven-

tion shall be limited thereby except as defined by the claims. The parts and percentages in the text and examples of this application are by weight unless otherwise indicated. Typically the gelatino-silver halide emulsions are coated at or below pH 7.

EXAMPLE I

A color reversal film was made by coating on a cellulose triacetate film support in order, a nonhalation layer of the type disclosed in Firestine and Stevenson, U.S. Ser. No. 183,759, filed Mar. 30, 1962 (abandoned), a red-sensitive, gelatino-silver iodobromide layer containing a cyan color-former; a gelatin separator layer, a green-sensitive, gelatino-silver iodobromide layer containing a magenta color-former; a gelatin, yellow collodial silver filter layer; and finally, a blue-sensitive, gelatino-silver iodobromide layer containing a yellow color-former. Two samples of the resulting film were each coated with an antiabrasion layer, one antiabrasion coating was plain gelatin and a second had added thereto 0.5 gram of Metol and 0.5 gram of acetone sodium bisulfite per 20 grams of gelatin. The antiabrasion layers were coated to give a gelatin coating weight of 10 milligrams per square decimeter, so that they contained 0.25 mg. of Metol and 0.25 mg. of acetone-sodium bisulfite per square decimeter. The cyan emulsions contained approximately 4.7% silver iodide, the remainder being silver bromide. The cyan color-former was that described in Example I of Umberger, U.S. Ser. No. 113,101, filed May 29, 1961 (abandoned), and was present in an amount of 1 part color-former per 1.79 parts of gelatin. The cyan layers were coated to give a coating weight of 39.0 mg. of silver halide per square decimeter. The magenta layers contained 3.4% silver iodide and the magenta color-former was made according to Firestine et al., U.S. Ser. No. 21,959, filed May 29, 1961, and was present in an amount of 1 part color-former per 1.79 parts of gelatin. The magenta layers were coated to give a silver halide coating weight of 24.6 milligrams per square decimeter.

The yellow layers contained 1.7% silver iodide and the yellow color-former was that disclosed in Example II of Chu, Firestine and Umberger, U.S. Ser. No. 113,100, filed May 29, 1961 (U.S. Patent 3,211,552, Oct. 12, 1965) and was present in an amount of 1 part color-former per 0.43 part of gelatin. The yellow layers were coated to give a silver halide coating weight of 25 milligrams per square decimeter. Also present in the emulsion layers was the non-color-forming polymer, polyethylacrylate in an amount of approximately 1 part of polymer per part of gelatin. The coatings were aged for 374 days at room temperature. The two films were exposed in an intensity scale sensitometer according to ASA–PH2.11 procedure and processed as follows:

(1) Black and white development in the following composition for 10 min. at 75° F.

Sodium phosphate (vitreous)	grams	2.0
Metol (N-methyl-p-aminophenol hydrosulfate)	grams	3.0
Sodium sulfite (anhyd.)	do	60.0
Hydroquinone	do	10.0
Sodium carbonate (monohydrate)	do	50.0
Potassium bromide	do	5.0
Potassium iodide 0.1% solution	ml	10.0

Water to make 1.0 liter.

(2) Immersed in the following Short Stop Composition for 1 minute.

Chrome alum	grams	30.0
Magnesium sulfate (anhyd.)	do	60.0
Boric acid	do	7.5

Water to make 1.0 liter.
pH adjusted to 3.3±.05.

(3) Washed in water for 2 minutes.

(4) White light exposure to G.E. Photo-DXC3' from the film.

(5) Color development in the following composition for 12 min.

Sodium tetra-ethylenediamine tetraacetate	grams	2.0
Sodium sulfite (anhyd.)	do	30.0
Potassium bromide	do	0.5
Trisodium phosphate ($12H_2O$)	do	40.0
Potassium iodide 0.1% solution	ml	10.0
Sodium hydroxide 3 N	ml	16.0
4-amino - N - ethyl-N(β-methanesulfonamidoethyl)-m-toluidine sesquisulfate monohydrate	grams	10.0

Water to make 1.0 liter.
pH at 75° F. 11.50±0.05.

(6) Washed in water for 10 seconds.

(7) Immersed in above short stop for 2 minutes.

(8) Washed in water for 3 minutes.

