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3,201,242

ACCELERATORS FOR REVERSAL COLOR DEVELOPMENT

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This invention relates to color photography, and more particularly, to a method of processing multi-layer color films or papers by the technique of reversal color development.

In multi-layer photographic elements used for color photography, there are generally three selectively sensitive emulsion layers (each of which may consist of several strata finished to different speed levels) coated on the same side of a photographic support, such as film or paper. For example, the uppermost layer is frequently a blue-sensitive layer, the next light-sensitive layer is generally green-sensitive and the light-sensitive layer closest to the support is generally sensitized to the red region of the spectrum. Inasmuch as many photographic silver halide emulsions have substantial inherent sensitivity in the blue spectral region, such photographic elements generally have a yellow filter layer coated beneath the blue-sensitive outermost layer for the purpose of absorbing substantially all blue radiation which would otherwise be transmitted to the green-sensitized and red-sensitized layers. Such multi-layer photographic elements can also have other layers for specialized purposes including light-sensitive emulsion layers, gelatin or other subbing layers, antihalation layers, etc. Typical multi-layer photographic materials useful in our invention have been described in the prior art, such as Mannes et al. U.S. Patent 2,252,718, issued August 19, 1951.

Color materials of the type advantageously employed in the present invention are those intended primarily for reversal color processes, in which the photoexposed material is given a conventional black-and-white development to produce a negative silver image but no color image, followed by at least one reversal re-exposure and color development to produce positive dye (and silver) images. The color materials used in our invention comprise those which contain the color-forming materials or couplers within the silver halide emulsions, or those materials designed for processing in developers which contain the color couplers or color-forming compounds within the color developer. The latter materials are particularly useful in practicing the present invention for reasons pointed out below.

It is, therefore, an object of our invention to provide an improved process for producing photographic images in color by reversal color photography. Another object is to provide improved developers for such reversal color photographic processes. Still another object is to provide a method of increasing the color density in certain of the emulsion layers of photographic color elements, particularly in the red-sensitive of cyan-producing layer. Still another object is to provide a convenient means for avoiding re-exposure by light, by simultaneously fogging and color developing photographic silver halide emulsion to produce a colored image of high maximum density. Other objects will become apparent from a consideration of the following description and examples.

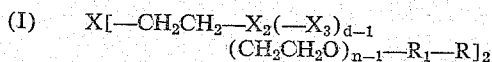
In the processing of photographic multi-layer materials by the reversal technique using color couplers in the developing compositions rather than in the emulsion layers, the conventional procedure is to selectively re-expose with colored light (or chemicals) each of the selectively sensitized layers and to separately develop each of these

layers to a colored image in a color developer which contains the appropriate color-forming ingredient in the color developer. In color processes of this type, it is frequently desired to accelerate color development so that the rate of development is increased without fogging the silver halide grains which have not been exposed by the selective exposure. Such accelerators increase the maximum color density with little or no increase in color fog.

In the processing of multi-layer photographic elements to produce a colored image, it is sometimes desired to have a color development bath which results in development of all silver halide remaining in the respective layers and to couple the color-forming compound with the oxidation products of the appropriate color developer to produce dye images in the respective photographic silver halide emulsion layers. Such results are desired principally in photographic multi-layer materials which contain the color-forming component or coupler within the silver halide emulsion layers, or in the final color development step in a color process in which the color-forming component is incorporated within the color developing solution.

We have now found that the afore-mentioned effects can be advantageously attained by incorporating certain non-polymeric, thioether compounds in color developers intended for use in reversal color development. The compounds of our invention can be used to increase the development rate of multi-layer photographic materials which are processed in developing solutions containing the color-forming components in the color developing solutions so that substantially all silver halide, which has been selectively re-exposed to a particular region of the spectrum, becomes developed in the subsequent color developing solution, thus preventing the formation of undesirable color fog as a consequence of further color development in a subsequent color developer for producing different colored images. Thus, it is possible to prevent the formation of cyan dye in the green- and blue-sensitive layers of such multi-layer color elements and to form cyan dye substantially only in the red-sensitive layer. It is also possible according to our invention to render substantially all residual silver halide in such multi-layer photographic elements developable by incorporating such thioether compounds in the color developers.

The thioether compounds useful in practicing our invention by incorporation in the color developer (or color developers) comprise compounds represented by the following general formula:



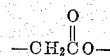
wherein X represents a divalent linkage, such as oxygen, sulfur,



or the group:



wherein X_1 and X_2 each represents an oxygen atom or a sulfur atom, provided at least one of the groups selected from X_1 and X_2 is a sulfur atom, X_3 represents a methylene carboxy radical, i.e.,



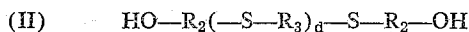
R represents a hydroxyl group, an alkoxy group (e.g., methoxy, ethoxy, propoxy, butoxy, etc.), a carbamyl group (i.e., an aminocarbonyl group), or a carboxylic acyloxy group, such as acetoxy, butyryloxy, etc., R_1 represents an ethylene radical, such as ethylene or ethylene

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substituted by an alkyl radical, such as methyl, ethyl, etc., d represents a positive integer of from 1 to 2 and n represents a positive integer of from 1 to 3.

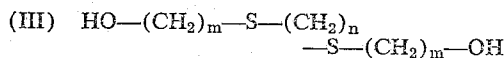
The compounds of Formula I above can be prepared according to methods which have been previously described in the technical literature. Preparations for a number of compounds coming within the scope of this formula are described in Dann, Chiesa and Lovett, U.S. application Serial No. 846,230, filed October 14, 1959.

Another group of compounds coming with the scope of Formula I above which can advantageously be employed in our invention comprise compounds represented by the following general formula:



(13)

wherein R_2 and R_3 each represents an alkylene group, such as ethylene, trimethylene, tetramethylene (butylene), methyl-substituted trimethylene, pentamethylene, ethyl-substituted tetramethylene, hexamethylene, heptamethylene, octamethylene, nonamethylene, decamethylene, etc. (e.g., a hydrocarbon alkylene group containing from about 2 to 10 carbon atoms), and d represents a positive integer of from 1 to 3. Especially useful sensitizing compounds, according to our invention, are dithiaalkylenediols, such as those embraced by the following general formula:



wherein m and n each represents a positive integer of from about 2 to 10.

