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(54) Photographic element having reduced color contamination.

(57) A multilayer color photographic element having improved reduction in dye stain while having reduced color contamination comprises at least one cyan color-forming silver halide layer which contains a thiacyanine sensitizing dye and at least one non-imaging layer containing a dialkyhydroquinone. The non-imaging layer is adjacent the layer containing the thiacyanine sensitizing dye or is in an antihalation layer.

Rank Xerox (UK) Business Services
(3.10/3.09/3.3.4)

Field of the Invention

This invention relates to a color photographic film element and in particular, a color photographic film element having improved reduction in dye stain while having reduced color contamination.

Background of the Invention

Multilayer color photographic film elements contain at least one silver halide emulsion layer sensitive to blue light and containing a yellow color-forming coupler, at least one silver halide emulsion layer sensitive to green light and containing a magenta color-forming coupler and at least one silver halide emulsion layer sensitive to red light and containing a cyan color-forming coupler. To enhance the sensitivity to light of the desired color, the silver halide grains in the layers can be treated with a sensitizing dye. It is known to use a thiacyanine dye to increase the sensitivity of a silver halide emulsion to red light.

After imagewise exposure to light, the element is processed to develop the desired colored image. The exposed silver halide grains react with the developing agent in the processing solution and oxidized developer (hereinafter referred to as "Dox") is produced. The Dox reacts with the dye forming couplers to form the desired color. Since Dox is created only at exposed silver halide grains, color development takes place imagewise. If Dox migrates from the layer in which it is produced to an adjacent layer containing dye forming coupler of a different color, dyes of the wrong color form which results in color contamination. To inhibit such undesired color formation, an intermediate layer containing a compound that reacts with Dox, (hereinafter called a scavenger) is positioned between layers of different sensitivity.

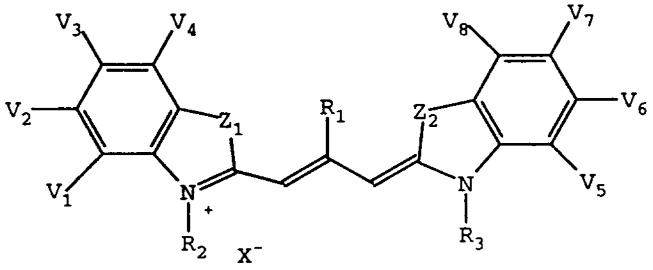
Certain photographic elements are processed using a reversal process which involves developing the exposed silver halide grains in one step and then later developing the color image in a separate second step. Other photographic elements are developed in a single step process in which development of the silver halide grains and reaction of Dox with color-forming couplers to create the color image takes place at the same time. In single step processes, the photographic element is in contact with the processing solution for a much shorter period of time than in a two step process. Color negative films are generally processed by single step development processing.

Problem to be Solved by the Invention

It has been found that when an intermediate layer containing certain common scavengers is used in a photographic film element in which a thiacyanine dye is used to sensitize silver halide grains in the red sensitive layer, unacceptable dye stain due to re-aggregation of excessive residual thiacyanine dye is formed during single step processing of the exposed photographic film element.

Summary of the Invention

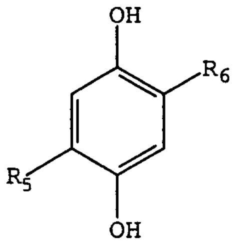
One aspect of this invention comprises a multilayer silver halide photographic film element for processing in a single step development process, said element comprising a transparent support having thereon at least one yellow color-forming silver halide emulsion layer, at least one magenta color-forming silver halide emulsion layer, at least one cyan color-forming layer and at least one non-imaging layer, wherein the cyan color-forming silver halide layer contains a sensitizing dye according to Formula A:



Formula A

wherein Z_1 represents a sulfur or a selenium atom; Z_2 represents a sulfur or selenium atom or $-NR_4$; R_1 represents a hydrogen atom or an unsubstituted or substituted alkyl group; R_2, R_3 and R_4 each independently represent an unsubstituted or substituted alkyl or alkenyl group of less than 18 carbon atoms; V_1, V_2, V_3, V_4, V_5, V_6, V_7 and V_8 each represent a hydrogen atom, a halogen atom, an alkyl group, an alkyloxy group, an aryl group, a heterocyclic group (such as furanyl), a cyano group, a hydroxy group, an amino group, a carbonamido group, a trifluoromethyl group, an acyloxy group, an alkylthio group or maybe connected to form one or more additional aromatic rings; and X represents a counter ion, as necessary to balance the overall charge of the dye;

wherein said non-imaging layer contains a dialkylhydroquinone according to Formula B:



Formula B

where R_5 and R_6 each represent an unsubstituted or substituted alkyl group, said dialkylhydroquinone being present in an amount effective to inhibit aggregation of said sensitizing dye remaining after processing;

and wherein said non-imaging layer is substantially free of reactive imaging components and (a) is positioned adjacent to said cyan color-forming layer between said cyan color forming layer and the support, or is (b) an antihalation layer.

In preferred embodiments of the invention the photographic film element further comprises an antihalation layer containing colloidal silver and/or organic dyes that absorb light having a wavelength in the range of 400-700 nm. The dialkyl hydroquinone is preferably incorporated into the antihalation layer.

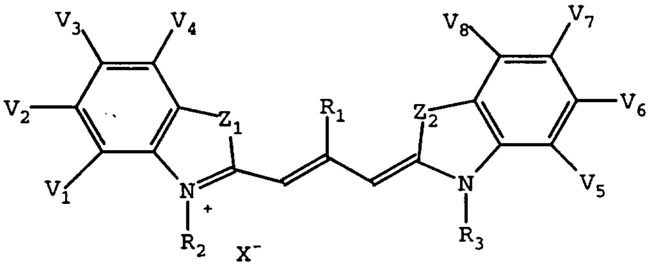
Advantageous Effect of the Invention

In the photographic element of this invention there is reduced dye stain due to aggregation of the thiacyanine sensitizing dye in the red sensitive silver halide emulsion layer, while color contamination due to migration of Dox from the layer in which it is generated is inhibited.

Detailed Description of the Invention

As stated above, the multilayer silver halide photographic film element of this invention is processed in a single step development process, as discussed more fully below. The multilayer film comprises a transparent support having thereon at least one yellow color-forming silver halide emulsion layer, at least one magenta color-forming silver halide emulsion layer, at least one cyan color-forming layer and at least one non-imaging layer. This invention is concerned with reducing dye stain due to re-aggregation of excessive residual thiacyanine dye used as a sensitizing dye in the red sensitizing layer. This dye stain is produced when certain scavengers are used in the intermediate layer to prevent migration of the Dox produced in one layer migrating to another layer. These scavengers include disulfonamidophenols, which are commonly used in color negative film.

In the photographic film of this invention a thiacyanine sensitizing dye according to formula A is used to sensitize the emulsion in the red sensitive layer.



Formula A

wherein Z_1 represents a sulfur or a selenium atom; Z_2 represents a sulfur or selenium atom or $-NR_4$; R_1 represents a hydrogen atom or an unsubstituted or substituted alkyl group; R_2, R_3 and R_4 each independently represent an unsubstituted or substituted alkyl or alkenyl group of less than 18 carbon atoms; V_1, V_2, V_3, V_4, V_5, V_6, V_7 and V_8 each represent a hydrogen atom, a halogen atom, an alkyl group, an alkyloxy group, an aryl group, a heterocyclic group (such as furanyl), a cyano group, a hydroxy group, an amino group, a carbonamido group, a trifluoromethyl group, an acyloxy group, an alkylthio group or may be connected to form one or more additional aromatic rings; and X represents a counterion, if necessary to balance the overall charge of the dye.

R_1 represents a hydrogen or a substituted or unsubstituted alkyl group, preferably containing 1-4 carbon atoms. Preferred examples of alkyl groups include methyl, ethyl, propyl, butyl, 2-methoxyethyl, 2-ethoxyethyl, methoxymethyl, ethoxymethyl, benzyl, p-methoxybenzyl, p-chlorobenzyl and 2-chloroethyl.

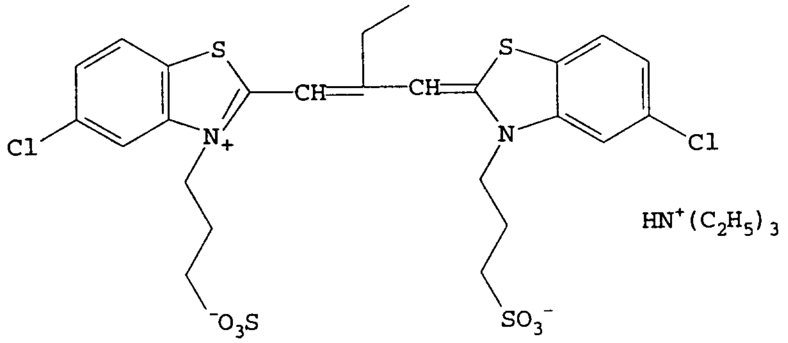
R_2, R_3 and R_4 are each independently a substituted or unsubstituted alkyl or alkenyl group, preferably having 1-18 carbon atoms. It is preferred that at least one of R_2, R_3 and R_4 contain an acid solubilizing group such as carboxy ($-CO_2^-$), sulfo (SO_3^-),phosphono($-PO_3H_2$), sulfato ($-OSO_3^-$), sulfocarbonamido ($-CONHSO_2-$) or imido (-CONHCO-). Further, additional solubilizing groups such as hydroxy, sulfonamido or carbonamido may be present. Preferred examples include ethyl, propyl, butyl, 3-sulfopropyl, 3-sulfobutyl, 4-sulfobutyl, and 2-hydroxy-3-sulfopropyl.

Preferred V_1-V_8 groups include H, methyl, chloro, phenyl, furanyl or annuated benzene rings.

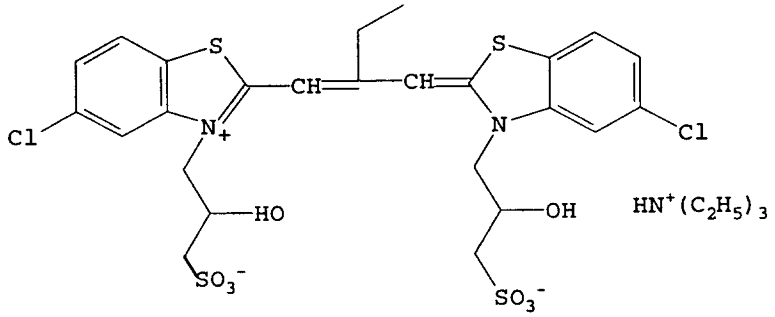
Preferred X ions are salts of sodium, potassium, triethylamine, pyridine, tetramethyl guanidine, morpholine, N-ethylpiperdine or N-ethylpyridinium.