(9) Immersed in following silver bleaching composition for 6 minutes.

Potassium ferricyanide	grams	105.0
Potassium bromide	do	35.0
Sodium sulfate	do	45.0
Borax	do	43.0
Acetic acid, glacial	ml	10.0
Potassium alum	grams	25.0

Water to make 1.0 liter.
pH adjusted to 4.85±0.05.

(10) Washed in water for 2 minutes.

(11) Fixed in the following composition for 3 minutes.

Sodium thiosulfate (anhyd.)	grams	127.0

Water to make 1.0 liter.

(12) Washed in water for 8 minutes.

(13) The resulting films were immersed in a dilute aqueous solution of a wetting agent to obviate water spots and dried.

Examination of a control sensitometric strip which had been aged 374 days between exposure and processing showed that the latent image in the yellow layer had faded 1.4 units on a logarithmic intensity scale to the base 2 (i.e., $\log_2$) e.g., from ASA speed index 25 to index 10. The cyan layer had faded 0.7 unit, e.g., from ASA speed index 25 to about index 15 and the latent image of the magenta layer had intensified or grown 0.2 unit, e.g., from ASA speed index 25 to about index 29. Examination of a sensitometric strip which contained Metol-acetone-sodium bisulfite mixture in the abrasion layer and which had been exposed and aged in the same manner as the control showed a decrease of about 50% in the amount of fading in the yellow layer, i.e., from 1.4 units to 0.7 unit or from ASA speed index of 10 to index 15. The cyan layer showed a decrease in fading of about 30%, i.e., 0.7 unit to 0.4 unit, or from ASA speed index of 15 to 19 and a complete suppression of unwanted latent image growth in the magenta layer. In fact there was some latent image fading in the magenta layer, however it balanced well with the yellow and cyan layers so as to allow an over-all adjustment in speed to give good exposure balance. The above results provided a colored image having good color balance with no untoward defects such as any substantial speed loss or fogging. By raising the amount of acetone-sodium bisulfite to 0.50 milligram per square decimeter, there was substantially no change in the amount of magenta latent image growth and the amount of fading in the other two layers was decreased about the same as when 0.25 milligram was used.

EXAMPLE II

Example I was repeated except that sufficient amounts of p-aminodiethylaniline and acetone sodium bisulfite were added to the gelatin antiabrasion layer to provide 0.25 milligram of the former and 0.375 milligram of the latter per square decimeter. Examination of the results showed that approximately the same degree of improvement was

obtained as in Example I using Metol and acetone-sodium bisulfite although the p-aminodiethylaniline caused some speed loss in the magenta layer in the above quantity, e.g., about 0.7 unit or from ASA speed index 29 to index 15. Further tests showed that the use of 0.05 milligram of the developing agent per square decimeter greatly reduced this speed loss without any reduction in the beneficial effect of decreasing latent image fading in the yellow and cyan layers.

EXAMPLE III

Example I was repeated except that sufficient amounts of hydroquinone and acetone-sodium bisulfite were added to the antiabrasion layer to provide 0.05 milligram per square decimeter of hydroquinone and 0.50 milligram per square decimeter of acetone-sodium bisulfite. Examination of the data resulting from processing 374 days after exposure showed a decrease of about 36% in the amount of latent image fading of the yellow layer, e.g., from 1.4 units to 0.9 or from ASA speed index of 10 to index 13, a decrease of about 57% in the amount of latent image fading in the cyan layer, e.g., from 0.7 unit to 0.1 or from ASA speed index 15 to index 23 and complete suppression of latent image growth in the magenta layer as compared to a control. The exposure of the material to a colored scene and subsequent processing more than one year after exposure produced colored images showing good color balance. A similar test using 0.50 milligram of hydroquinone and 0.50 milligram of acetone-sodium bisulfite per square decimeter in the antiabrasion layer showed some slight improvement over the use of 0.05 milligram of hydroquinone.

EXAMPLE IV

Example I was repeated except that sufficient amounts of catechol and acetone-sodium bisulfite were added to the antiabrasion layer to provide 0.50 milligram of each per square decimeter. Examination of the results after processing the latent images 374 days after exposure showed a decrease in fading from 1.4 units to 0.6 unit or a speed increase from ASA speed index of 10 to speed index of 17 in the yellow layer, a decrease in fading from 0.7 unit to 0.5 unit or from ASA speed index of 15 to speed index 18 in the cyan layer and a complete suppression of latent image growth in the magenta layer as compared to a control.