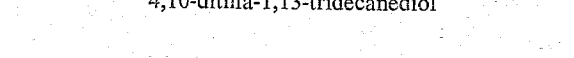
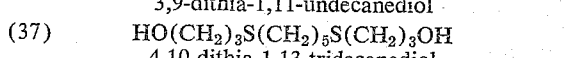
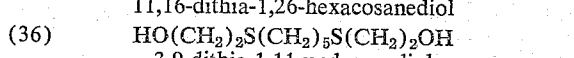
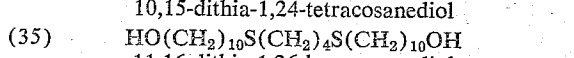
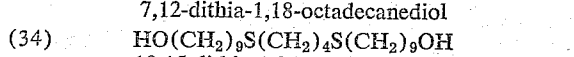
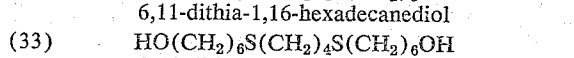
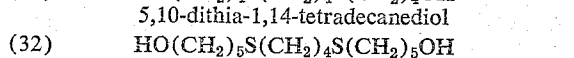
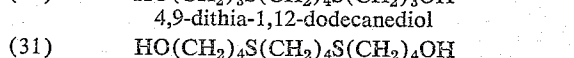
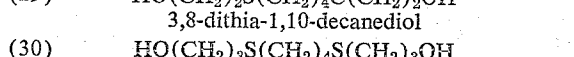
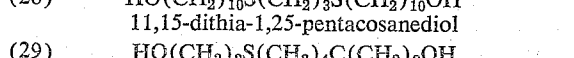
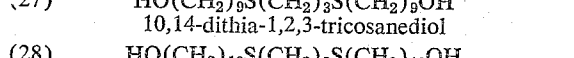
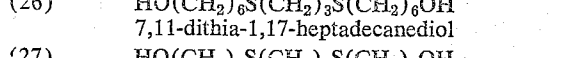
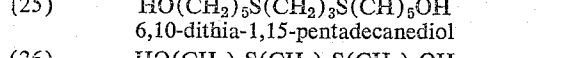
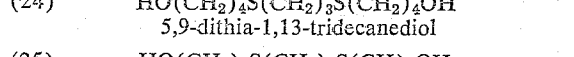
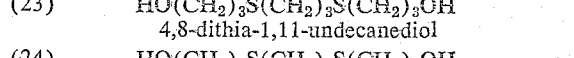
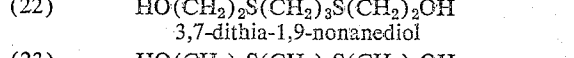
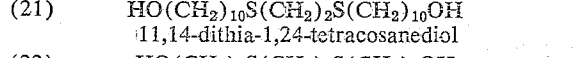
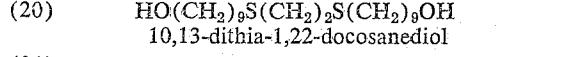
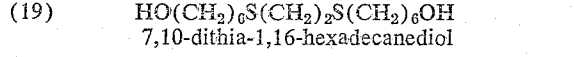
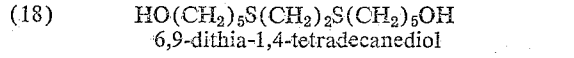
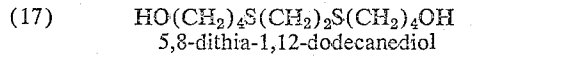
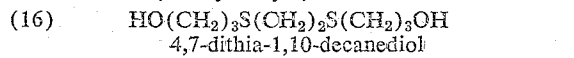
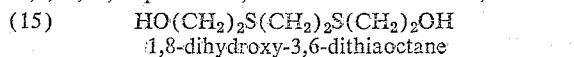
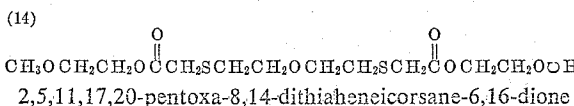
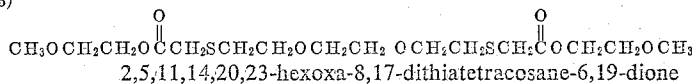
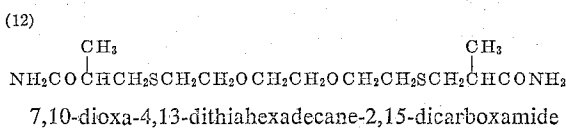
Compounds represented by Formulas II and III above can be prepared according to methods which have been previously described in the technical literature. The preparation having a number of such compounds is given in Williams and Cossar U.S. application Serial No. 843,638, filed October 1, 1959 (now U.S. Patent 3,021,215, issued February 13, 1962).

Typical compounds useful in our invention embraced by the above general formulas include the following:

- (1) $HOCH_2CH_2SCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2OH$
1,14-dihydroxy-6,9-dioxa-3,12-dithiatetradecane
- (2) $CH_3CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2OCH_2CH_2SCH_2CH_2OCH_2CH_2CH_3$
3,6,12,18,21-pentoxa-9,15-dithiatricosane
- (3) $C_2H_5OCH_2CH_2OCH_2CH_2SCH_2CH_2OCH_2CH_2OC_2H_5$
3,6,12,15-tetraoxa-10-thiaheptadecane
- (4) $CH_3OCH_2CH_2SCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2OCH_2CH_3$
2,8,11,17-tetroxa-5,14-dithiaoctadecane
- (5) $CH_3CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2CH_3$
3,6,9,15,18,21-hexoxa-12-thiatricosane
- (6) $CH_3CH_2OCH_2CH_2SCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2OCH_2CH_2OCH_2CH_2CH_3$
3,9,12,18-tetroxa-6,15-dithiaieicosane
- (7) $CH_3CH_2OCH_2CH_2SCH_2CH_2OCH_2CH_2SCH_2CH_2OCH_2CH_2OCH_2CH_2CH_3$
3,9,15-trioxa-6,12-dithiaheptadecane
- (8) $CH_3CH_2OCH_2CH_2OCH_2CH_2SCH_2CH_2OCH_2CH_2SCH_2CH_2OCH_2CH_2OCH_2CH_2CH_3$
3,6,15,18-tetroxa-9,12-dithiaieicosane
- (9) $HOCH_2CH_2OOCCH_2SCH_2CH_2OCH_2CH_2SCH_2COOCH_2CH_2OH$
1,17-dihydroxy-3,9,15-trioxa-6,12-dithiaheptadecane-4,14-dione

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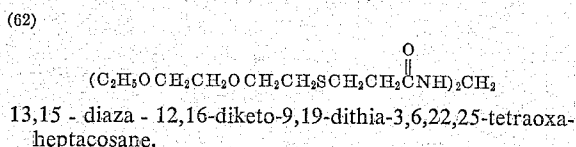
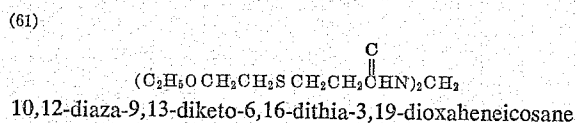
- (10) $HOCH_2CH_2OCH_2CH_2OOCCH_2SCH_2CH_2OCH_2CH_2SCH_2COOCH_2CH_2OCH_2CH_2OH$
1,23-dihydroxy-3,6,12,18,21-pentoxa-9,15-dithiatricosane-7,17-dione
- (11) $HOCH_2CH_2OOCCH_2SCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_2COOCH_2CH_2OH$
1,20-dihydroxy-3,9,12,18-tetroxa-6,15-dithiaieicosane-4,17-dione