In preferred thiacyanine dyes, Z_1 represents a sulfur atom and Z_2 represents a sulfur or selanium atom. In particularly preferred dyes, each of Z_1 and Z_2 represents a sulfur atom. Preferably the dye molecule contains a solubilizing group attached to the nitrogen atom of one of the thiazole rings and more preferably it contains a solubilizing group attached to the nitrogen atoms of each thiazole ring.

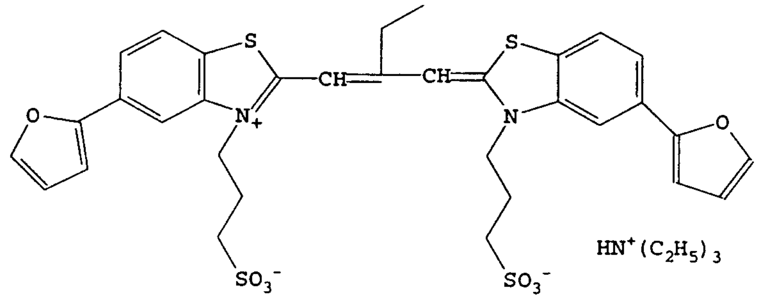
Illustrative thiacyanine dyes are shown below by their structural formulas:


Cl
S
N+
CH
CH
S
N
Cl
$HN^+(C_2H_5)_3$
^-O_3S
SO_3^-

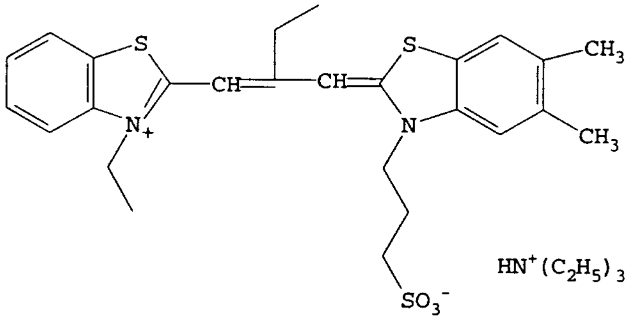
DYE-1


Cl
S
N+
CH
CH
S
N
Cl
HO
OH
$HN^+(C_2H_5)_3$
SO_3^-
SO_3^-

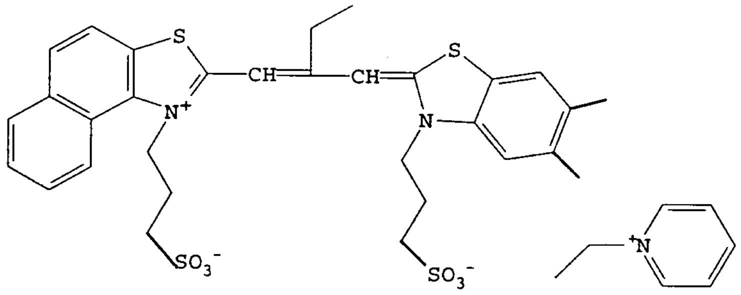
DYE-2



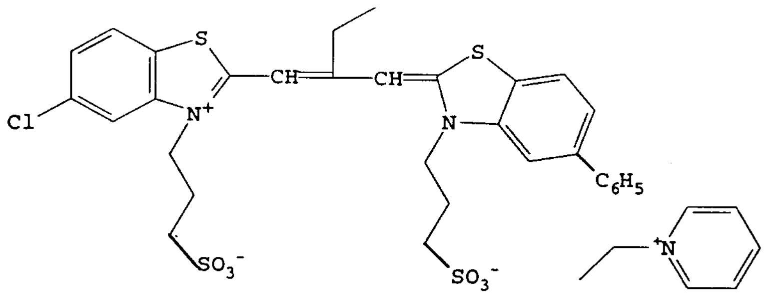
DYE-3



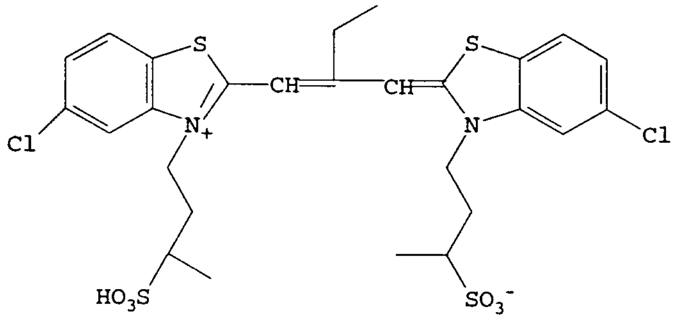
DYE-4



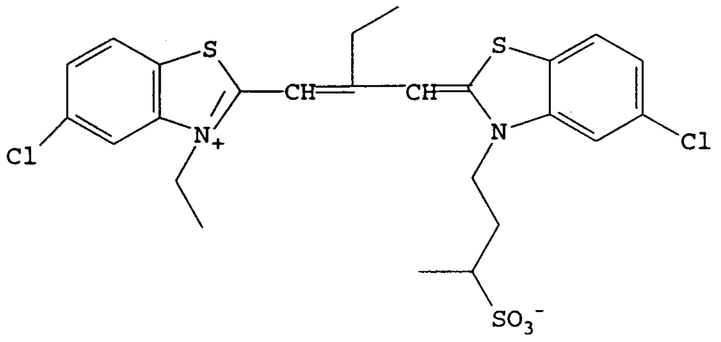
DYE-5



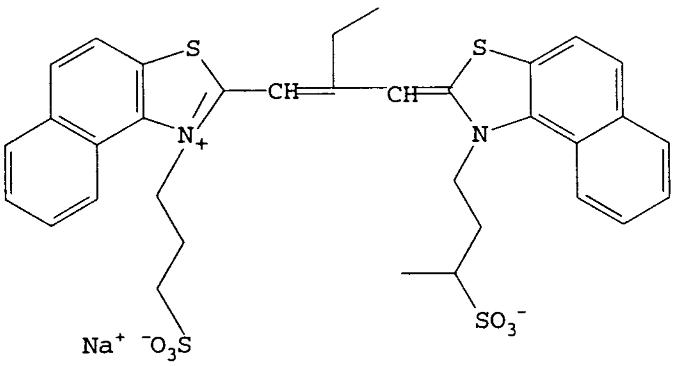
DYE-6



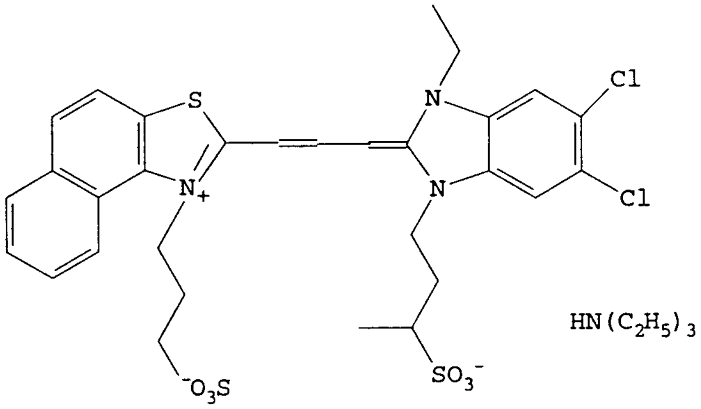
DYE-7



DYE-8



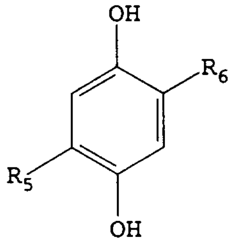
DYE-9



DYE-10

The red sensitizing dye is used to sensitize the silver halide emulsion used in the cyan color-forming layer as described in U.S. Patents Nos. 3,463,640 and 3,522,052, the entire disclosures of which are incorporated herein by reference. Preferably the amount of sensitizing dye used is from about 0.1 mmol, to about 5 mmol per mole of silver, more preferably about 0.3 mmol, to about 3.0 mmol per mole of silver. In the film of this invention, a scavenger is located in at least one non-imaging layer, such as an antihalation layer or an interlayer positioned adjacent the cyan color-forming layer.

Preferred dialkylhydroquinones have the structure represented by formula B.

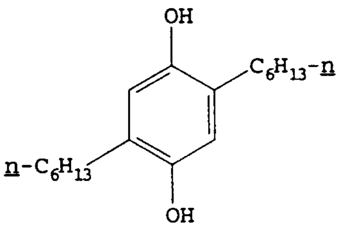


Formula B

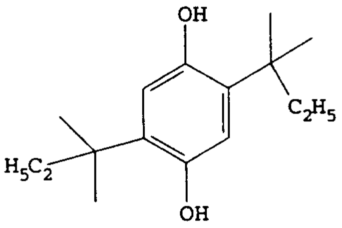
where R_5 and R_6 each independently represents an unsubstituted or substituted alkyl group. Particularly preferred are hydroquinones in which each of R_5 and R_6 are tertiary alkyl groups in which the tertiary carbon atom is adjacent to the aromatic ring.

R_4 and R_5 each independently represents an unsubstituted or substituted alkyl group, preferably having 1-30 carbon atoms. Examples of preferred R_4 and R_5 groups are methyl, ethyl, propyl, isopropyl, butyl, t-butyl, t-amyl, hexyl, t-hexyl, octyl, t-octyl, decyl, t-decyl, dodecyl, t-dodecyl or n-or t octadecyl. It is preferred than R_4 and R_5 are identical and that they each contain more than 5 carbon atoms. Examples of substituents which may be present include ether groups, carbonyl groups, carbamoyl, sulfamoyl, sulfonyl, or amino groups or substituted phenyl groups, such as p-methoxyphenyl, m-carboxyphenyl, p-chlorophenyl and the like.