EXAMPLE V

Example I was repeated except that sufficient amounts of pyrogallol and acetone-sodium bisulfite were added to the gelatin antiabrasion coating to provide 0.50 milligram of each per square decimeter. Examination of the results after processing the latent images 374 days after exposure showed a decrease in fading from 1.4 units to 0.6 unit or a speed increase from ASA speed index 10 to 16 in the yellow layer, a decrease in fading from 1.4 units to 0, or a speed increase from ASA speed index 10 to speed index 25 in the cyan layer and complete suppression of latent image growth in the magenta layer as compared to the control.

EXAMPLE VI

Example I was repeated except that sufficient amounts of p-aminodiethylaniline and sodium bisulfite were added to the antiabrasion layer to provide 0.05 milligram of the former and 0.25 milligram of the latter per square decimeter. A control in which the antiabrasion layer did not contain the above mixture showed latent image fading in the yellow layer equivalent to a loss of ASA speed from 25 to 22 after aging 41 days between exposure and processing. The cyan layer showed a speed loss from ASA 25 to 24 during the same aging period. The magenta layer showed a latent image growth equivalent to a gain in ASA speed from 25 to 30 during the 41 day aging period. Examination of the results from the element containing the stabilizing mixture in the antiabrasion layer which had been aged for 41 days showed only slight latent image fading in the yellow layer and no fading in the cyan layer. There was no image growth in the magenta layer during the 41 days aging period. Similar results were obtained using 0.05 milligram of p-aminodiethylaniline and 0.25 milligram of formaldehyde-sodium bisulfite and also with 0.05 milligram of p-aminodiethylaniline and 0.50 milligram of acetaldehyde-sodium bisulfite per square decimeter. While the range of quantities of carbonyl alkali metal sulfite or alkali metal sulfite per se may vary to a considerable degree, it has been found that an excessive amount, i.e., 1 mg. per square decimeter in the antiabrasion layer, it will have a tendency to destroy the latent image. Quantities of the order of 0.10 to 0.50 milligram per square decimeter have generally been found to be satisfactory.

EXAMPLE VII

Example I was repeated except that a sufficient amount of acetone-sodium bisulfite alone was added to the antiabrasion layer to provide 0.50 milligram per square decimeter. Examination of the results after processing the latent images 374 days after exposure showed a decrease of fading from 1.4 units to 1.1 units or a speed increase from ASA speed index 10 to about 12 because of the reduced latent image fading in the yellow layer; and a decrease of fading from 0.7 unit to 0.2 unit or a speed increase from ASA speed index 15 to 22 in the cyan layer. There was no image growth in the magenta layer. Doubling the amount of acetone-sodium bisulfite in the absence of reducing agent destroyed the latent images however.

EXAMPLE VIII

Example I was repeated except that a sufficient amount of 2-amino-5-diethylaminotoluene hydrochloride and acetone-sodium bisulfite was added to the gelatin antiabrasion layer to provide .05 milligram of the former and 0.25 milligram of the latter per square decimeter. Examination of the results after processing an exposed film after one month aging showed that latent image fading in the yellow layer had been decreased about 60% e.g., from 0.5 unit to 0.2 unit or from approximately ASA speed index 18 to approximately ASA speed index 22, there was a complete suppression of latent image growth in the magenta layer and no change in the cyan layer which had shown no latent image fading in the control at the one month's aging period.

EXAMPLE IX

Example I was repeated except that a sufficient amount of 4-amino-N-(β - methanesulfonamidoethyl)-m-toluidine sesquisulfate monohydrate and acetone-sodium bisulfite were added to the antiabrasion layer to provide 0.05 milligram of the former and 0.25 milligram of the latter per square decimeter. Examination of the results after processing the exposed film after one month of aging showed as compared to a control strip that latent image fading in the yellow and cyan layers and the latent image growth in the magenta layers had been completely suppressed so that there was no substantial change as indicated by the speed of the film.