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- (38) $\text{HO}(\text{CH}_2)_5\text{S}(\text{CH}_2)_5\text{S}(\text{CH}_2)_5\text{OH}$
6,12-dithia-1,17-heptadecanediol
- (39) $\text{HO}(\text{CH}_2)_6\text{S}(\text{CH}_2)_5\text{S}(\text{CH}_2)_6\text{OH}$
7,13-dithia-1,19-nonadecanediol
- (40) $\text{HO}(\text{CH}_2)_9\text{S}(\text{CH}_2)_5\text{S}(\text{CH}_2)_9\text{OH}$
10,16-dithia-1,25-pentacosanediol
- (41) $\text{HO}(\text{CH}_2)_{10}\text{S}(\text{CH}_2)_5\text{S}(\text{CH}_2)_{10}\text{OH}$
11,17-dithia-1,27-heptacosanediol
- (42) $\text{HO}(\text{CH}_2)_2\text{S}(\text{CH}_2)_6\text{S}(\text{CH}_2)_2\text{OH}$
3,10-dithia-1,12-dodecanediol
- (43) $\text{HO}(\text{CH}_2)_3\text{S}(\text{CH}_2)_6\text{S}(\text{CH}_2)_3\text{OH}$
4,11-dithia-1,14-tetradecanediol
- (44) $\text{HO}(\text{CH}_2)_4\text{S}(\text{CH}_2)_6\text{S}(\text{CH}_2)_4\text{OH}$
5,12-dithia-1,16-hexadecanediol
- (45) $\text{HO}(\text{CH}_2)_5\text{S}(\text{CH}_2)_6\text{S}(\text{CH}_2)_5\text{OH}$
6,13-dithia-1,18-octadecanediol
- (46) $\text{HO}(\text{CH}_2)_6\text{S}(\text{CH}_2)_6\text{S}(\text{CH}_2)_6\text{OH}$
7,14-dithia-1,20-eicosanediol
- (47) $\text{HO}(\text{CH}_2)_9\text{S}(\text{CH}_2)_6\text{S}(\text{CH}_2)_9\text{OH}$
10,17-dithia-1,26-hexacosanediol
- (48) $\text{HO}(\text{CH}_2)_{10}\text{S}(\text{CH}_2)_6\text{S}(\text{CH}_2)_{10}\text{OH}$
11,18-dithia-1,28-octacosanediol
- (49) $\text{HO}(\text{CH}_2)_2\text{S}(\text{CH}_2)_9\text{S}(\text{CH}_2)_2\text{OH}$
3-13-dithia-1,15-pentadecanediol
- (50) $\text{HO}(\text{CH}_2)_3\text{S}(\text{CH}_2)_9\text{S}(\text{CH}_2)_3\text{OH}$
4,14-dithia-1,17-heptadecanediol
- (51) $\text{HO}(\text{CH}_2)_4\text{S}(\text{CH}_2)_9\text{S}(\text{CH}_2)_4\text{OH}$
5,15-dithia-1,19-nonadecanediol
- (52) $\text{HO}(\text{CH}_2)_6\text{S}(\text{CH}_2)_9\text{S}(\text{CH}_2)_6\text{OH}$
7,17-dithia-1,23-tricosanediol
- (53) $\text{HO}(\text{CH}_2)_9\text{S}(\text{CH}_2)_9\text{S}(\text{CH}_2)_9\text{OH}$
10,20-dithia-1,29-nonacosanediol
- (54) $\text{HO}(\text{CH}_2)_{10}\text{S}(\text{CH}_2)_9\text{S}(\text{CH}_2)_{10}\text{OH}$
11,21-dithia-1,31-hentriacontanediol
- (55) $\text{HO}(\text{CH}_2)_2\text{S}(\text{CH}_2)_{10}\text{S}(\text{CH}_2)_2\text{OH}$
3,14-dithia-1,16-hexadecanediol
- (56) $\text{HO}(\text{CH}_2)_3\text{S}(\text{CH}_2)_{10}\text{S}(\text{CH}_2)_3\text{OH}$
4,16-dithia-1,18-octadecanediol
- (57) $\text{HO}(\text{CH}_2)_4\text{S}(\text{CH}_2)_{10}\text{S}(\text{CH}_2)_4\text{OH}$
5,16-dithia-1,20-eicosanediol
- (58) $\text{HO}(\text{CH}_2)_5\text{S}(\text{CH}_2)_{10}\text{S}(\text{CH}_2)_5\text{OH}$
6,17-dithia-1,22-docosanediol
- (59) $\text{HO}(\text{CH}_2)_9\text{S}(\text{CH}_2)_{10}\text{S}(\text{CH}_2)_9\text{OH}$
10,21-dithia-1,30-tricoanediol
- (60) $\text{HO}(\text{CH}_2)_{10}\text{S}(\text{CH}_2)_{10}\text{S}(\text{CH}_2)_{10}\text{OH}$
11,22-dithia-1,32-dotriacontanediol



The above thioether compounds useful in practicing our invention can be utilized in various concentrations, depending upon the particular silver halide emulsions employed, the thickness of the emulsion layers, the concentration of silver halides in the emulsions, the concentration of developing agents in the color developers, the pH of the color developers, etc. In general, we have found that useful results are obtained when the concentration of the thioether compound in the color developer is at least 0.1 gram per liter. Larger amounts of thioether compounds can be employed in the color developers, and concentrations as high as 5 grams (or higher) per liter

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are useful. The activity of the color developers will obviously depend upon the development temperature, duration of development and the like. All of these variables are well understood by those skilled in the art of photography. The most advantageous concentration for a particular developer can be determined by developing a series of test strips of silver halide emulsions wherein the concentration of thioether compound is varied. The color developers useful in our invention can also contain conventional addenda, such as alkaline salts (e.g., sodium carbonate, potassium carbonate, sodium hydroxide, sodium metaborate, etc.), restraining agents, such as potassium bromide, stain preventives, such as alkali metal sulfites, etc.

The photographic emulsions used in practicing our invention are of the developing-out type.

The emulsions can be chemically sensitized by any of the accepted procedures. The emulsions can be digested with naturally active gelatin, or sulfur compounds can be added such as those described in Sheppard U.S. Patent 1,574,944, issued March 2, 1926, Sheppard et al. U.S. Patent 1,623,499, issued April 5, 1927, and Sheppard et al. U.S. Patent 2,410,689, issued November 5, 1946.

The emulsions 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. Patent 2,448,060, issued August 31, 1948, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245, issued August 28, 1951, and 2,566,263, issued August 28, 1951.

The emulsions can also be chemically sensitized with gold salts as described in Waller et al. U.S. Patent 2,399,083, issued April 23, 1946, and Damschroder et al. U.S. Patent 2,642,361, issued June 16, 1953. Suitable compounds are potassium chloraurate, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurisulfobenzothiazole methochloride.

The emulsions can also be chemically sensitized with reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850, issued November 15, 1949), polyamines, such as diethylene triamine (Lowe and Jones U.S. Patent 2,518,698, issued August 15, 1950), polyamines, such as spermine (Lowe and Allen U.S. Patent 2,521,925, issued September 12, 1950), or bis(β -aminoethyl) sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926, issued September 12, 1950).