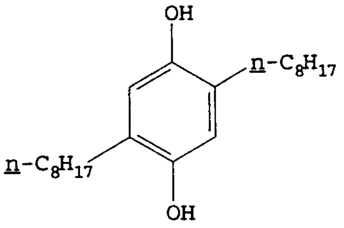
Illustrative hydroquinones include compounds of the following structural formulas:



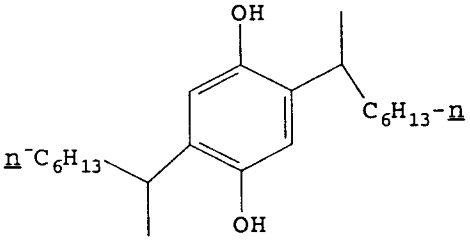
S-1



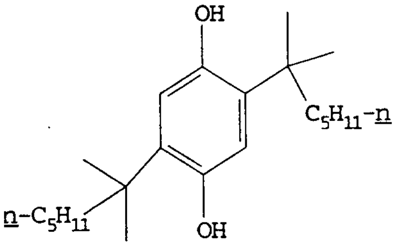
S-2



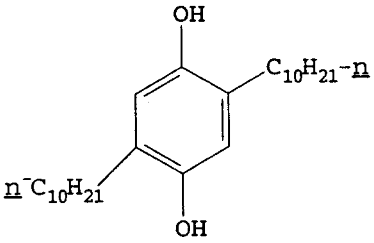
S-3



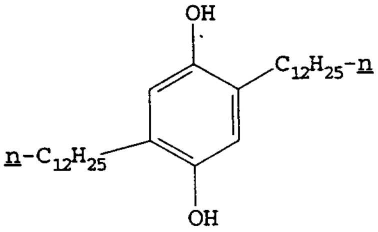
S-4



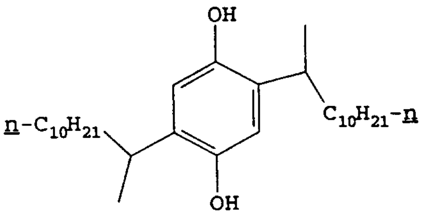
S-5



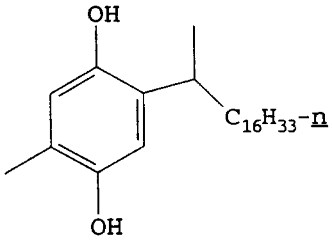
S-6

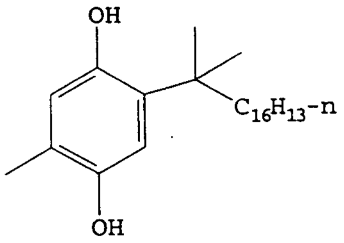


S-7



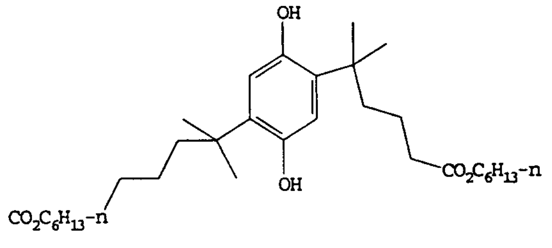
S-8



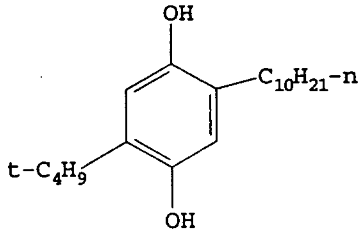


S-9

S-10



S-11



S-12

A particularly preferred dialkyl hydroquinone is dioctyl hydroquinone. Use of dioctyl hydroquinone as a scavenger in multilayer photographic film elements has been limited due to the relative instability of dispersions of dioctyl hydroquinone. A solution to this problem is described in copending commonly assigned patent application 07/978104 of Zengerle et al filed November 18, 1992, the entire disclosures of which are incorporated herein by reference. Preferably the amount of dialkyl hydroquinone used in the non-imaging layer is from about 1 x 10^{-3} g/m^2 to about 1 g/m^2, more preferably from about 1 x 10^{-2} g/m^2 to about 0.25 g/m^2.

The multilayer silver halide photographic film element of this invention can be prepared by coating the various layers onto a transparent support. The transparent support is preferably a polymeric film support or cellulose ester support, such as the supports described in Research Disclosure 308,119, (published by Kenneth Mason Publications, Ltd., Dudley Annex 12a North Street, Emsworth, Hampshire P010 7DQ, England) December 1989 (hereinafter *Research Disclosure*), Section XVII, in particular paragraphs B, E, F and G. Particularly preferred are supports of cellulose acetate or polyethylene terephthalate. The support may be provided with one or more subbing layers to enhance the adhesive, antistatic, dimensional, abrasive, hardness, frictional, antihalation and/or other properties of the support surface. In a preferred embodiment of this invention the support is provided with an antihalation layer containing absorbing materials, such described in the *Research Disclosure* Section VIII, in particular paragraph C thereof. The antihalation layer preferably comprises colloidal silver and/or one or more organic dyes.

The support may also contain a transparent magnetic recording layer such as a layer containing particles on the underside of the support as described in U.S. Patents No. 4,279,945 and 4,302,523 and in Research Disclosure 34390 November, 1992. (also published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire P010 7DQ, ENGLAND).

In the following discussion of suitable materials for use in the film element of this invention, reference will be made to the above mentioned Research Disclosure, December 1989, Item 308119, (*Research Disclosure*). The contents of the *Research Disclosure*, including the patents and publications referenced therein, are incorporated herein by reference, and the Sections hereafter referred to are Sections of the *Research Disclosure*.

The silver halide emulsions employed in the elements of this invention can be either negative-working or positive-working. Suitable emulsions and their preparation as well as methods of chemical and spectral sensitization are described in Sections I through IV. Color materials and development modifiers are described in Sections V and XXI. Vehicles are described in Section IX, and various additives such as brighteners, antifoggants, stabilizers, light absorbing and scattering materials, hardeners, coating aids, plasticizers, lubricants and matting agents are described , for example, in Sections V, VI, VIII, X, XI, XII, and XVI. Manufacturing methods are described in Sections XIV and XV, other layers and supports in Sections XIII and XVII, processing methods and agents in Sections XIX and XX, and exposure alternatives in Section XVIII.

Coupling-off groups are well known in the art. Such groups can determine the chemical equivalency of a coupler, i.e., whether it is a 2-equivalent or a 4-equivalent coupler, or modify the reactivity of the coupler. Such groups can advantageously affect the layer in which the coupler is coated, or other layers in the photographic recording material, by performing, after release from the coupler, functions such as dye formation, dye hue adjustment, development acceleration or inhibition, bleach acceleration or inhibition, electron transfer facilitation, color correction and the like.

The presence of hydrogen at the coupling site provides a 4-equivalent coupler, and the presence of another coupling-off group provides a 2-equivalent coupler. Representative classes of such coupling-off groups include, for example, chloro, alkoxy, aryloxy, hetero-oxy, sulfonyloxy, acyloxy, acyl, heterocyclyl, sulfonamido, mercaptotetrazole, benzothiazole, mercaptopropionic acid, phosphonyloxy, arylthio, and arylazo. These coupling-off groups are described in the art, for example, in U.S. Pat. Nos. 2,455,169, 3,227,551, 3,432,521, 3,476,563, 3,617,291, 3,880,661, 4,052,212 and 4,134,766; and in U.K. Patents and published application Nos. 1,466,728, 1,531,927, 1,533,039, 2,006,755A and 2,017,704A, the disclosures of which are incorporated herein by reference.

The red sensitive layer (or layers) contain one or more couplers that form cyan dyes upon reaction with oxidized color developing agents are described in such representative patents and publications as: U.S. Pat. Nos. 2,772,162, 2,895,826, 3,002,836, 3,034,892, 2,474,293, 2,423,730, 2,367,531, 3,041,236, 4,883,746 and "Farbkuppler-eine LiteratureUbersicht" published in Agfa Mitteilungen, Band III, pp. 156-175 (1961). Preferably such couplers are phenols and naphthols that form cyan dyes on reaction with oxidized color developing agent.

The green sensitive layer (or layers) contain one or more couplers that form magenta dyes upon reaction with oxidized color developing agent are described in such representative patents and publications as: U.S. Pat; Nos. 2,600,788, 2,369,489, 2,343,703i 2,311,082, 3,152,896, 3,519,429, 3,062,653, 2,908,573 and "Farbkupplereine LiteratureUbersicht," published in Agfa Mitteilungen, Band III, pp. 126-156 (1961). Preferably such couplers are pyrazolones, pyrazolotriazoles, or pyrazolobenzimidazoles that form magenta dyes upon reaction with oxidized color developing agents.

The blue sensitive layer (or layers) contain one or more couplers that form yellow dyes upon reaction with oxidized and color developing agent are described in such representative patents and publications as: U.S. Pat. Nos. 2,875,057, 2,407,210, 3,265,506, 2,298,443, 3,048,194, 3,447,928 and "Farbkuppler-eine LiteratureUbersicht," published in Agfa Mitteilungen, Band III, pp. 112-126 (1961). Such couplers are typically open chain ketomethylene compounds.

It may be useful to use a combination of couplers any of which may contain known ballasts or coupling-off groups such as those described in U.S. Patent 4,301,235; U.S. Patent 4,853,319 and U.S. Patent 4,351,897. The coupler may also be used in association with "wrong" colored couplers (e.g. to adjust levels of interlayer correction) and, in color negative applications, with masking couplers such as those described in EP 213.490; Japanese Published Application 58-172,647; U.S. Patent 2,983,608; German Application DE 2,706,117C; U.K. Patent 1,530,272; Japanese Application A-113935; U.S. Patents 4,070,191 and 4,273,861; and German Application DE 2,643,965. The masking couplers may be shifted or blocked.

The film element may also contain materials that accelerate or otherwise modify the processing steps e.g. of developing, bleaching or fixing to improve the quality of the image. Bleach accelerator releasing couplers such as those described in EP 193,389; EP 301,477; U.S. 4,163,669; U.S. 4,865,956; and U.S. 4,923,784, may be useful. Also contemplated is use of the compositions in association with nucleating agents, development accelerators or their precursors (UK Patent 2,097,140; U.K. Patent 2,131,188); electron transfer agents (U.S. 4,859,578; U.S. 4,912,025); antifogging and anti color-mixing agents such as derivatives of hydroquinones, aminophenols, amines, gallic acid; catechol; ascorbic acid; hydrazides; sulfonamidophenols; and non color-forming couplers.

A typical film element of this invention comprises a sensitizing dye as defined above and a dialkyl hydroquinone scavenger. The film element may comprise, for example, the following layers from top to bottom:

(1) one or more overcoat layers containing ultraviolet absorber(s);

(2) a two-coat yellow pack with a fast yellow layer containing "Coupler 1": Benzoic acid, 4-chloro-3-((2-(4-ethoxy-2,5-dioxo-3-(phenylmethyl)-1-imidazolidinyl)-3-(4-methoxyphenyl)-1,3-dioxopropyl)amino)-, dodecyl ester and a slow yellow layer containing the same compound together with "Coupler 2": Propanoic acid, 2-[[5-[[4-[2-[[[2,4-bis(1,1-dimethylpropyl)phenoxy]acetyl]amino]-5-[(2,2,3,3,4,4,4-heptafluoro-1-oxobutyl)amino]-4-hydroxyphenoxy]-2,3-dihydroxy-6-[(propylamino)carbonyl]phenyl]thio]-1,3,4-thiadiazol-2-yl]thio]-, methyl ester and "Coupler 3": 1-((dodecyloxy)carbonyl) ethyl(3-chloro-4-((3-(2-chloro-4-((1-tridecanoylethoxy) carbonyl)anilino)-3-oxo-2-((4)(5)(6)-(phenoxycarbonyl)-1H-benzotriazol-1-yl)propanoyl)amino))benzoate;

(3) an interlayer containing fine metallic silver;