EXAMPLE X

Example I was repeated except that a sufficient amount of 4 - amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline sulfate and acetone-sodium bisulfite was added to the antiabrasion layer to provide 0.05 milligram of the former and 0.25 milligram of the latter per square decimeter. Examination of the results from processing the film one month after exposure showed a decrease of 80% in the amount of latent image fading as compared by a control strip aged for one month, in the yellow layer, e.g., from 0.5 unit to 0.1 unit or from ASA speed index of 18 to ASA speed index of about 23. There was complete sup-

pression of latent image fading in the cyan layer and latent image growth in the magenta layer.

EXAMPLE XI

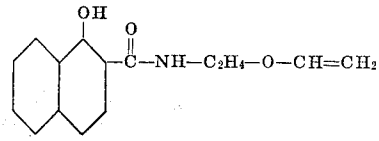
The procedure set forth in Example VI was repeated except that the antiabrasion layer contained 0.25 mg. of p-aminodiethylaniline and 0.25 g. of sodium metabisulfite per dm.^{2}. The control was the same as in Example VI, i.e., it showed latent image fading in the yellow layer equivalent to a loss of ASA speed from 25 to 22, loss in the cyan layer from ASA 25 to 24, and latent image growth in the magenta layer equivalent to a gain in ASA speed from 25 to 30 during the 41-day aging period between exposure and processing. The stabilized film of the present example, during the same period of aging, showed no (zero) change in the yellow and cyan layer and a very slight latent image growth in the magenta layer equivalent to a gain in ASA speed from 25 to 26.

EXAMPLE XII

Example I was repeated except that sufficient amounts of p-aminodiethylaniline and acetone-sodium bisulfite were added to the yellow emulsion layer to provide 0.085 milligram of each per square decimeter. The color film did not have an antiabrasion layer coated thereon. A control in which the yellow emulsion layer did not contain the above components showed latent image fading in the yellow layer which in terms of units on a logarithmic intensity scale to the base 2, showed a speed loss of 0.2 for four days between exposure and processing. The latent image of the magenta layer had intensified or grown 0.4 unit. Examination of the sensitometric strip which contained the p-aminodiethylaniline and acetone-sodium bisulfite in the yellow emulsion layer and which had been exposed, aged and processed in the same manner as the control showed complete suppression of latent image fading in the yellow layer and substantially complete suppression of latent image growth in the magenta layer.

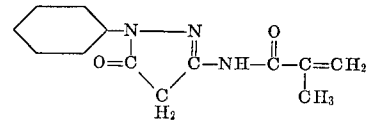
EXAMPLE XIII

Three color reversal films were made by coating on a film support in order, a red-sensitive gelatino-silver iodobromide emulsion layer containing a cyan color former, a gelatin separator layer, a green-sensitive, gelatino-silver iodobromide emulsion layer containing a magenta color former, a yellow filter layer containing a dye made as described in Example I of Belgian Patent 588,055, a blue-sensitive, gelatino-silver iodobromide emulsion layer containing a yellow color former and finally a gelatin antiabrasion layer. On the opposite side of the film support there was coated a monhalation layer. The red sensitized gelatino-silver iodobromide emulsions for the cyan layers contained approximately 7.0 mole percent iodide, the remainder being silver bromide. The cyan color former was a lipophilic addition copolymer comprising units from ethyl acrylate and the naphthol cyan color forming monomer having the formula:



as disclosed in Belgian Patent 618,202. The resulting color former was dispersed in the emulsion with the aid of a surface active agent and was present in an amount of 1.0 gram of color former per 1.4 grams of gelatin. The cyan layers were coated to give a coating weight of 22 milligrams of silver halide per square decimeter.

The green sensitized gelatino-silver iodobromide emulsion for the magenta layers contained approximately 7.0 mole percent silver iodide, the remainder being silver bromide. The magenta color former was a lipophilic addition copolymer comprising units from a methacrylate ester and a pyrazolone monomer having the formula:



as disclosed in Belgian Patent 602,516. The resulting copolymer was dispersed in the silver halide emulsion using the alcohol-alkali method and was present in an amount of 1.0 part of color former per 1.5 parts of silver halide. The magenta layers were coated to give a coating weight of 11 grams of silver halide per square decimeter.