The emulsions can also be optically sensitized with cyanine and merocyanine dyes, such as those described in Brooker U.S. Patents 1,846,301, issued February 23, 1932; 1,846,302, issued February 23, 1932; and 1,942,854, issued January 9, 1934; White U.S. Patent 1,990,507, issued February 12, 1935; Brooker and White U.S. Patents 2,112,140, issued March 22, 1938; 2,165,338, issued July 11, 1939; 2,493,747 issued January 10, 1950, and 2,739,964, issued March 27, 1956; Brooker and Keyes U.S. Patent 2,493,748, issued January 10, 1950; Sprague U.S. Patents 2,503,776, issued April 11, 1950, and 2,519,001, issued August 15, 1950; Heseltine and Brooker U.S. Patent 2,666,761, issued January 19, 1954; Heseltine U.S. Patent 2,734,900, issued February 14, 1956; Van Lare U.S. Patent 2,739,149, issued March 20, 1956; and Kodak Limited British Patent 450,958, accepted July 15, 1936.

The emulsions can also be stabilized with the mercury compounds of Allen, Byers and Murray U.S. Patent 2,728,663, issued December 27, 1955; Carroll and Murray U.S. Patent 2,728,664, issued December 27, 1955; and Leubner and Murray U.S. Patent 2,728,665, issued December 27, 1955; or with gold salts as described in Damschroder U.S. Patent 2,597,856, issued May 27, 1952, and Yutzy and Leermakers U.S. Patent 2,597,915, issued

May 27, 1952; the triazoles of Heimbach and Kelly U.S. Patent 2,444,608, issued July 6, 1948; the azaindenes of Heimbach and Kelly U.S. Patents 2,444,605 and 2,444,606, issued July 6, 1948; Heimbach U.S. Patents 2,444,607, issued July 6, 1948, and 2,450,397, issued September 28, 1948; Heimbach and Clark U.S. Patent 2,444,609, issued July 6, 1948; Allen and Reynolds U.S. Patents 2,713,541, issued July 19, 1955, and 2,743,181, issued April 24, 1956; Carroll and Beach U.S. Patent 2,716,062, issued August 23, 1955; Allen and Beiffuss U.S. Patent 2,735,769, issued February 21, 1956; Reynolds and Sagal U.S. Patent 2,756,147, issued July 24, 1956; Allen and Sagura U.S. Patent 2,772,164, issued November 27, 1956, and those disclosed by Birr in "Z. wiss. Phot.," vol. 47, 1952, pages 2-28; the disulfides of Kodak Belgian Patent 569,317, issued July 31, 1958; the quaternary benzothiazolium compounds of Brooker and Staud U.S. Patent 2,131,038, issued September 27, 1938, or the polymethylene bis-benzothiazolium salts of Allen and Wilson U.S. Patent 2,694,716, issued November 16, 1954; the zinc and cadmium salts of Jones U.S. Patent 2,839,405, issued June 17, 1958; and the carboxymethylmercapto compounds of Murray, Reynolds and Van Allan U.S. Patent 2,819,965, issued January 14, 1958.

The emulsions may also contain speed increasing compounds of the quaternary ammonium type of Carroll U.S. Patent 2,271,623, issued February 3, 1942; Carroll and Allen U.S. Patent 2,288,226, issued June 30, 1942; and Carroll and Spence U.S. Patent 2,334,864, issued November 23, 1943; or the polyethylene glycol type of Carroll and Beach U.S. Patent 2,708,162, issued May 10, 1955; or the quaternary ammonium salts and polyethylene glycols of Piper U.S. Patent 2,886,437, issued May 12, 1959; as well as the thiopolymers of Graham and Sagal U.S. application Serial No. 779,839, filed December 12, 1958 (now U.S. Patent 3,046,129, issued July 24, 1962), and the Dann and Chechak U.S. application Serial No. 779,874, filed December 12, 1958 (now U.S. Patent 3,046,134, issued July 24, 1962).

The emulsions may contain a suitable gelatin plasticizer such as glycerin; a dihydroxy alkane such as 1,5-pentane diol as described in Milton and Murray U.S. application Serial No. 588,951, filed June 4, 1956 (now U.S. Patent 2,960,404, issued November 15, 1960); an ester of an ethylene bis-glycolic acid such as ethylene bis(methyl glycolate) as described in Milton U.S. Patent 2,904,434, issued September 15, 1959; bis-(ethoxy diethylene glycol) succinate as described in Gray U.S. application Serial No. 604,333, filed August 16, 1956 (now U.S. Patent 2,940,854, issued June 14, 1960), or a polymeric hydrosol as results from the emulsion polymerization of a mixture of an amide of an acid of the acrylic acid series, an acrylic acid ester and a styrene-type compound as described in Tong U.S. Patent 2,852,386, issued September 16, 1958. The plasticizer may be added to the emulsion before or after the addition of a sensitizing dye, if used.

The emulsions may be hardened with any suitable hardener for gelatin such as formaldehyde; a halogen-substituted aliphatic acid such as mucobromic acid as described in White U.S. Patent 2,080,019, issued May 11, 1937; a compound having a plurality of acid anhydride groups such as 7,8-diphenylbicyclo(2,2,2)-7-octene-2,3,5,6-tetra-carboxylic dianhydride, or a dicarboxylic or a disulfonic acid chloride such as terephthaloylchloride as described in Allen and Carroll U.S. Patents 2,725,294, and 2,725,295, both issued November 29, 1955; a cyclic 1,2-diketone such as cyclopentane-1,2-dione as described in Allen and Byers U.S. Patent 2,725,305, issued November 29, 1955; a bisester of methane-sulfonic acid such as 1,2-di-(methanesulfonyl)-ethane as described in Allen and Laakso U.S. Patent 2,726,162, issued December 6, 1955; 1,3-dihydroxymethylbenzimidazol-2-one as described in July, Knott and Pollak U.S. Patent 2,732,316, issued January 24, 1956; a dialdehyde or a sodium bisulfite derivative thereof, such as β -methyl glutaraldehyde

bis-sodium bisulfite as described in Allen and Burness U.S. patent application Serial No. 556,031, filed December 29, 1955 (now abandoned); a bis-aziridine carboxamide such as trimethylene bis(1-aziridine carboxamide) as described in Allen and Webster U.S. patent application Serial No. 599,891, filed July 25, 1956 (now U.S. Patent 2,950,197, issued August 23, 1960); 2,3-dihydroxy dioxane as described in Jeffreys U.S. Patent 2,870,013, issued January 20, 1959; or bisisocyanate as described in Henn et al. U.S. patent application Serial No. 805,357, filed April 10, 1959.