(4) a triple-coat magenta pack with a fast magenta layer containing "Coupler 4": Benzamide, 3-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-N-(4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)-,"Coupler 5": Benzamide, 3-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-N-(4',5'-dihydro-5'-oxo-1'-(2,4,6-trichlorophenyl) (1,4'-bi-1H-pyrazol)-3'-yl)-,"Coupler 6": Carbamic acid, (6-(-((3-(dodecyloxy)propyl) amino)carbonyl)-5-hydroxy-1-naphthalenyl)-, 2-methylpropyl ester , "Coupler 7": Acetic acid, ((2-((3-(((3-(dodecyloxy)propyl)amino) carbonyl)-4-hydroxy-8-(((2-methylpropoxy)carbonyl) amino)-1-naphthalenyl)oxy)ethyl)thio)-, and "Coupler 8" Benzamide, 3-((2-(2,4-bis(1,1-dimethylpropyl)

phenoxy)-1-oxobutyl)amino)-N-(4,5-dihydro-4-((4-methoxyphenyl) azo)-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)-; a mid-magenta layer and a slow magenta layer each containing "Coupler 9": a ternary copolymer containing by weight in the ratio 1:1:2 2-Propenoic acid butyl ester, styrene, and N-[1-(2,4,6-trichlorophenyl)-4,5-dihydro-5-oxo-1H-pyrazol-3-yl]-2-methyl-2-propenamide; and "Coupler 10": Tetradecanamide, N-(4-chloro-3-((4-((4-((2,2-dimethyl-1-oxopropyl) amino)phenyl)azo)-4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)amino)phenyl)-, in addition to Couplers 3 and 8;

(5) an interlayer;

(6) a triple-coat cyan pack, in which at least one of the layers contains the red-sensitizing dye defined above, with a fast cyan layer containing Couplers 6 and 7; a mid-cyan containing Coupler 6 and "Coupler 11": 2,7-Naphthalenedisulfonic acid, 5-(acetylamino)-3-((4-(2-((3-(((3-(2,4-bis(1,1-dimethylpropyl)phenoxy) propyl)amino)carbonyl)-4-hydroxy-1-naphthalenyl) oxy)ethoxy)phenyl)azo)-4-hydroxy-, disodium salt; and a slow cyan layer containing Couplers 2 and 6;

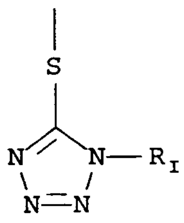
(7) an undercoat layer containing Coupler 8; and

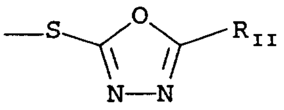
(8) an antihalation layer, which preferably contains colloidal silver and/or an organic dye.

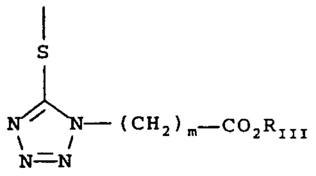
The film element may also contain filter dye layers comprising colloidal silver sol or yellow, cyan, and/or magenta filter dyes, either as oil-in-water dispersions, latex dispersions or as solid particle dispersions. Additionally, they include "smearing" couplers (e.g. as described in U.S. 4,366,237; EP 96,570; U.S. 4,420,556; and U.S. 4,543,323.) Also, compositions used in the film element may be blocked or coated in protected form as described, for example, in Japanese Application 61/258,249 or U.S. 5,019,492.

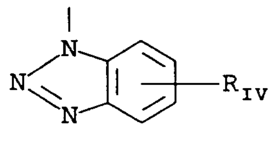
The film element may also contain image-modifying compounds such as "Developer Inhibitor-Releasing" compounds (DIR's). DIR's useful in conjunction with the compositions of the invention are known in the art and examples are described in U.S. Patent Nos. 3,137,578; 3,148,022; 3,148,062; 3,227,554; 3,384,657; 3,379,529; 3,615,506; 3,617,291; 3,620,746; 3,701,783; 3,733,201; 4,049,455; 4,095,984; 4,126,459; 4,149,886; 4,150,228; 4,211,562; 4,248,962; 4,259,437; 4,362,878; 4,409,323; 4,477,563; 4,782,012; 4,962,018; 4,500,634; 4,579,816; 4,607,004; 4,618,571; 4,678,739; 4,746,600; 4,746,601; 4,791,049; 4,857,447; 4,865,959; 4,880,342; 4,886,736; 4,937,179; 4,946,767; 4,948,716; 4,952,485; 4,956,269; 4,959,299; 4,966,835; 4,985,336 as well as in patent publications GB 1,560,240; GB 2,007,662; GB 2,032,914; GB 2,099,167; DE 2,842,063, DE 2,937,127; DE 3,636,824; DE 3,644,416 as well as the following European Patent Publications: 272,573; 335,319; 336,411; 346, 899; 362, 870; 365,252; 365,346; 373,382; 376,212; 377,463; 378,236; 384,670; 396,486; 401,612; 401,613.

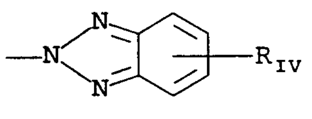
Such compounds are also disclosed in "Developer-Inhibitor-Releasing (DIR) Couplers for Color Photography," C.R. Barr, J.R. Thirtle and P.W. Vittum in Photographic Science and Engineering, Vol. 13, p. 174 (1969), incorporated herein by reference. Generally, the developer inhibitor-releasing (DIR) couplers include a coupler moiety and an inhibitor coupling-off moiety (IN). The inhibitor-releasing couplers may be of the time-delayed type (DIAR couplers) which also include a timing moiety or chemical switch which produces a delayed release of inhibitor. Examples of typical inhibitor moieties are: oxazoles, thiazoles, diazoles, triazoles, oxadiazoles, thiadiazoles, oxathiazoles, thiatriazoles, benzotriazoles, tetrazoles, benzimidazoles, indazoles, isoindazoles, mercaptotetrazoles, selenotetrazoles, mercaptobenzothiazoles, selenobenzothiazoles, mercaptobenzoxazoles, selenobenzoxazoles, mercaptobenzimidazoles, selenobenzimidazoles, benzodiazoles, mercaptooxazoles, mercaptothiadiazoles, mercaptothiazoles, mercaptotriazoles, mercaptooxadiazoles, mercaptodiazoles, mercaptooxathiazoles, telleurotetrazoles or benzisodiazoles. In a preferred embodiment, the inhibitor moiety or group is selected from the following formulas:







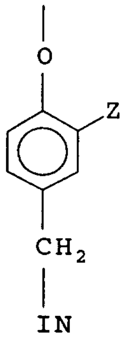


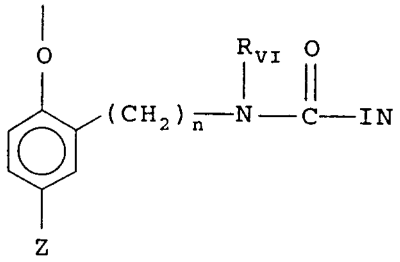


wherein R_I is selected from the group consisting of straight and branched alkyls of from 1 to about 8 carbon atoms, benzyl, phenyl, and alkoxy groups and such groups containing none, one or more than one such substituent; R_{II} is selected from R_I and $-SR_I$; R_{III} is a straight or branched alkyl group of from 1 to about 5 carbon atoms and m is from 1 to 3; and R_{IV} is selected from the group consisting of hydrogen, halogens and alkoxy, phenyl and carbonamido groups, $-COOR_V$ and $-NHCOOR_V$ wherein R_V is selected from substituted and unsubstituted alkyl and aryl groups.

Although it is typical that the coupler moiety included in the developer inhibitor-releasing coupler forms an image dye corresponding to the layer in which it is located, it may also form a different color as one associated with a different film layer. It may also be useful that the coupler moiety included in the developer inhibitor-releasing coupler forms colorless products and/or products that wash out of the photographic material during processing (so-called "universal" couplers).

As mentioned, the developer inhibitor-releasing coupler may include a timing group which produces the time-delayed release of the inhibitor group such as groups utilizing the cleavage reaction of a hemiacetal (U.S. 4,146,396, Japanese Applications 60-249148; 60-249149); groups using an intramolecular nucleophilic substitution reaction (U.S. 4,248,962); groups utilizing an electron transfer reaction along a conjugated system (U.S. 4,409,323; 4,421,845; Japanese Applications 57-188035; 58-98728; 58-209736; 58-209738) groups utilizing ester hydrolysis (German Patent Application (OLS) No. 2,626,315; groups utilizing the cleavage of imino ketals (U.S. 4,546,073); groups that function as a coupler or reducing agent after the coupler reaction (U.S. 4,438,193; U.S. 4,618,571) and groups that combine the features describe above. It is typical that the timing group or moiety is of one of the formulas:

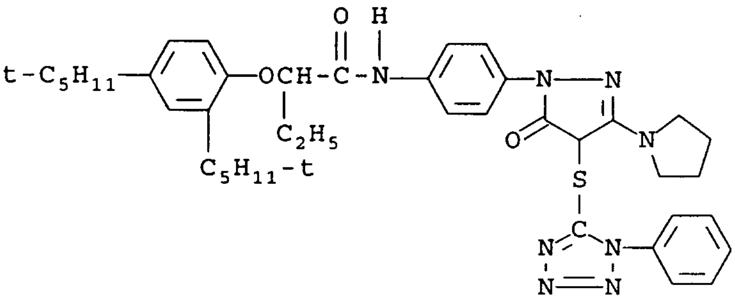




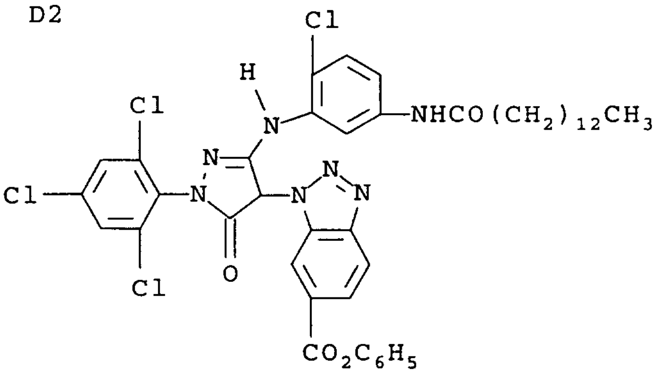
wherein IN is the inhibitor moiety, Z is selected from the group consisting of nitro, cyano, alkylsulfonyl; sulfamoyl ($-SO_2NR_2$); and sulfonamido ($-NRSO_2R$) groups; n is 0 or 1; and R_{VI} is selected from the group consisting of substituted and unsubstituted alkyl and phenyl groups. The oxygen atom of each timing group is bonded to the coupling-off position of the respective coupler moiety of the DIAR.