The blue sensitive gelatino silver iodobromide emulsions for the yellow layers contained equal parts by weight of gelatino-silver iodobromide emulsion containing 7.0 mole percent AgI and a gelatino-silver bromide emulsion containing no other silver halide. The yellow color former was a lipophilic addition copolymer comprising units from 2-ethylhexyl acrylate and alpha-benzoyl-2-methoxy-5 - methacrylamido - acetanilide. The copolymer was dispersed by stirring into the emulsion with the aid of a surface active agent and was present in an amount of 1.0 part of color former per 1.4 parts of silver halide. The yellow layers were coated to give a coating weight of 17 milligrams of silver halide per square decimeter.

One color reversal element (A) was used as a control, another color reversal element (B) contained a stabilizing mixture of 0.25 milligram of Metol and 0.25 milligram of acetone-sodium bisulfite per square decimeter in the antiabrasion layer. The third color reversal element contained 0.08 milligram of Metol and 0.08 milligram of acetone-sodium bisulfite per square decimeter in the yellow emulsion layer, 0.05 milligram of each of the above compounds per square decimeter in the magenta emulsion layer and 0.11 milligram of each per square decimeter in the cyan emulsion layer. The color reversal elements were exposed as described in Example I and aged for three days at room temperature and processed in substantially the same manner as described in Example I. Examination of the control (A) sensitometric strip showed a color shift which in terms of units on a logarithmic intensity scale to the base 2, showed a loss in speed of 0.8 in the blue sensitive layer, 0.2 in the green-sensitive layer and 0.2 in the red-sensitive layer.

The sensitometric strip for the color reversal element containing the Metol and acetone-sodium bisulfite in the antiabrasion layer showed that the speed loss for the blue-sensitive layer had been reduced from 0.8 to 0.3, and the green-sensitive and red sensitive speeds showed no substantial change.

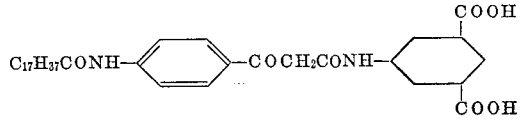
The sensitometric strip for the color reversal element containing the varying quantities of Metol and acetone-sodium bisulfite in the separate emulsion layers showed that the speed loss for the blue-sensitive layer had been reduced from 0.8 to 0.2 and the speeds for the green-sensitive and red-sensitive layers showed no substantial change. A comparison with the control shows that all color layers in color reversal element (C) show the same speed loss, namely 0.2 and therefore no color shift on aging after exposure. This, of course, results in good color balance in the processed films.

The above experiment was repeated with the exception that the aging period between exposure and processing was extended to seven days. Examination of the control strip showed a speed loss of 1.0 for the blue-sensitive yellow layer, 0.4 for the green-sensitive magenta layer and 0.6 for the red-sensitive cyan layer. The strip (B) containing the stabilizing mixture in the abrasion layer showed the speed loss in the yellow layer had been reduced to 0.2, in the magenta layer to 0.3 and in the cyan layer to 0.1. The sensitometric strip (C) where the stabilizing mixture had been added to the various layers, showed that the speed loss in the yellow layer had been

reduced to 0.3, in the magenta layer to 0.3 and in the cyan layer to 0.3.

EXAMPLE XIV

Two color reversal films were made by coating on a film support in order, a red-sensitive gelatino-silver iodobromide emulsion containing 7 mole percent silver iodide and containing a cyan color former, a gelatin separation layer, a green-sensitive gelatino-silver iodobromide emulsion containing 7 mole percent silver iodide and a magenta color former, a yellow filter layer containing a dye made as described in Example I of Belgian Patent 588,055 and a blue-sensitive gelatino-silver iodobromide emulsion layer containing equal parts of a silver iodobromide emulsion containing 7 mole percent silver iodide and a gelatino-silver bromide emulsion and containing a yellow color former. The cyan and magneta color formers were made and incorporated in the respective emulsion layers in the manner described in Example XIII. The ratio of color former to silver halide on a weight basis was 1:2 for cyan and 1:2.1 for magenta. The yellow layer contained 40% by weight of the yellow color former disclosed in Example II of Belgain Patent 618,201 and 60% by weight of a yellow color former having the formula:



The ratio of the former to silver halide is 1:3.1 and the ratio of the latter color former to silver halide is 1:2 parts by weight.