The emulsions may contain a coating aid such as saponin; a lauryl or oleyl monoether of polyethylene glycol as described in Knox and Davis U.S. Patent 2,831,766, issued April 22, 1958; a salt of a sulfated and alkylated polyethylene glycol ether as described in Knox and Davis U.S. Patent 2,719,087, issued September 27, 1955; an acylated alkyl taurine such as the sodium salt of N-oleoyl-N-methyl taurine as described in Knox, Twardokus and Davis U.S. Patent 2,739,891, issued March 27, 1956; the reaction product of a dianhydride of tetracarboxybutane with an alcohol or an aliphatic amine containing from 8 to 18 carbon atoms which is treated with a base, for example, the sodium salt of the monoester of tetracarboxybutane as described in Knox, Stenberg and Wilson U.S. Patent 2,843,487, issued July 15, 1958; a water-soluble maleopimarate as described in Knox and Fowler U.S. Patent 2,823,123, issued February 11, 1958; an alkali metal salt of a substituted amino acid such as disodium N-(carbo-p-tert. octylphenoxy)pentaoxyglutamate as described in Knox and Wilson U.S. patent application Serial No. 600,679, filed July 30, 1956 (now U.S. Patent 3,038,804, issued June 12, 1962); or a sulfosuccinamate such as tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate as described in Knox and Stenberg U.S. Patent Application Serial No. 691,125, filed October 21, 1957 (now U.S. Patent 2,992,108, issued July 11, 1961), or a sodium salt of an alkylaryl polyether sulfonate of Baldisiefen U.S. Patent 2,600,831, issued June 17, 1952.

The addenda which we have described may be used in various kinds of photographic emulsions. In addition to being useful in X-ray and other nonoptically sensitized emulsions they may also be used in orthochromatic, panchromatic, and infrared sensitive emulsions. They may be added to the emulsion before or after any sensitizing dyes which are used. Various silver salts may be used as the sensitive salt such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide or silver bromiodide. The agents may be used in emulsions intended for color photography, for example, emulsions containing color-forming couplers or emulsions to be developed by solutions containing couplers or other color-generating materials, emulsions of the mixed-packet type, such as described in Godowsky U.S. Patent 2,698,794, issued January 4, 1955; or emulsions of the mixed-grain type, such as described in Carroll and Hanson U.S. Patent 2,592,243, issued April 8, 1952. These agents can also be used in emulsions which form latent images predominantly on the surface of the silver halide crystal or in emulsions which form latent images predominantly inside the silver halide crystal, such as those described in Davey and Knott U.S. Patent 2,592,250, issued April 8, 1952.

These may also be used in emulsions intended for use in diffusion transfer processes which utilize the undeveloped silver halide in the nonimage areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a receiving layer in close proximity to the original silver halide emulsion layer. Such processes are described in Rott U.S. Patent 2,352,014, issued June 20, 1944, and Land U.S. Patents 2,584,029, issued January 29, 1952; 2,698,236, issued December 28, 1954, and 2,543,181, issued February 27, 1951; and Yackel et al. U.S. patent application Serial No.

586,705, filed May 23, 1956 (now U.S. Patent 3,020,155, issued February 6, 1962). They may also be used in color transfer processes which utilize the diffusion transfer of an image-wise distribution of developer, coupler or dye, from a light-sensitive layer to a second layer, while the two layers are in close proximity to one another. Color processes of this type are described in Land U.S. Patents 2,559,643, issued July 10, 1951, and 2,698,798, issued January 4, 1955; Land and Rogers Belgian Patents 554,933 and 554,934, granted August 12, 1957; International Polaroid Belgian Patents 554,212, granted July 16, 1957, and 554,935, granted August 12, 1957; Yutzy U.S. Patent 2,756,142, granted July 24, 1956 and Whitmore and Mader U.S. patent application Serial No. 734,141; filed May 9, 1958 (now abandoned). They may also be used in emulsions intended for use in a monobath process such as described in Haist et al. U.S. Patent 2,875,048, issued February 24, 1959, and in web-type processes, such as the one described in Fregillus et al. U.S. patent application Serial No. 835,473, filed August 24, 1959.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions, there may be employed as the dispersing agent for the silver halide in its preparation, gelatin or some other colloidal material such as colloidal albumin, a cellulose derivative or a synthetic resin, for instance, a polyvinyl compound. Some colloids which may be used are polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in Lowe U.S. Patent 2,286,215, issued June 16, 1942; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19-26% as described in U.S. Patent 2,327,808 of Lowe and Clark, issued August 24, 1943; a water-soluble ethanolamine cellulose acetate as described in Yutzy U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamide or an imidized polyacrylamide as described in Lowe, Minsk and Kenyon U.S. Patent 2,541,474, issued February 13, 1951; zein as described in Lowe U.S. Patent 2,563,791, issued August 7, 1951; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith U.S. Patent 2,768,154, issued October 23, 1956; or containing cyano-acetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in Unruh, Smith and Priest U.S. Patent 2,808,331, issued October 1, 1957; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in U.S. Patent 2,852,382, of Illingsworth, Dann and Gates, issued September 16, 1958.

If desired, compatible mixtures of two or more of these colloids may be employed for dispersing the silver halide in its preparation. Combinations of these antifoggants, sensitizers, hardeners, etc., may be used.

As mentioned above, the advantages of our invention are particularly outstanding in reversal color photographic processes. Couplers or color-forming compounds which are soluble in the strongly alkaline developing solutions are well known to those skilled in the art. Typical couplers include the following:

COUPLERS FOR USE IN COLOR DEVELOPERS

Cyan couplers:

- (1) 5-benzenesulfonamino-1-naphthol
- (2) 2,4-dichloro-5-benzenesulfamino-1-naphthol
- (3) 2,4-dichloro-5-(p-toluenesulfamino)-1-naphthol
- (4) 5-(1,2,3,4-tetrahydronaphthalene-6-sulfonamino)-1-naphthol
- (5) 2,4-dichloro-5-(4'-bromodiphenyl-4-sulfonamino)-1-naphthol
- (6) o-(β -Naphthalenesulfonamino)phenol
- (7) 5-(m-nitrobenzenesulfonamino)-1-naphthol
- (8) 5-(quinoline-5-sulfonamino)-1-naphthol
(U.S. 2,362,598)
- (9) 2-acetylamino-5-methylphenol