Suitable developer inhibitor-releasing couplers for use in the present invention include, but are not limited to, the following:

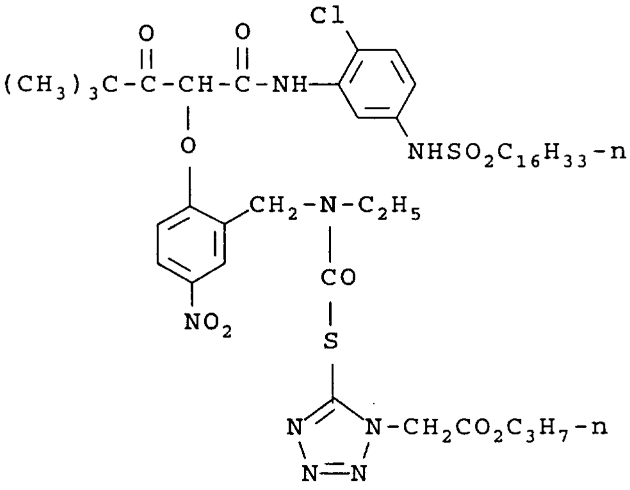
D1



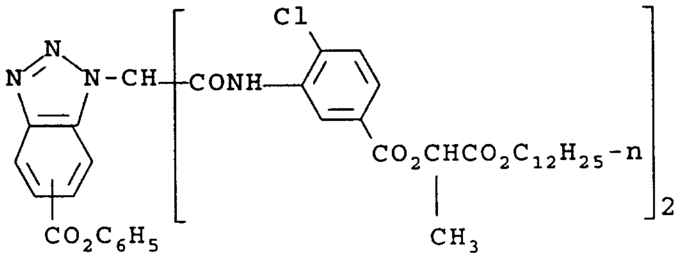
D2



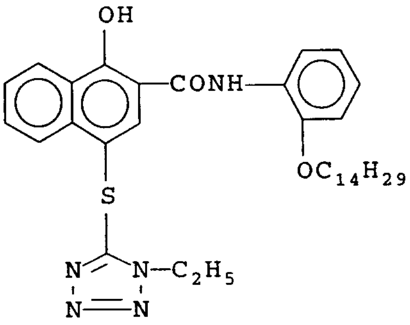
D3



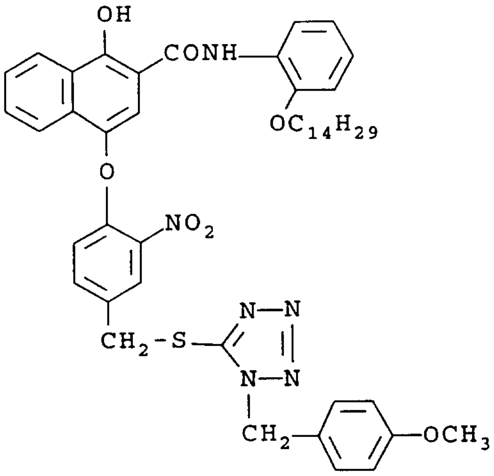
D4



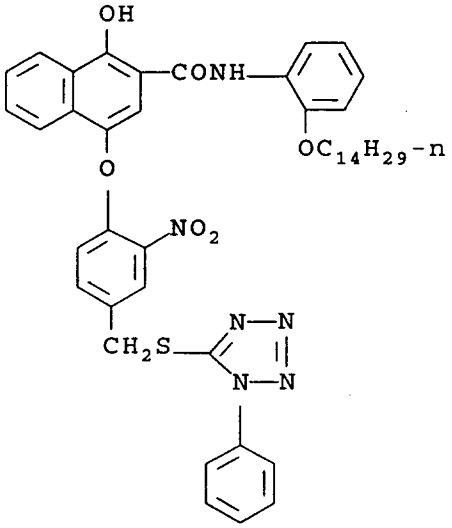
D5



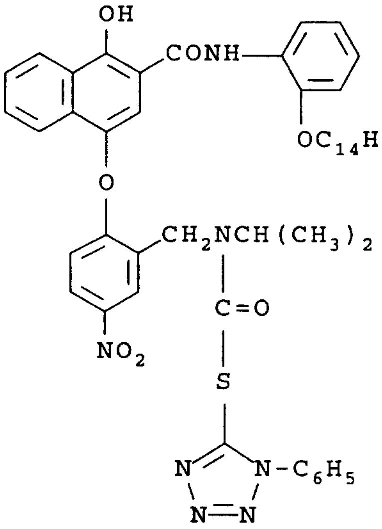
D6



D7



D8



Especially useful in this invention are tabular grain silver halide emulsions. Specifically contemplated tabular grain emulsions are those in which greater than 50 percent of the total projected area of the emulsion grains are accounted for by tabular grains having a thickness of less than 0.3 micron (0.5 micron for blue sensitive emulsion) and an average tabularity (T) of greater than 25 (preferably greater than 100), where the term "tabularity" is employed in its art recognized usage as

$$T = ECD/t^2$$

where

ECD is the average equivalent circular diameter of the tabular grains in microns and

t is the average thickness in microns of the tabular grains.

The average useful ECD of photographic emulsions can range up to about 10 microns, although in practice emulsion ECD's seldom exceed about 4 microns. Since both photographic speed and granularity increase with increasing ECD's, it is generally preferred to employ the smallest tabular grain ECD's compatible with achieving aim speed requirements.

Emulsion tabularity increases markedly with reductions in tabular grain thickness. It is generally preferred that aim tabular grain projected areas be satisfied by thin (t < 0.2 micron) tabular grains. To achieve the lowest levels of granularity it is preferred that aim tabular grain projected areas be satisfied with ultrathin (t < 0.06 micron) tabular grains. Tabular grain thicknesses typically range down to about 0.02 micron. However, still lower tabular grain thicknesses are contemplated. For example, Daubendiek et al U.S. Patent 4,672,027 reports a 3 mole percent iodide tabular grain silver bromoiodide emulsion having a grain thickness of 0.017 micron.

As noted above tabular grains of less than the specified thickness account for at least 50 percent of the total grain projected area of the emulsion. To maximize the advantages of high tabularity it is generally preferred that tabular grains satisfying the stated thickness criterion account for the highest conveniently attainable percentage of the total grain projected area of the emulsion. For example, in preferred emulsions, tabular grains satisfying the stated thickness criteria above account for at least 70 percent of the total grain projected area. In the highest performance tabular grain emulsions, tabular grains satisfying the thickness criteria above account for at least 90 percent of total grain projected area.

Suitable tabular grain emulsions can be selected from among a variety of conventional teachings, such as those of the following: Research Disclosure, Item 22534, January 1983, published by Kenneth Mason Publications, Ltd., Emsworth, Hampshire P010 7DD, England; U.S. Patent Nos. 4,439,520; 4,414,310; 4,433,048; 4,643,966; 4,647,528; 4,665,012; 4,672,027; 4,678,745; 4,693,964; 4,713,320; 4,722,886; 4,755,456; 4,775,617; 4,797,354; 4,801,522; 4,806,461; 4,835,095; 4,853,322; 4,914,014; 4,962,015; 4,985,350; 5,061,069 and 5,061,616.

The emulsions can be surface-sensitive emulsions, i.e., emulsions that form latent images primarily on the surfaces of the silver halide grains, or the emulsions can form internal latent images predominantly in the interior of the silver halide grains. The emulsions can be negative-working emulsions, such as surface-sensitive emulsions or unfogged internal latent image-forming emulsions, or direct-positive emulsions of the unfogged, internal latent image-forming type, which are positive-working when development is conducted with uniform light exposure or in the presence of a nucleating agent.

The photographic elements of this invention elements can be exposed to actinic radiation, typically in the visible region of the spectrum, to form a latent image and can then be processed to form a visible dye image. Processing to form a visible dye image includes the step of contacting the element with a color developing agent to reduce developable silver halide and oxidize the color developing agent. Oxidized color developing agent in turn reacts with the coupler to yield a dye.

The processing step described above is a single process step process and provides a negative image. The described elements can be processed in the known C-41 color process as described in The British Journal of Photography Annual of 1982, pages 209 - 211 and 1988, pages 191-198. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

Preferred color developing agents are p-phenylenediamines such as:

4-amino-N,N-diethylaniline hydrochloride,
4-amino-3-methyl-N,N-diethylaniline hydrochloride,
4-amino-3-methyl-N-ethyl-N-(b-(methanesulfonamido) ethyl)aniline sesquisulfate hydrate,
4-amino-3-methyl-N-ethyl-N-(b-hydroxyethyl)aniline sulfate,
4-amino-3-b-(methanesulfonamido)ethyl-N,N-diethylaniline hydrochloride and
4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluene sulfonic acid.

Development is usually followed by the conventional steps of bleaching, fixing, or bleach-fixing, to remove silver or silver halide, washing, and drying.

The following examples illustrate the preparation of color negative films in accordance with this invention and evaluation thereof for dye stain due to the aggregation of thiacyanine dye used in the red sensitive layer.

Example 1(comparative)

A comparative photographic element was produced by coating the following layers on a cellulose triacetate film support (for each of the various components, coverage is given in grams per square meter). The chemical structures of the various components are set forth following Example 2.

Layer 1 (antihalation layer): black colloidal silver sol containing silver at 0.26; gelatin at 2.44; and UV-1 at 0.13 and UV-2 at 0.075.

Layer 2 (slow cyan layer): a blend of three red-sensitized iodobromide tabular grains: (i) a medium sized tabular emulsion (4.1% iodide, 2.33 x 0.127 µm, dye set 1 at 0.95 mmole/Ag mole) at 0.92 (ii) smaller grain size tabular emulsion (4.1% iodide, 1.13 x 0.116 µm dye set 1 at 0.92 mmole/Ag mole) at 0.22 and (iii)a much smaller sizes tabular emulsion (4.5% iodide, 0.57 x 0.138 µm, dye set 1 at 1.0 mmole/Ag mole) at 0.36; bleach accelerator releasing coupler B-1 at 0.07; antifoggant 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene at 0.02; cyan dye-forming coupler C-1 at 1.1; DIR coupler DIR-1 at 0.04; magenta colored cyan dye forming masking coupler MC-1 at 0.04 and gelatin at 2.8. Dye set 1, set forth below, contains a thiacyanine dye of Formula A.

Layer 3 (interlayer): oxidized developer scavenger S-A (a commonly uses disulfonamidophenol oxidized developer scavenger) at 0.05 and gelatin at 0.97.

Layer 4 (slow magenta layer): a blend of two green-sensitized iodobromide grains: (i) a medium sized tabular emulsion (2.8% iodide, 2.18 x 0.134 μm, dye set 2 at 0.85 mmole/Ag mole) at 0.70, (ii) a smaller sized tabular emulsion (4.1% iodide, 0.80 x 0.09 mm, dye set 3 at 0.87 mmole/Ag mole) at 0.64; magenta-dye forming coupler M-1 at 0.31; masking coupler MC-2 at 0.09; DIR coupler DIR-4 at 0.005; gelatin at 1.43 and antifoggant 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene at 0.02.

Layer 5 (interlayer): oxidized developer scavenger S-A at 0.05 and gelatin at 0.97.