One color reversal element was used as a control and the other element was coated with a gelatin antiabrasion layer in an amount of 10 milligrams per square decimeter, said coating containing 0.25 milligram each of Metol and acetone-sodium bisulfite per square decimeter.

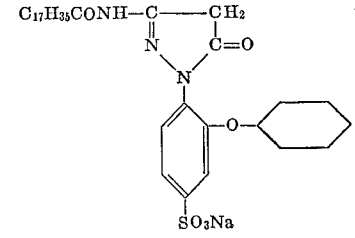
The resulting film elements were exposed and aged for seven days at room temperature and processed in substantially the manner described in Example I. Examination of the control sensitometric strip showed a loss of color speed of 1.5 for the yellow layer, 2.7 for the magenta layer and 2.2 for the cyan layer. The loss in color speed for the color reversal element having the antiabrasion layer containing the Metol and acetone-sodium bisulfite mixture showed a reduction in speed loss from 1.5 to 0.8 for the yellow layer, from 2.7 to 0.9 for the magenta and from 2.2 to 0.6 for the cyan. The overall color balance was of course greatly improved.

EXAMPLE XV

Two color reversal film elements were made by coating a film support with the cyan and magenta color former gelatino-silver halide emulsions described in Example XIII and to the green-sensitive magenta layer of one of the elements there was incorporated 0.24 milligram of Metol and 0.24 milligram of acetone-sodium bisulfite per square decimeter. The other coated element was used as a control and showed in the processed sensitometric strips, which had been room-temperature-aged for 11 days between exposure and processing, a color shift in terms of speed loss of 1.2 in both the cyan and magenta layers. This speed loss in the magenta layer containing the Metol and acetone-sodium bisulfite was reduced to 0.3 and in the cyan layer to 0.8. Latent image fading, of course, had been essentially completely suppressed.

EXAMPLE XVI

Example XV was repeated except that the magenta color former used had the formula:



Examination of the control sensitometric strip showed a color shift represented by a speed loss of 1.2 for the magenta and 2.4 for the cyan layer. The presence of the Metol and acetone-sodium bisulfite in the magenta layer reduced the speed loss of the magenta layer to 0.2 and the speed loss of the cyan layer to 0.0 thus the tendency toward a shifting of color balance had been overcome.

EXAMPLE XVII

Single gelatino-silver halide emulsion layer films were made using the cyan color former emulsion of Example I. In one of the cyan layers there was incorporated .01 milligram of p-aminodiethylaniline and .05 milligram of acetone-sodium bisulfite per square decimeter.

Examination of the control sensitometric strip which had been aged at room temperature for 36 days after exposure before processing showed a color shift as indicated by color speed loss of 0.9. The presence of the p-aminodiethylaniline and acetone-sodium bisulfite reduced this speed loss to 0.3. This and the above examples show that significant improvement can be obtained by incorporating even very small quantities of the stabilizing mixture directly in the emulsion layers or in auxiliary layers.

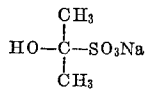
Although this invention is particularly applicable to the reversal color film described above, it is by no means limited to these particular structures. It is also applicable to other color films which may have other than the conventional layer arrangement. The invention is also applicable to any color photographic film structures where colored images are subject to color shift due to latent image instability between the time of exposure and development. Thus, in addition to color reversal films, the invention may also be applied to color negative and color positive films and to films used for cine or still use. It is understood that this invention applies to integral color coupler films containing those hydrophilic color couplers having a high molecular weight hydrocarbon group and an acid group attached to the color-forming nucleus and those lipophilic color couplers containing only a high molecular weight group attached to the color-forming nucleus, hydrophilic gelatin compatible polymeric color couplers and dispersed lipophilic polymeric couplers. However, this invention applies particularly to those polymeric couplers used to make thin, high definition multilayer color films by replacing part of the normal gelatin binder.