- (10) 2-benzoylamino-3,5-dimethylphenol
 - (11) 2- α -(p-tert. amylphenoxy)-n-butyrylamino-5-methylphenol
 - (12) 2- α -(p-tert. amylphenoxy)-n-butyrylamino-4-chloro-5-methylphenol
 - (13) 2-(p'-tert. amylphenoxy-p-benzoyl)amino-4-chloro-5-methylphenol
 - (14) 2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3,5-dimethyl-1-phenol
 - (15) 2-phenylacetylamino-4-chloro-5-methylphenol
 - (16) 2-benzoylamino-4-chloro-5-methylphenol
 - (17) 2-anilinoacetylamino-4-chloro-5-methylphenol
 - (18) 2-{4'-[α -(4''-tert. amylphenoxy)-n-butyrylamino]-benzoylamino}-4-chloro-5-methylphenol
 - (19) 2-{4'-[3''-(4'''-tert. amylphenoxy)-benzoylamino]-benzoylamino}-4-chloro-5-methylphenol
 - (20) 2-p-nitrobenzoylamino-4-chloro-5-methylphenol
 - (21) 2-m-aminobenzoyl-4-chloro-5-methylphenol
 - (22) 2-acetamino-4-chloro-5-methylphenol
 - (23) 2-(4'-sec. amylbenzamino)-4-chloro-5-methylphenol
 - (24) 2-(4'-n-amyloxybenzamino)-4-chloro-5-methylphenol
- Magenta couplers:
- (25) 1-phenyl-3-acetylamino-5-pyrazolone
 - (26) 1-phenyl-3-propionylamino-5-pyrazolone
 - (27) 1-phenyl-3-dichloroacetylamino-5-pyrazolone
 - (28) 1-phenyl-3-benzoylamino-5-pyrazolone
 - (29) 1-phenyl-3(m-aminobenzoyl)-amino-5-pyrazolone hydrochloride
 - (30) 1-phenyl-3-(diamylbenzoyl)amino-5-pyrazolone
 - (31) 1-phenyl-3-phenylcarbonylamino-5-pyrazolone
 - (32) 1-phenyl-3-phenoxyacetylamino-5-pyrazolone
 - (33) 1-phenyl-3-p-aminobenzoylamino-5-pyrazolone
 - (34) 1-phenyl-3-(o-carboxybenzoyl)amino-5-pyrazolone
 - (35) 1-phenyl-3-palmitylamino-5-pyrazolone
 - (36) 1-phenyl-3-(p-sec. amylbenzenesulfonylamino)-5-pyrazolone
 - (37) 1-phenyl-3-[p-(p'-sec. amylbenzoyl)aminobenzoylamino]-5-pyrazolone
 - (38) 1-m-tolyl-3-[m-(β -phenylpropionyl)aminobenzoylamino]-5-pyrazolone
 - (39) 1-m-tolyl-3-(2,4-di-tert. butyl-m-tolyloxyacetylamino)-5-pyrazolone
 - (40) 1-[p-(p'-tert. butylphenoxy)phenyl]-3-3[p-(benzoyl-amino)-benzoylamino]-5-pyrazolone
 - (41) 1-(p-tert. butylphenoxyphenyl)-3-(p-m-amyloxybenzoyl-amino)-5-pyrazolone
 - (42) 1-[p-(p'-tert. butylphenoxy)phenyl]-3-(3,5-dimethoxy-benzoyl)amino-5-pyrazolone
 - (43) 1-[p-(p'-tert. butylphenoxy)phenyl]-3-[m-(p-toluene-sulfonylamino)benzoylamino]-5-pyrazolone
 - (44) 1-[p-(3,5-dimethylphenoxy)phenyl]-3-(4-n-amyloxy-3-methylbenzoylamino)-5-pyrazolone
 - (45) 3-(p-nitrophenoxyacetylamino)-1-(2',4',6',-trichloro-phenyl)-5-pyrazolone
- Yellow couplers:
- (46) p-(ω -Benzoylacetamino)benzenesulfonamide
 - (47) p-(ω -Benzoylacetamino)benzenesulfonmethanamide
 - (48) p-(ω -Benzoylacetamino)benzenesulfonanilide
 - (49) 4-benzenesulfonamino- ω -benzoylacetanilide
 - (50) 4-(p-toluenesulfonamino) ω -benzoylacetanilide
 - (51) 4-(p-laurylbenzenesulfonamino)- ω -benzoylacetanilide
 - (52) 1,4-di-[p-(benzoylacetamino)benzenesulfonamino]benzene
 - (53) N,N'-di-(p-benzoylacetaminophenyl)benzene-1,3-disulfonamide
 - (54) N-(p-benzoylacetaminophenyl)-4-[p-(benzoylacetamino)-benzenesulfonamido]benzenesulfonamide
 - (55) N⁴-benzoylacetyl-N'-(2-benzoylthiazolyl)sulfanilamide
 - (56) p-Acetoacetaminobenzenesulfon- β -naphthalide

- (57) p-Furoylacetaminobenzenesulfon-N-cyclohexylamide
 (58) p-(4-ethoxybenzoylacetamino)benzenesulfonamide
 (59) Terephthaloyl-bis(p-N-amylsulfonamido)acetanilide
 (60) p-(Quinoline-8-sulfonamino)-*o*-benzoylacetanilide
 (61) p-Acetoacetamino-*o*-methylbenzenesulfon-N-anilide
 (62) N,N'-di-(p-benzoylacetaminophenol)naphthalene-1,5-disulfonamide
 (63) p-(Benzenesulfonamino)benzoylacetone
 (64) N-benzoylacetate-*o*-anisidine

Typical couplers that are primarily useful in the photographic silver halide emulsion layers of our invention comprise the following:

Coupler:

- (65) 1-hydroxy-2[δ -(2',4'-di-tert. amylphenoxy)-*n*-butyl]-naphthamide (U.S. Patent 2,474,293)
 (66) 1-hydroxy-4-phenylazo-4'-(p-tert. butylphenoxy)-2-naphthanilide (U.S. Patent 2,521,908)
 (67) 2-(2,4-di-tert. amylphenoxyacetamino)-4,6-dichloro-5-methylphenol (U.S. Patent 2,725,291)
 (68) 2-(α -di-tert. amylphenoxy-*n*-butyrylamino)-4,6-dichloro-*t*-methylphenol
 (69) 6-{ α -{4-[α -(2,4-di-tert. amylphenoxy)butyramido]-phenoxy}acetamido}-2,4-dichloro-3-methylphenol
 (70) 2-[3'-(2'',4''-diamylphenoxy)-acetamido]-benzamido-4-chloro-5-methylphenol
 (71) 1-(2',4',6'-trichlorophenyl)-3-[3''-(2''',4'''-di-tert. amylphenoxyacetamido)-benzamido]-5-pyrazolone (U.S. Patent 2,600,788)
 (72) 1-(2,4',6'-trichlorophenyl)-3-[3''-(2''',4'''-di-tert. amylphenoxyacetamido)-benzamido]-4-(p-methoxyphenylazo)-5-pyrazolone
 (73) N-(4-benzoylacetaminobenzenesulfonyl)-N-(γ -phenylpropyl)-*p*-toluidine (U.S. Patent 2,298,443)
 (74) α -*o*-Methoxybenzoyl- α -chloro-4-[α -(2,4-di-tert. amylphenoxy)-*n*-butyramido]-acetanilide (McCrosen U.S. Patent 2,728,658)
 (75) α -{3-[α -(2,4-di-tert. amylphenoxy)acetamido]-benzoyl}-2-methoxyacetanilide
 (76) 3-benzoylacetamido-4-methoxy-2',4'-di-tert. amylphenoxyacetanilide
 (77) benzoylacetamido-3-methoxy-2',4'-di-tert. amylphenoxyacetanilide

Other couplers suitable for use in the emulsions of our invention comprise those disclosed in Spence and Carroll U.S. Patent 2,640,776, issued June 2, 1953, Weissberger et al. U.S. Patent 2,407,210, issued September 3, 1946, and Weissberger et al. U.S. Patent 2,474,293, issued June 28, 1949.