Layer 6 (fast cyan layer): a red-sensitized silver iodobromide tabular emulsion (4.1% iodide, 3.5 x 0.127 μm, dye set 1 at 0.86 mmole/Ag mole) at 1.24; gelatin at 1.85; cyan dye-forming coupler C-2 at 0.24; DIR coupler DIR-2 at 0.05; bleach accelerator releasing coupler B-1 at 0.003 and antifoggant 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene at 0.03.

Layer 7 (interlayer): oxidized developer scavenger S-A at 0.05 and gelatin at 0.97.

Layer 8 (mid magenta layer): a green-sensitized tabular silver iodobromide emulsion (2.75% iodide, 2.2 X 0.13 μm, dye set 2 at 0.85 mmole/Ag mole) at 0.97; gelatin at 1.16; magenta dye-forming coupler M-1 at 0.08; masking coupler MC-2 at 0.04; bleach accelerator releasing coupler B-1 at 0.011 and antifoggant 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene at 0.02.

Layer 9 (fast magenta layer): a green-sensitized silver bromoiodide tabular emulsion (2.75% iodide, 3.35 x 0.128 μm, dye set 2 at 0.952 mmole/Ag mole) at 0.86; gelatin at 2.5; magenta dye-forming coupler M-1 at 0.07; masking coupler MC-2 at 0.019 and antifoggant 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene at 0.02.

Layer 10 (interlayer): oxidized developer scavenger S-A at 0.05 and gelatin at 0.97.

Layer 11 (slow yellow layer): a blend of 3 blue-sensitized emulsions: (i) a tabular silver iodobromide emulsion (4.5% iodide, 3x 0.13 μm, sensitized with YD-A) at 0.624, (ii) a smaller tabular silver iodobromide emulsion (4.5% iodide, 0.8 x 0.08 μm, sensitized with YD-A) at 0.194, (iii) a very small silver iodobromide emulsion (3% iodide, 0.50 x 0.08 μm, sensitized with YD-A) at 0.13; yellow dye-forming coupler Y-1 at 1.24; DIR coupler DIR-3 at 0.05 and antifoggant 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene at 0.025.

Layer 12 (fast yellow layer): a blue-sensitized silver iodobromide emulsion (15% iodide, 2.2 μm, YD-A at 0.05 mmole/Ag mole) at 1.08; yellow dye-forming coupler Y-1 at 0.32; gelatin at 2.04 and antifoggant 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene at 0.333.

Layer 13 (UV filter layer): gelatin at 0.54; silver bromide Lippmann at 0.27; and UV-1 and UV-2 both at 0.11.

Layer 14 (protective overcoat layer): gelatin at 0.89 and bis (vinylsulfonyl) methane added at 1.6% of total gelatin weight.

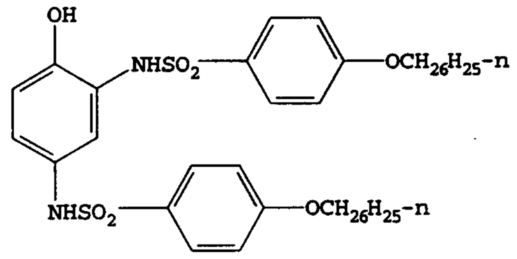
Conventional surfactants coating aids, soluble absorber dyes, inert tinting dyes and stabilizers were added to the various layers (where appropriate) as is practiced routinely in the art.

Example 2 (invention)

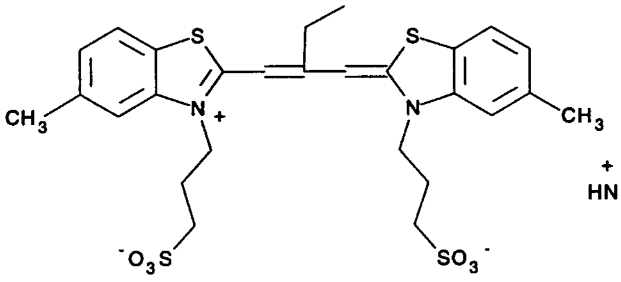
A second photographic element, designated Example 2, was prepared in similar manner as Example 1, except that in interlayers 3,5,7 and 10 S-A was replaced with S-5 (a dialkyl hydroquinone) at 0.86. Samples of each element were exposed imagewise through a stepped density test object and subjected to the KODAK FLEXICOLOR (C41) Process as described in British Journal of Photography Annual, 1988, pp. 196-198. The red D-min for Example 2 decreased by 0.06 red density compared to the film element of Example 1. Analysis of the spectral dye density data indicated that the elimination of stain was due to the absence of aggregated red-sensitizing dye (Dmax about 650 nm) while maintaining low color contamination between the color records.

The chemical formulas of components specified in Examples 1 and 2 are as follows:

S-A



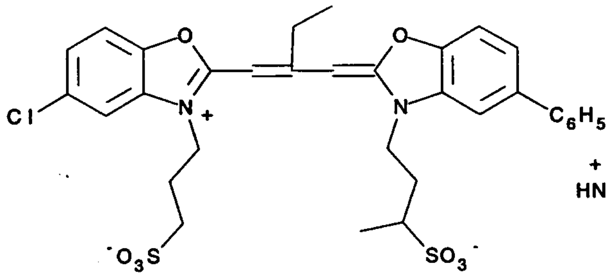
DYE SET 1: DYE-1/CD-A at 9:1



CD-A

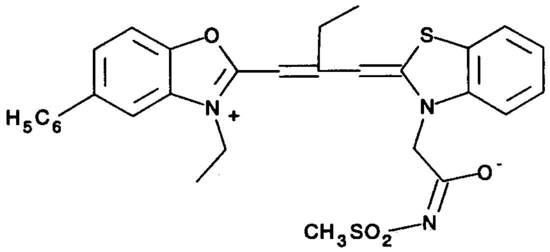
$^{+}HN(C_2H_5)_3$

DYE SET 2: MD-A/MD-B at 6:1



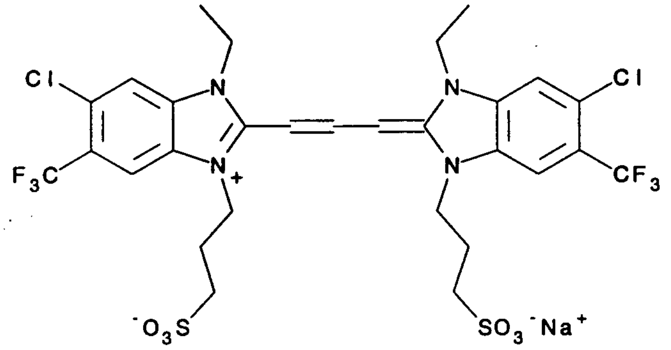
MD-A

$^{+}HN(C_2H_5)_3$



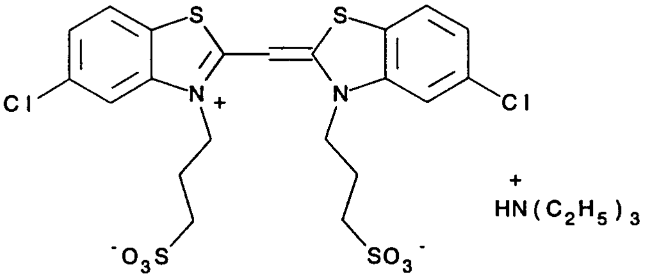
MD-B

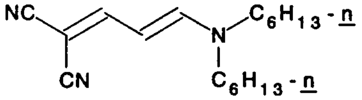
DYE SET 3: MD-A/MD-C at 6:1

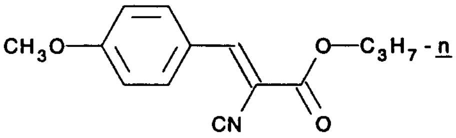


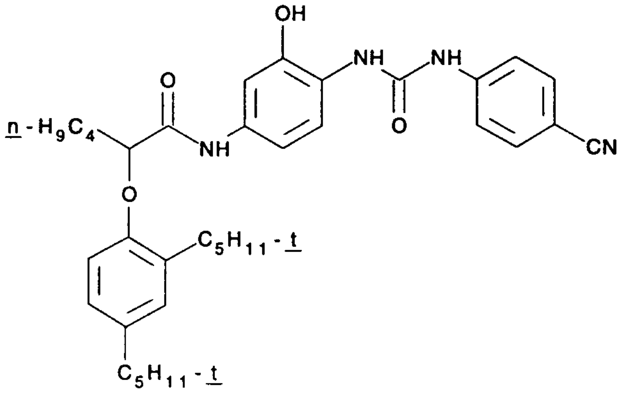
MD-C

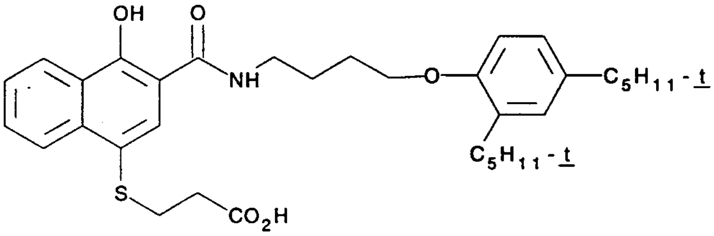
YD-A:

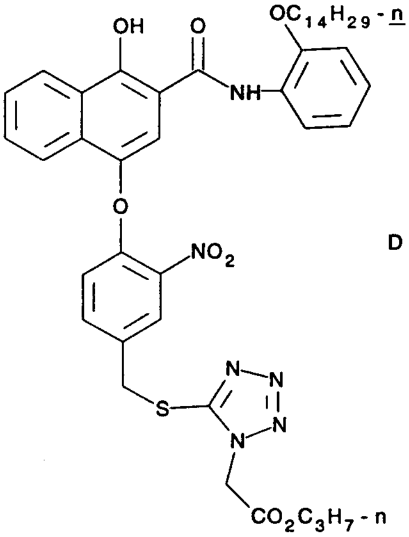


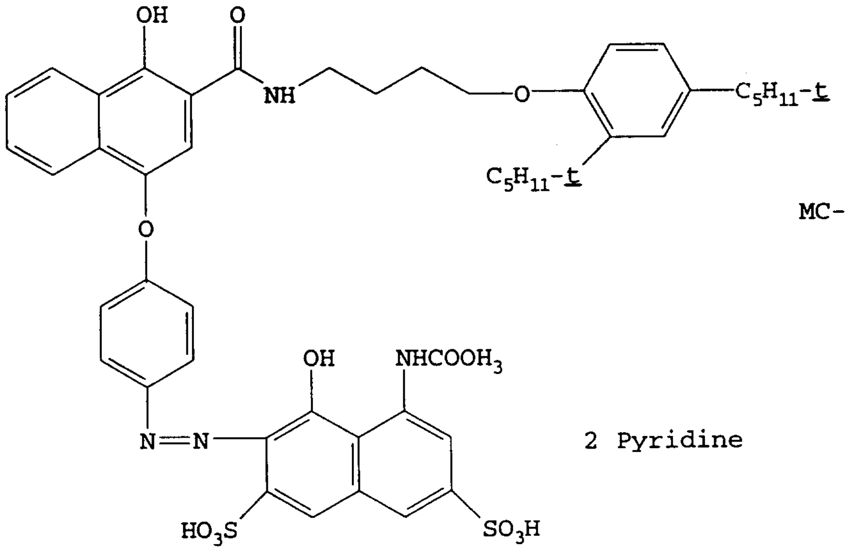

UV-1


UV-2


C-1

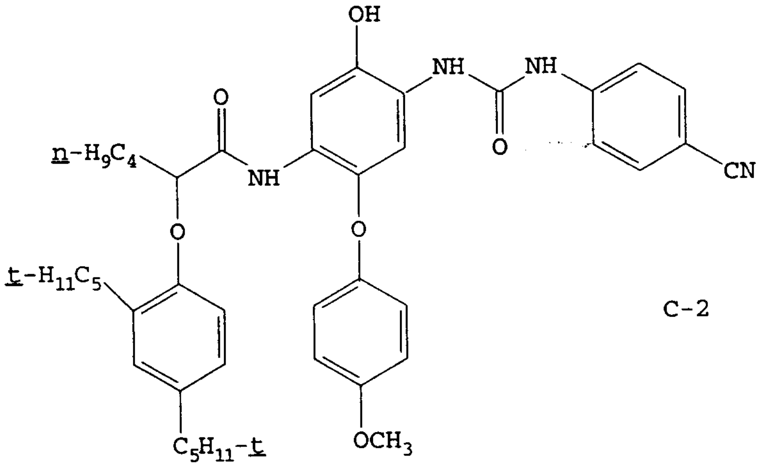

B-1


DIR-1

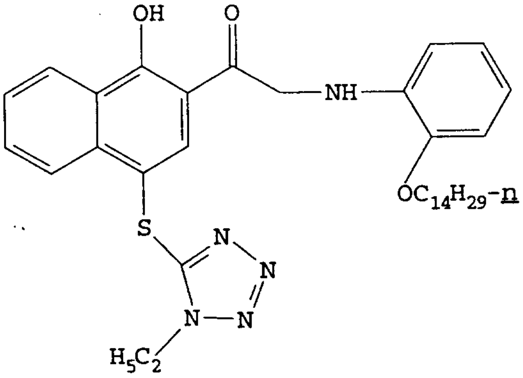


2 Pyridine

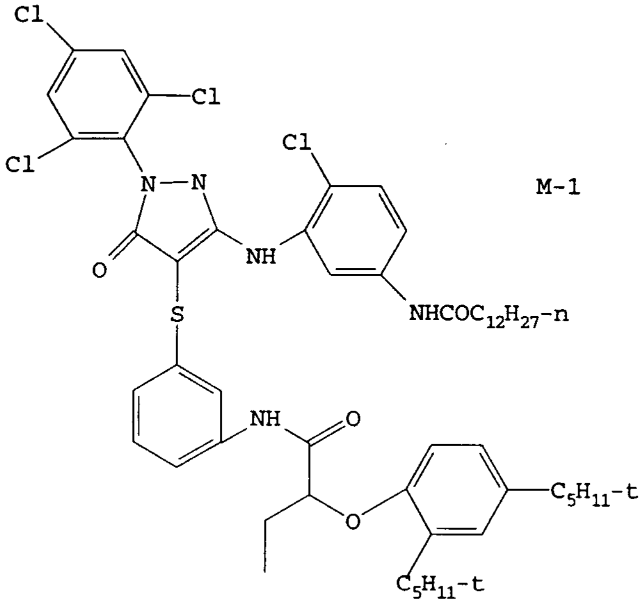
MC-1



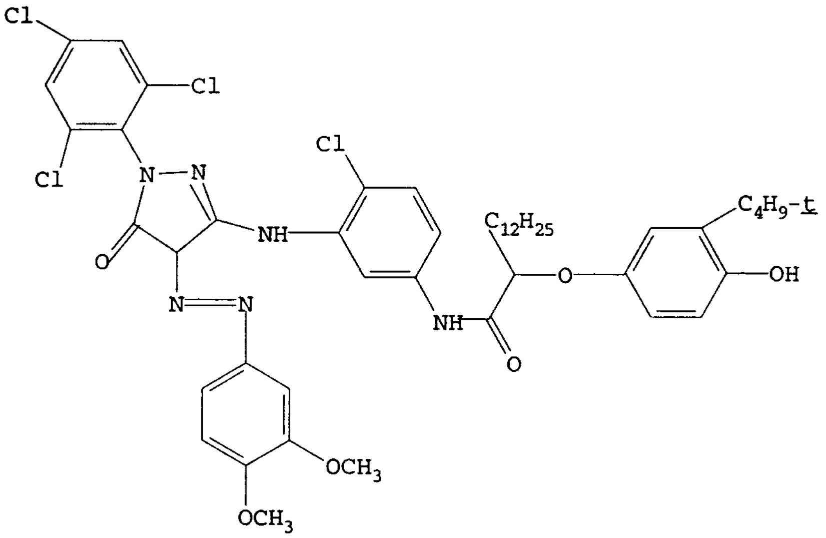
C-2



DIR-2


Cl
Cl
Cl
N
N
O
NH
Cl
S
NHCOC$_{12}$H$_{27}$-n
NH
O
O
C$_5$H$_{11}$-t
C$_5$H$_{11}$-t

M-1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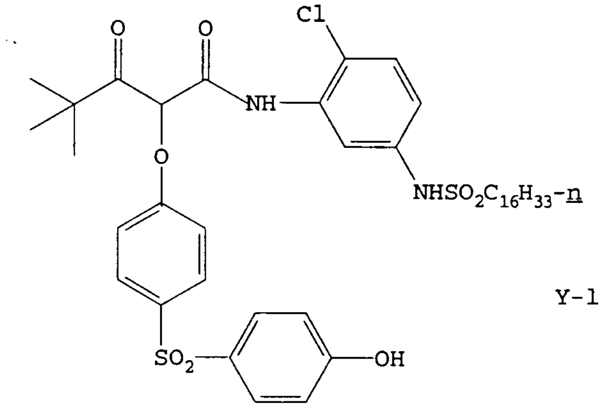
N
N
O
NH
Cl
N
N
NH
O
C$_{12}$H$_{25}$
O
C$_4$H$_9$-t
OH
OCH$_3$
OCH$_3$

MC-2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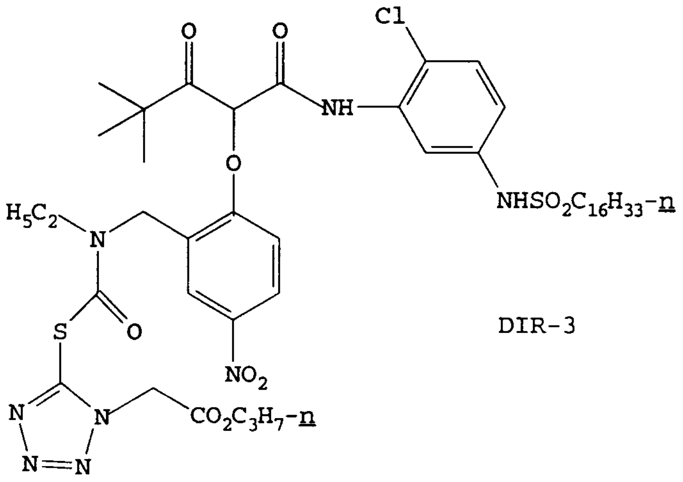
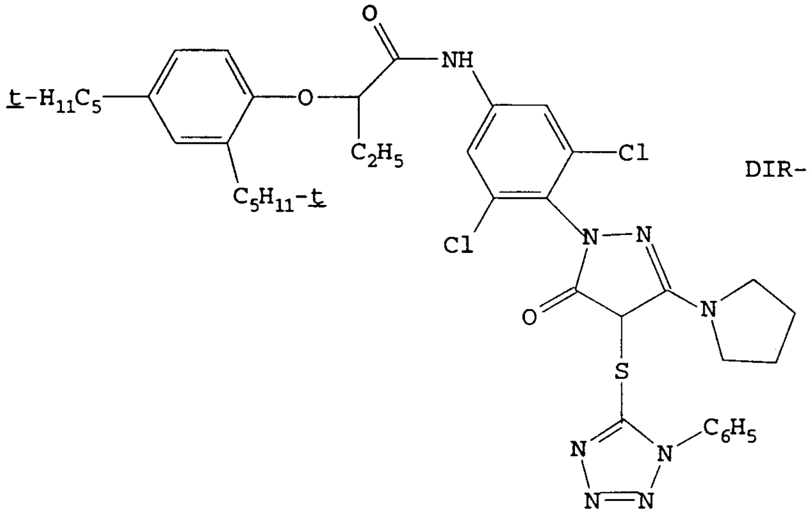
O
Cl
NH
O
NHSO$_2$C$_{16}$H$_{33}$-n
SO$_2$
OH

Y-1



DIR-3



DIR-4

Example 3

Bilayer Comparative Example

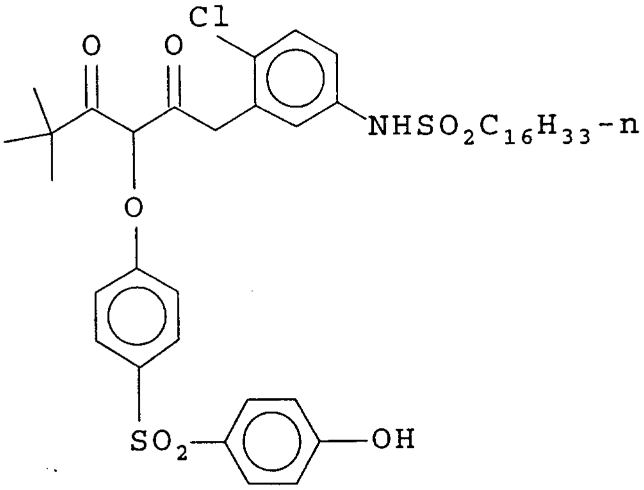
Four layer test photographic elements were prepared by coating a cellulose acetate butyrate film support first with an antihalation layer containing 4.89 g/m^2 of gelatin and 0.32 g/m^2 of gray colloidal silver followed by a photosensitive layer consisting of 2.0 g/m^2 of silver iodobromide emulsion prepared as described below, 1.08 g/m2 of yellow image coupler Y-1 (formula given below), 0.325 g/m^2 of antifoggant 5-methyl-s-triazole-[2-3-a]-pyrimidine-7-ol and 2.15 g/m^2 of gelatin. These layers were then overcoated with an interlayer consisting of 0.65 g/m^2 of gelatin with 0.108 g/m2 of the scavenger specified in Table 1, below followed by a non-photosensitive layer of 2.69 g/m^2 of gelatin with 0.33 g/m^2 of magenta image coupler M-1 (formula given below) and finally, with an overcoat of 5.4 g/m^2 of gelatin with bis-vinylsulfonyl methyl ether hardener at 1.75 weight percent based on total gel.

The photosensitive emulsions used to generate these test elements were a tabular AgIBr (1.07 micron x 0.110 microns, 4.5% iodide, designated as T in TABLE 1), an octahedral AgIBr (0.32 micron edge, 3.1% iodide, designated as O) and a cubic AgIBr (0.29 micron edge, 3.1% iodide, designated as C), and were prepared as known in the art. The emulsion was then chemically and spectrally sensitized by adding in the following sequence: NaSCN (100 mg/mole silver, as 68% aqueous solution), held for 20 minutes at 40 ° C; 3-(3-((methylsulfonyl)amino)-3-oxopropyl)-benzothiazolium tetrafluoroborate (40 mg/mole silver, as 0.23% aqueous solution); sensitizing dye as indicated in Table 1 (0.993 mg/mole silver for the tabular emulsion, 1.296 mg/mole silver for the cubic emulsion and 0.878 mg/mole silver for the octahedral emulsion, as 5% MeOH solution held for 20 minutes at 40 ° C; Sodium Aurous(I)dithiosulfate dihydrate (3.5 mg/mole silver, 0.03% aqueous solution); Sodium thiosulfate pentahydrate (1.75 mg/mole silver); held for 5 minutes at 62 degrees C; and then cooled.

Samples of each element were exposed imagewise through a stepped density test object and subjected to the KODAK FLEXICOLOR (C41) Process as described in British Journal of Photography Annual, 1988, pp. 196-198. Process A in Table 1 used fresh processing solutions. Process B used solutions that are seasoned and aged by processing enough exposured multilayer film to reach a steady state of development by-products.

In this format, magenta dye can be formed only by the wandering of oxidized developer from the layer in which it is generated through an interlayer to the layer containing the magenta coupler. Thus, the ability of the scavenger to prevent oxidized developer from wandering can be measured by the difference in green density measured at minimum and maximum exposure. In Table 1, Δgreen D (Delta green density) = green density at maximum exposure minus green density at minimum exposure. Smaller differences reflect improved scavenging ability. At the same time, the only source of red density at Dmin will be cyan stain due to re-aggregation of the retained cyan sensitizing dye, which is normally magenta colored after processing. Less red density at Dmin implies reduced re-aggregation.

Y-1



M-1

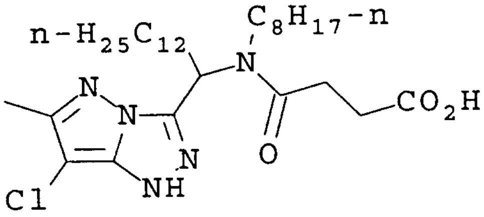


Table 1

Comparison or Invention	Dye	Emulsion	ILS	Process A		Process B	
				Δ Green D	Red D @ Dmin	Δ Green D	Red D @ Dmin
C	DYE-1	T	--	0.554	0.064	0.491	0.115
C	DYE-1	O	--	0.528	0.062	0.458	0.094
C	DYE-1	C	--	0.231	0.139	0.327	0.175
C	DYE-1	T	S-A	0.226	0.140	0.208	0.203
C	DYE-1	O	S-A	0.221	0.092	0.203	0.163
C	DYE-1	C	S-A	0.168	0.180	0.147	0.220
I	DYE-1	T	S-5	0.251	0.062	0.220	0.112
I	DYE-1	O	S-5	0.225	0.061	0.202	0.101
I	DYE-1	C	S-5	0.163	0.081	0.150	0.169
C	DYE-7	T	S-A	0.236	0.063	0.192	0.072
C	DYE-7	O	S-A	0.261	0.065	0.220	0.074
C	DYE-7	C	S-A	0.185	0.063	0.161	0.072
I	DYE-7	T	S-5	0.264	0.060	0.217	0.070
I	DYE-7	O	S-5	0.265	0.065	0.226	0.073
I	DYE-7	C	S-5	0.180	0.060	0.159	0.070
C	DYE-10	T	S-A	0.265	0.062	0.223	0.073
C	DYE-10	O	S-A	0.236	0.062	0.211	0.071
C	DYE-10	C	S-A	0.189	0.063	0.173	0.073
I	DYE-10	T	S-5	0.315	0.059	0.253	0.070
I	DYE-10	O	S-5	0.219	0.062	0.199	0.071
I	DYE-10	C	S-5	0.190	0.060	0.173	0.069
C	DYE-8	T	S-A	0.219	0.062	0.203	0.070
I	DYE-8	T	S-5	0.210	0.059	0.202	0.070
C	DYE-9	T	S-A	0.273	0.174	0.245	0.184
I	DYE-9	T	S-5	0.287	0.139	0.258	0.154
C	DYE-2	T	S-A	0.229	0.108	0.196	0.199
I	DYE-2	T	S-5	0.253	0.059	0.199	0.072
C	DYE-4	T	S-A	0.208	0.062	0.190	0.071
I	DYE-4	T	S-5	0.194	0.060	0.186	0.073
C	DYE-5	T	S-A	0.276	0.253	0.249	0.288
I	DYE-5	T	S-5	0.324	0.256	0.280	0.279
C	DYE-6	T	S-A	0.259	0.061	0.215	0.070
I	DYE-6	T	S-5	0.308	0.060	0.254	0.070

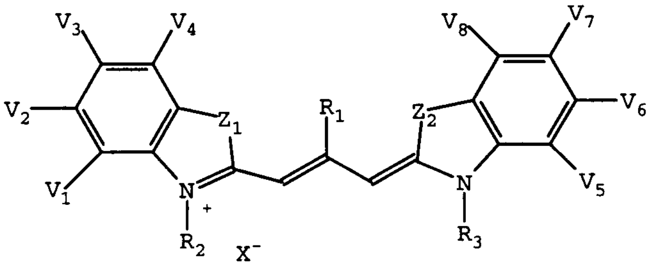
Summary

The data in Table 1 demonstrates that only the inventive combination of the thiacyanine dye with an dialkylhydroquinone scavenger gives low red stain while minimizing color contamination. Table 1 also show that this effect applies to all classes of emulsion type.

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

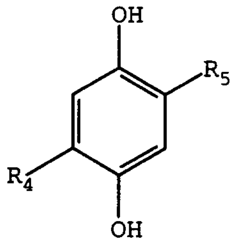
Claims

1. A multilayer silver halide photographic film element for processing in a single step development process, said element comprising a transparent support having thereon at least one yellow color-forming silver halide emulsion layer, at least one magenta color-forming silver halide emulsion layer, at least one cyan color-forming layer and at least one non-imaging layer,
   wherein the cyan color-forming silver halide layer contains a sensitizing dye according to Formula A:



Formula A

   where Z_1 represents a sulfur or a selenium atom; Z_2 represents a sulfur or selenium atom or $-NR_4$; R_1 represents a hydrogen atom or an unsubstituted or substituted alkyl group; R_2, R_3 and R_4 each independently represent an unsubstituted or substituted alkyl or alkenyl group of less than 18 carbon atoms; V_1, V_2, V_3, V_4, V_5, V_6, V_7 and V_8 each represent a hydrogen atom, a halogen atom, an alkyl group, an alkyloxy group, an aryl group, a heterocyclic group, a cyano group, a hydroxy group, an amino group, a carbonamido group, a trifluoromethyl group, an acyloxy group, an alkylthio group or maybe connected to form one or more additional aromatic rings; and X represents a counterion, as necessary to balance the overall charge of the dye;
   wherein said non-imaging layer contains a dialkylhydroquinone according to Formula B



Formula B

   where R4, and R5 each represent an unsubstituted or substituted alkyl group
   and wherein said non-imaging layer is adjacent said cyan color-forming layer or is an antihalation layer.

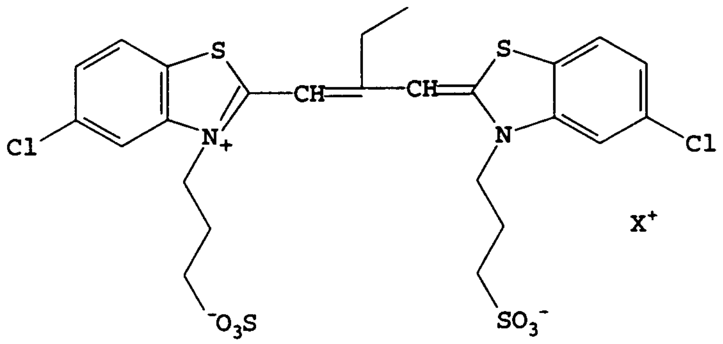
2. An element in accordance with claim 1, wherein Z_1, is a sulfur and Z_2 is sulfuR or selenium.

3. An element in accordance with claim 2, wherein Z_2 is sulfur.

4. An element in accordance with claim 1, wherein R_2 and R_3 are alkyl groups, at least one of which is substituted with an acid solubilizing group.

5. An element in accordance with claim 4, wherein each of R_2 and R_3 are substituted with an acid solubilizing group.

6. An element in accordance with claim 1, wherein the sensitizing dye is a dye having the formula:

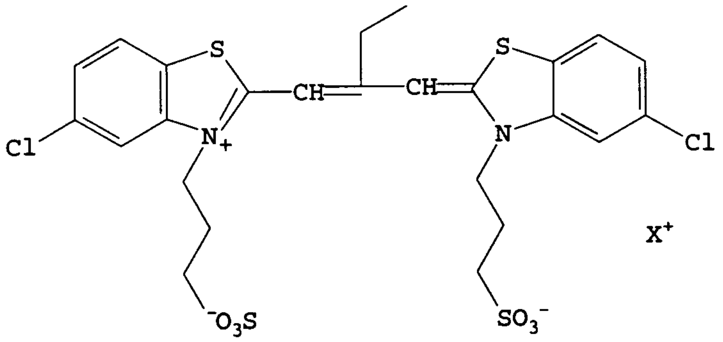


where X is a cation.

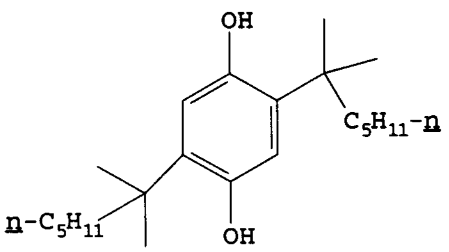
7. An element in accordance with claim 1, wherein R_5 and R_6 are tertiary alkyl groups in which the tertiary carbon atom is adjacent to the aromatic nucleus.

8. An element in accordance with claim 7, wherein R_5 and R_6 are each tertiary octyl groups.

9. An element in accordance with claim 1, wherein the red sensitizing dye has the formula:



where X is a cation
and the dialhylhydroquinone has the formula:



10. An element in accordance with claim 1, wherein said non-imaging layer is an antihalation layer.