Suitable other layer arrangements are disclosed, Jennings 2,397,864; Woodward and Chu U.S. 2,927,019 and US. 2,927,024 and Blanchard U.S. 2,997,388. However the invention will be most appreciated in a configuration as shown in the above mentioned Chu and Umberger application U.S. Ser. No. 287,746, filed June 14, 1963, where the upper blue-sensitive layer is thin and contains a high proportion of polymeric yellow color-former based on the gelatin.

The invention, moreover, is not limited to the specific light-sensitive silver halides described in the detailed examples. Various other samples and mixed silver halides may be used to formulate the light sensitive emulsions. Mixtures of silver bromides, chlorides, and/or iodides can be made by adding mixtures of soluble halides in like manner.

As described above, the manner of addition of the sulfur compounds, carbonyl derivatives thereof and the admixture of a reducing agent therewith is not critical and

may be added either to the antiabrasion layer or to the yellow color-forming layer. The ingredients may be added separately or together or in the form of chemical complexes. For example acetone and sodium bisulfite are believed to form the compound



Inert ingredients, e.g., pigments, colloidal silver, polymer latices, matting agents, etc. may be present in all of the element layers including the support. The element may also contain, where needed, chemical sensitizers, optical sensitizers, coating aids, antifoggants, non-halation dyes and pigments, optical brightening agents as is well known in the art.

In addition to the cellulosic film support, of course other synthetic resins which have been described in the art as suitable for photographic supports may be used. For example, the supports disclosed and claimed in Alles and Saner, U.S. 2,627,088, dated Feb. 3, 1953, may be used.

An advantage of this invention is that it is simple and easy to carry out and does not necessitate the use of difficult to obtain or unusual apparatus or material. A further advantage is that this invention affords an easy method of positively controlling the latent image stability and thereby assuring good color balance in color photographic images where the color generated is dependent on the amount of exposed silver halide which is developable. Another advantage is that this invention provides a photographic film which may be exposed to images over a period of time and then color processed to give images having little or no discernable difference in color balance.

While some reducing agents provide limited independent specific control on one or more of the three record layers, the action of the developers in the photographic films of this invention provides greater independent control of each individual layer. For example, Metol preferentially induces more magenta latent image fading than other reducing agents do, and this is desirable in obtaining good color balance.

We claim:

1. A multilayer color film having a film support bearing in order on one surface:

(1) a red-sensitive gelatino-silver halide emulsion layer containing a nondiffusing cyan color former,

(2) a green-sensitive gelatino-silver halide emulsion layer containing a nondiffusing magenta color former,

(3) a yellow filter layer,

(4) a blue-sensitive gelatino-silver halide emulsion layer containing a nondiffusing yellow color former, and

(5) a water-permeable colloid antiabrasion layer; said photographic film being characterized in that at least one of the contiguous layers contain

(i) at least one member selected from the group consisting of a bisulfite ion, its water soluble salts, and their complexes with an organic carbonyl compound of the formula

where R and R′ are hydrogen, methane, or ethyl; in admixture with

(ii) a water-soluble photographic silver halide hydroxybenzene or aromatic amine developing agent; at least one of the color formers being polymeric.

2. A film according to claim 1 wherein said support is clear and transparent to visible light.

3. A film according to claim 1 wherein the color formers in the red-sensitive and green-sensitive layers are copolymers of a vinyl ether containing a color former nucleus and maleic anhydride, and of acrylic acid, acrylamide and acrylamidopyrazolone, respectively.

4. A film according to claim 1 wherein the agent is an aromatic amine photographic silver halide developing agent.

5. A film according to claim 1 wherein the salt is an alkali metal metasulfite and the reducing agent is an aromatic amine photographic silver halide developing agent.

6. A film according to claim 1 wherein the complex is acetone-sodium bisulfite and the agent is p-aminodiethylaniline.

7. A film according to claim 1 wherein the complex is acetone-sodium bisulfite and the agent is N-methyl-p-aminophenol.

8. A film according to claim 1 wherein the complex is present in an amount from 0.01 to 2.5% based on the weight of gelatin in the layer, and the reducing agent is present in an amount of 0.1 to 1.0 parts per part of the sulfur salt.

9. A color film according to claim 1 wherein the color formers are polymeric compounds.

10. A color film according to claim 1 wherein said color formers are lipophilic addition copolymers.

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J. TRAVIS BROWN, *Primary Examiner.*

U.S. Cl. X.R.

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