The color-forming developers useful in our invention have been previously described in the prior art, and our invention is not to be restricted to the use of any particular color-forming developer. The color-forming developers previously mentioned which we have found to be especially useful in our invention comprise aromatic primary amines containing an amino (substituted or not) or hydroxyl substituent. Phenylenediamines and substituted derivatives thereof containing a primary amino group have been found to provide excellent results when employed in combination with the formamidinothiomethyl compounds of our invention. Typical of such color-forming developers are the sulfonamido substituted *p*-phenylenediamines disclosed in Weissberger U.S. Patent 2,548,574, issued April 10, 1951, the substituted *p*-phenylenediamines disclosed in Weissberger et al. U.S. Patent 2,566,271, issued August 28, 1951. Other phenylenediamine color-forming developers can be employed to like advantage in the process of our invention.

The first developer employed in the process of our invention is generally a rapid developer of the MQ type,

i.e., a combination of hydroquinone and Elon (*p*-N-methylaminophenyl) developer.

The following examples will serve to illustrate the manner of obtaining improved images in multi-layer photographic elements according to our invention.

An ordinary photographic multi-layer color film of the type described in Mannes et al. U.S. Patent 2,252,718 and containing no color-formers or couplers in the selectively sensitized photographic silver halide emulsion layers (i.e., blue, green and red) was cut into a number of strips. Each of the strips was then exposed for $\frac{1}{100}$ second on an Eastman Type Ib Sensitometer to a 500-watt light source equipped with a 0.6 neutral density filter in combination with a Wratten No. 29 filter (i.e., a filter transmitting only visible light beyond about 600 $m\mu$ with maximum transmittance at about 700 $m\mu$) so that the illuminant had a color temperature of about 3000° K. Each of the strips was then developed to a black-and-white negative image by development for 10 minutes at 80° F. in an ordinary hydroquinone-Elon developer, such as one having the following formula:

Kodak developer D-19

	Grams
25 N-methyl- <i>p</i> -aminophenol sulfate	2.0
Sodium sulfite, desiccated	90.0
Hydroquinone	8.0
Sodium carbonate, monohydrated	52.5
Potassium bromide	5.0
30 Cold water to make 1.0 liter.	

The strips were then washed for 2 minutes at 80° F., followed by an additional two minutes' treatment at 80° F. in a fog-reducing bath having the following composition:

3-(2-benzothiazolylmethyl)benzothiazolin <i>p</i> -toluenesulfonate	0.5
Methanol	100
40 Water	900

Each of the strips was then again washed for two minutes with water heated to 80° F. and given reversal reexposure for 15 seconds to a RFL No. 2 Lamp placed at a distance of one meter through a Wratten No. 92 filter (i.e., a filter transmitting only visible radiation beyond about 620 $m\mu$ with maximum transmittance of about 88 percent at 700 $m\mu$).

Each of the strips was developed for ten minutes at 80° F. in a cyan developer having the composition given below. One of the film strips served as a control and contained no thioether compound, while the other strips were developed in cyan developers containing thioether compounds in amounts identified in the following table. The compound numbers in the table correspond to the compound numbers given above for the thioether compounds. The cyan developer which served as a control and to which the thioether compounds were added had the following formula:

60 Sulfuric acid (concentrated)	1.5
Calgon (sodium hexametaphosphate)	0.5
Sodium sulfite	5.0
2-amino-5-diethylamino toluene.HCl	0.6
65 Sodium carbonate monohydrate	15.0
Sodium bromide	0.25
Potassium iodide	.002
Color coupler ¹	1.2
70 H acid	0.5
Water to 1 liter.	

(Sufficient sodium hydroxide added to give a pH of 10.5.)

¹ 5-*p*-toluene sulfonamido-2,4-dichloro- α -naphthol.

Each of the strips was then washed for 10 minutes in

water heated to 80° F. and bleached for two minutes at 80° F. in a bath having the following composition:

	Grams
Calgon	1.0
Potassium ferricyanide	80.0
Sodium bromide	34.4
Water to 1 liter.	

The strips were then fixed for two minutes at 80° F. in a bath having the following composition:

	Grams
Calgon	10.0
Sodium sulfite	10.0
Sodium thiosulfate pentahydrate	32.0
Water to make 1 liter.	

The strips were then washed for five minutes in 80° F. water and dried. The following results were obtained.

TABLE I

Compound Number	Conc. in Cyan Dev., g./l.	10' Cyan Development Time	
		Cyan D _{max}	Cyan Fog
None.....		2.04	0.16
2.....	0.5	4.0+	.21
3.....	.5	2.98	.14
5.....	.5	3.66	.14
6.....	.5	4.0+	.28
7.....	.2	2.25	.09
8.....	.2	2.60	.13
61.....	.5	3.06	.14
62.....	.5	2.60	.17
4.....	.5	4.0+	.22

+ exceeds scale of densitometer.

During the development of a color film such as described above in a black-and-white developer, fog centers are introduced in the unexposed regions which then develop in the coupler containing developers. For example, after negative development and red re-exposure, development in a color developer containing a cyan coupler results not only in development of the red sensitive layer, but also in development of cyan fog in the blue- and green-sensitive layers. Such cyan fog is tabulated in the table above.

The following example will serve to illustrate the useful effect of our thioether compound in a magenta reversal developer.

A multi-layer color film of the type used in Example 1 was cut into several strips and each of these exposed for 1/25 second to a 500-watt 3000° K. light source on an Eastman Type Ib Sensitometer. Each of the strips was then developed for nine minutes at 80° F. to a black-and-white negative developer of the type described in the above example and washed for five minutes in 80° F. water. Strips were then treated in an antifoggant bath of the type described in the above example for two minutes at 80° F. and washed for two minutes in 80° F. water. The strips were then given a reversal re-exposure to red illumination as described in Example 1 and developed for 15 minutes at 80° F. in the above cyan developer containing no thioether compound. The strips were then washed for five minutes at 80° F. in water and exposed to blue illumination through the emulsion side of the support and developed for 20 minutes at 80° F. in a yellow-forming developer having the following composition:

	Grams
Calgon	0.5
Sodium sulfite	5.0
N,N-diethyl-p-phenylenediamine HCl	2.0
Sodium carbonate monohydrate	20.0
Sodium bromide	0.25
Potassium iodide	0.22
ω-Benzoyl-4-p-toluenesulfonamido acetanilide	2.0
H acid	0.7
Hydroxylamine hydrochloride	1.0
Water to make 1 liter.	

(Sufficient sodium hydroxide to give a pH of 11.5.)

The strips were again washed for 5 minutes at 80° F. in water and given a flash exposure to white light and developed in a magenta developer for the times indicated in the following table, the developing composition being as follows:

	Grams
Sulfuric acid (concentrated)	1.5
Calgon	0.5
Sodium sulfite	5.0
2-amino-5-diethylamino toluene HCl	1.6
Sodium carbonate monohydrate	15.0
Sodium bromide	0.25
Potassium iodide	0.002
Coupler ¹	4.0
H acid	0.2

Water to make 1 liter.

(Sufficient sodium hydroxide to give a pH of 11.0.)

¹ 1-(2,4,6-trichlorophenyl) - 3[α - (4 - nitrophenoxy) - acetamido] - 5-pyrazolone.

The strips were then washed for 5 minutes in 80° F. water, bleached for 2 minutes at 80° F. in the bleach bath of the above example, fixed for two minutes at 80° F. in a fixing bath of the type used in the above example, washed for five minutes at 80° F. and dried. The following data were obtained:

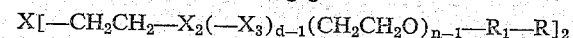
TABLE II

Compound Number	Conc. in Magenta Dev., g./l.	Magenta Dev. Time, Minutes	Magenta D _{max}
Control.....		20	2.26
1.....	2.0	15	3.30

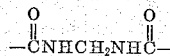
The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

What we claim as our invention and desire secured by Letters Patent of the United States is:

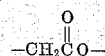
1. A photographic color developer comprising an aqueous alkaline solution of an arylendiamine color developer and a non-polymeric compound selected from those represented by the following general formula:



wherein R represents a member selected from the class consisting of a hydroxyl group, an alkoxy group, and a carbamyl group, R₁ represents an ethylene radical, X represents a divalent radical selected from the class consisting of an oxygen atom, a sulfur atom



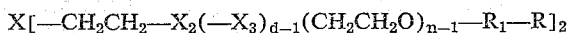
and the group $-X_1CH_2CH_2X_1-$, X₁ and X₂ each represents a divalent radical selected from the class consisting of an oxygen atom and a sulfur atom, provided at least one of the radicals selected from the class consisting of X, X₁ and X₂ represents a sulfur atom, X₃ represents the divalent radical



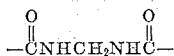
d represents a positive whole number of from 1 to 2 and n represents a positive whole number of from 1 to 3.

2. A photographic color developer comprising an aqueous alkaline solution of a p-phenylenediamine color developing agent, a color-forming compound capable of coupling with the oxidation products of said color developing agent to provide a colored image, and a non-pol-

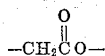
ymeric compound selected from those represented by the following general formula:



wherein R represents a member selected from the class consisting of a hydroxyl group, an alkoxy group, and a carbamyl group, R_1 represents an ethylene radical, X represents a divalent radical selected from the class consisting of an oxygen atom, a sulfur atom,



and the group $-X_1CH_2CH_2X_1-$, X_1 and X_2 each represents a divalent radical selected from the class consisting of an oxygen atom and a sulfur atom, provided at least one of the radicals selected from the class consisting of X, X_1 and X_2 represents a sulfur atom, X_3 represents the divalent radical

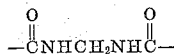


d represents a positive whole number of from 1 to 2 and n represents a positive whole number of from 1 to 3.

3. A photographic color developer comprising an aqueous alkaline solution of a p-phenylenediamine color developing agent, a phenolic compound capable of coupling with the oxidation products of said color developing agent to provide a cyan photographic image, and a non-polymeric compound selected from those represented by the following general formula:

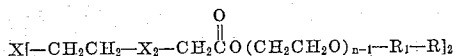


wherein R represents a member selected from the class consisting of a hydroxyl group, an alkoxy group and a carbamyl group, X represents a divalent radical selected from the class consisting of an oxygen atom, a sulfur atom,

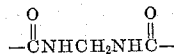


and the radical $-X_1CH_2CH_2X_1-$, X_1 and X_2 each represents a divalent radical selected from the class consisting of an oxygen atom and a sulfur atom, provided at least one of the radicals selected from the class consisting of X, X_1 and X_2 represents a sulfur atom, and n represents a positive whole number of from 1 to 3.

4. A photographic color developer comprising an aqueous alkaline solution of a p-phenylenediamine color developing agent, a phenolic compound capable of coupling with the oxidation products of said color developing agent to provide a cyan photographic image, and a non-polymeric compound selected from those represented by the following general formula:



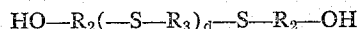
wherein R represents a member selected from the class consisting of a hydroxyl group, an alkoxy group, and a carbamyl group, R_1 represents an ethylene radical, X represents a divalent radical selected from the class consisting of an oxygen atom, a sulfur atom,



and the radical $-X_1CH_2CH_2X_1-$, X_1 and X_2 each represents a divalent radical selected from the class consisting of an oxygen atom and a sulfur atom, provided at least one of the radicals selected from the class consisting of X, X_1 and X_2 represents a sulfur atom, and n represents a positive whole number of from 1 to 3.

5. A photographic color developer comprising an aqueous alkaline solution of a p-phenylenediamine color developing agent, a compound capable of coupling with the

oxidation products of said color developing agent to produce a colored photographic image, and a non-polymeric compound selected from those represented by the following general formula:



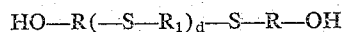
wherein R_2 and R_3 each represents a hydrocarbon alkylene group containing from about 2 to 10 carbon atoms and d represents a positive integer of from 1 to 3.

6. A photographic color developer comprising an aqueous alkaline solution of a p-phenylenediamine color developing agent, a compound capable of coupling with the oxidation products of said color developing agent to produce a colored photographic image, and a non-polymeric compound selected from those represented by the following general formula:



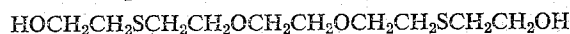
wherein m and n each represents a positive integer of from about 2 to 10.

7. A photographic color developer comprising an aqueous alkaline solution of a p-phenylenediamine color developing agent, a pyrazolone compound capable of coupling with the oxidation products of said color developing agent to produce a magenta photographic image and a non-polymeric compound selected from those represented by the following general formula:

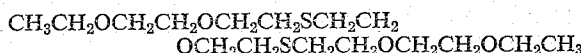


wherein R and R_1 each represents a hydrocarbon alkylene group containing from about 2 to 10 carbon atoms and d represents a positive integer of from 1 to 3.

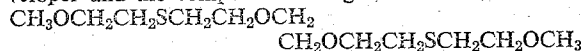
8. A photographic color developer comprising an aqueous alkaline solution of an arylenediamine color developer and the compound having the formula:



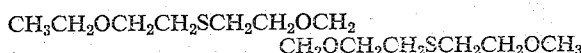
9. A photographic color developer comprising an aqueous alkaline solution of an arylenediamine color developer and the compound having the formula:



10. A photographic color developer comprising an aqueous alkaline solution of an arylenediamine color developer and the compound having the formula:



11. A photographic color developer comprising an aqueous alkaline solution of an arylenediamine color developer and the compound having the formula:



12. A photographic color developer comprising an aqueous alkaline solution of an arylenediamine color developer and the compound having the formula:



References Cited by the Examiner

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NORMAN G. TORCHIN, *Primary Examiner.*

HAROLD N. BURSTEIN, *Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,201,242

August 17, 196

Judith A. Schwan et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 16, lines 53 and 54, the right-hand portion of the formula reading

$\text{CH}_2\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OCH}_3$ read $\text{CH}_2\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$

Signed and sealed this 8th day of March 1966.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents