(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 566 415 A2**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number : **93302942.3**

(22) Date of filing : **15.04.93**

(51) Int. Cl.[5] : **G03C 7/30,** G03C 7/38, G03C 1/83

(30) Priority : **16.04.92 US 870136**

(43) Date of publication of application : **20.10.93 Bulletin 93/42**

(84) Designated Contracting States : **BE CH DE FR GB IT LI NL**

(71) Applicant : **EASTMAN KODAK COMPANY**
343 State Street
Rochester, New York 14650-2201 (US)

(72) Inventor : **Rieger, John Brian, c/o Eastman Kodak Company**
Patent Department, 343 State Street
Rochester, New York 14650-2201 (US)
Inventor : **Friday, James Anthony, c/o Eastman Kodak Company**
Patent Department, 343 State Street
Rochester, New York 14650-2201 (US)

(74) Representative : **Nunney, Ronald Frederick Adolphe et al**
Kodak Limited Patent Department Headstone Drive
Harrow Middlesex HA1 4TY (GB)

(54) **Photographic material having low fog.**

(57) An improved multilayered color photographic element having lowered levels of fog comprising a support having coated thereon photographic silver halide emulsion layers, the layers including a unit of at least one green sensitive silver halide emulsion layer and a yellow filter layer adjacent said green sensitive layer, the green sensitive layer comprising a pyrazolotriazole dye-forming coupler.

EP 0 566 415 A2

Technical Field

This invention relates to a photographic material having improved speed and fog levels comprising a support having at least one green sensitive silver halide emulsion layer having an active magenta dye-forming coupler and an adjacent yellow filter layer containing a dye for filtering blue light.

Prior Art

Color photographic materials comprising multiple layers containing photographic couplers are well known. Typical photographic materials are described in US-A-Patents 4,145,219; 4,724,198; 4,184,876; 4,186,016 and 4,724,198.

Assessment of the Art

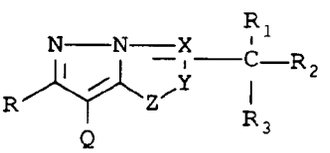
Prior photographic materials have exhibited problems with exposure reciprocity, speed, retained silver, color reproduction and neutral gray scale, flesh tone reproduction and image structure or granularity.

Various ways have been recognized in the photographic art for improving these problems. That is, for example, granularity can be improved but often it can be at the expense of another property such as speed. Or flesh tone color reproduction can be improved but neutral gray scale can be adversely affected. Further, when active couplers, such as certain magenta dye-forming couplers are used in a photographic element containing finely divided silver in adjacent interlayers, undesirable physical development is experienced which produces unacceptably high levels of fog. Prior solutions to this problem included the use of less active couplers, e.g., magenta dye forming couplers, however this results in slower film speed. Thus, there is a great need for a photographic material which enables improvement in these properties without serious adverse affects.

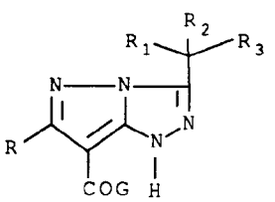
Disclosure of the Invention

Active couplers referred to such as magenta image dye forming couplers include couplers which, when coated at equal molar laydowns in the same format, exposed and processed substantially identically, produce higher gamma and more density at equal exposure than a less active coupler.

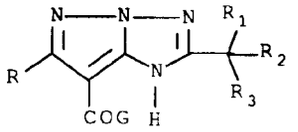
With respect to high fog, the present invention solves this problem by providing an improved multiple color layer photographic element having lowered levels of fog comprising a support having coated thereon photographic silver halide emulsion layers, the layers including a unit of at least one green sensitive silver halide emulsion layer and a yellow filter layer adjacent said green sensitive layer, the green sensitive layer comprising: a pyrazolotriazole dye-forming coupler, the coupler having the structure



or in the two preferred embodiments:



or



where

R is a substituent which does not adversely affect the desired properties of the coupler,

R_1, R_2, R_3 are linked to the alpha carbon and are selected from the group consisting of hydrogen, halogen, cyano or substituted or unsubstituted alkyl, aryl, heterocyclic, aliphatic residue, alkoxy, aryloxy, amino, alkylamino, acylamino, anilino, ureido, sulfamoylamino, alkylthio, arylthio, alkoxycarbonylamino, sulfonamido, carbamoyl, sulfamoyl, sulfonyl, heterocyclicoxy, acyloxy, carbamoyloxy, silyloxy, aryloxycarbonylamino, imido, heterocyclicthio, sulfinyl, phosphonyl, aryloxycarbonyl, acyl, or alkoxycarbonyl group wherein not more than one of R_1, R_2, R_3 is hydrogen,

Q is hydrogen or a coupling-off group (COG),

X, Y, Z are individually carbon or nitrogen atoms necessary to complete an azole ring, with unsaturated bonding being present in the ring as needed.

R may be a substituted or unsubstituted alkyl, aryl, alkoxy or carbonamido group suitably having 1 to 30 carbon atoms and preferrably 1 to 18 carbon atoms. R should aid solubility or diffusion resistance and produce a dye of desired hue upon reaction of the coupler with an oxidized color developing agent. These groups should not adversely affect the coupler. Exemplary substituent groups include alkyl (including C_{1-30}-alkyl, such as methyl, ethyl, propyl, n-butyl, t-butyl, octyl and eicosyl), aryl (including C_{6-30}-aryl, for example, phenyl, naphthyl and mesityl), cycloalkyl (such as cyclohexyl and cyclopentyl), alkoxy (including C_{1-30}-alkoxy, such as methoxy, i-butoxy and dodecyloxy), aryloxy (including C_{6-30}-aryloxy, for example, phenoxy and naphthoxy), alkoxycarbonyl (such as ethoxycarbonyl and dodecyloxycarbonyl), aryloxycarbonyl (such as phenoxycarbonyl), alkylthio (including C_{1-30}-alkylthio, such as methylthio and i-butylthio), arylthio (including C_{6-30}-arylthio such as phenylthio), alkanesulfonyl (such as ethanesulfonyl and butanesulfonyl), amino, acylamino (including C_{2-30}-acylamino, for example acetamido, benzamido and stearamido), ureido, carboxy, cyano, carbamyl (such as methyl carbamyl and hexyl carbamyl), sulfamyl (such as dioctyl sulfamyl and methyloctadecyl sulfamyl), sulfonamido, carboxamido, and heterocyclic groups, such as groups comprised of atoms selected from the group consisting of carbon, oxygen, nitrogen and sulfur atoms necessary to complete a 5- or 6-member heterocyclic ring, for example pyridyl, benzoxazolyl, furyl and thienyl.

The foregoing groups on the pyrazoloazole coupler are unsubstituted or optionally substituted with groups that do not adversely affect the desired properties of the coupler. Examples of useful substituents include ballast groups and coupler moieties known to be useful in the photographic art, and alkyl groups, such as C_{1-4}-alkyl, for example, methyl, ethyl and t-butyl.

R is preferably a tertiary carbon group where the individual substituents thereon do not adversely affect the coupler. Preferred substituents include halogen (such as chlorine, bromine and fluorine); alkyl, (including C_{1-30}-alkyl, such as methyl, ethyl, propyl, butyl, pentyl, ethylhexyl and eicosyl); aryl (for example C_{6-30}-aryl, such as phenyl, naphthyl and mesityl); carbonamido; ureido; carboxy; cyano; sulfamyl; sulfonamido; carboxamido; cycloalkyl (such as cyclohexyl and cyclopentyl); alkoxy (including C_{1-30}-alkoxy, such as methoxy, ethoxy, butoxy and dodecyloxy); aryloxy (including C_{6-30}-aryloxy, such as phenoxy and naphthoxy); alkylthio (such as C_{1-30}-alkylthio, including methylthio, ethylthio, propylthio, butylthio and dodecylthio); arylthio (including C_{6-30}-arylthio, such as phenylthio and naphthylthio); amino (including dioctylamino, dimethylamino and dodecylamino); acylamino (such as C_{1-30}-acylamino, including acetamido, benzamido and stearamido); and heterocyclyl (including 5- or 6-member heterocyclic rings such as pyrrolyl, oxazolyl and pyridyl).

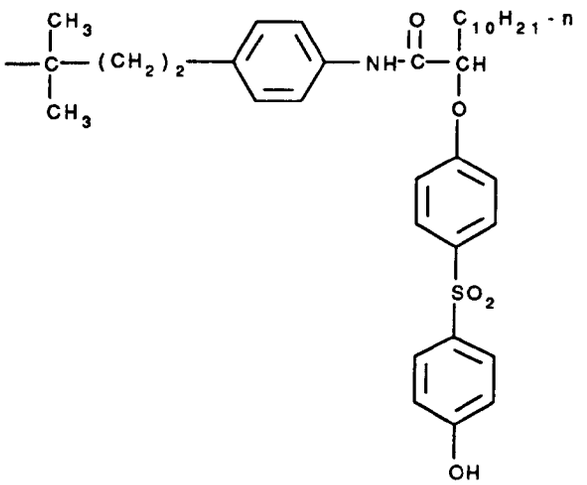
Optionally, in such a tertiary group, two substituent groups can form a heterocyclic ring, such as a heterocyclic ring comprised of atoms selected from carbon, oxygen, nitrogen and sulfur atoms necessary to complete a 5- or 6-member heterocyclic ring, for example pyrrole, oxazole, pyridine and thiophene; or a carbocyclic ring, such as cyclohexyl or norbornyl; or can comprise the carbon and hydrogen atoms necessary to complete a ring, such as an adamantyl ring.

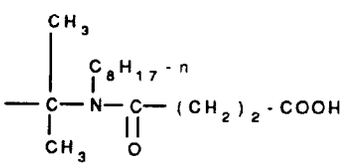
The possible R groups are unsubstituted or optionally further substituted with groups that do not adversely affect the desired properties of the pyrazolotriazole coupler. The groups can be optionally substituted with groups such as C_{1-20}-alkyl, including methyl, ethyl, propyl and butyl; C_{6-30}-aryl, such as phenyl and naphthyl; or phenolic, carboxylic acid and heterocyclic substituent groups. Substituents can include ballast groups and

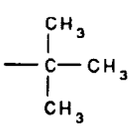
coupler moieties known to be useful in the photographic art.

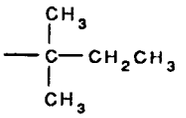
A ballast group, as is known to the art, is an organic radical of such size and configuration as to confer on the coupler molecule sufficient bulk to render the coupler substantially non-diffusible from the layer in which it is coated in a photographic element. Couplers of the invention can contain ballast groups, or be bonded to polymeric chains through one or more of the groups described herein. For example, one or more coupler moieties can be attached to the same ballast group. Representative ballast groups include substituted or unsubstituted alkyl or aryl groups containing 8 to 32 carbon atoms. Representative substituents include alkyl, aryl, alkoxy, aryloxy, alkylthio, arylthio, hydroxy, halogen, alkoxycarbonyl, aryloxycarbonyl, carboxy, acyl, acyloxy, carbonamido, carbamoyl, alkylsulfoxide, arylsulfoxide, alkanesulfonyl, arenesulfonyl, amino, anilino, sulfonamido and sulfamoyl groups where the alkyl and aryl substituents and the alkyl and aryl portions of the alkoxy, aryloxy, alkylthio, arylthio, alkoxycarbonyl, arylcarbonyl, acyl, acyloxy, carbonamido, carbamoyl, alkanesulfonyl, arenesulfonyl, sulfonamido and sulfamoyl substituents contain 1 to 30 carbon atoms and 6 to 30 carbon atoms, respectively, and can be further substituted with such substituents.

Examples of useful tertiary carbon groups are:





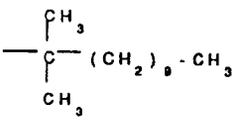


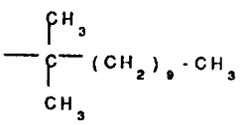


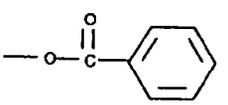
Another specific example of a group useful in the R position is phenoxyethoxy ($-O-CH_2CH_2-O-C_6H_5$).

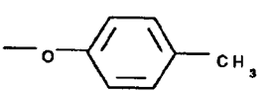
The pyrazoloazole couplers employed according to the invention contain, in the coupling position, hydrogen or a coupling-off group. Examples of specific coupling-off groups for Q or COG include:

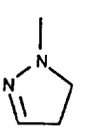
-Cl, -F, -SCN, $-OCH_3$, $-OC_6H_5$, $-OCH_2CONHCH_2CH_2OH$, $-OCH_2CONHCH_2CH_2OCH_3$, $-OCH_2CONHCH_2CH_2OCOCH_3$, $-NHSO_2CH_3$, $-OSO_2CH_3$, -S- $(-CH_2-)_2-COOH$,

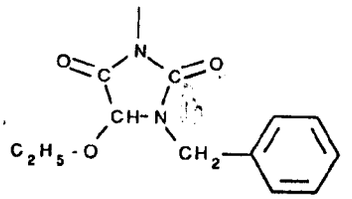


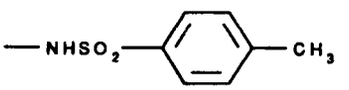


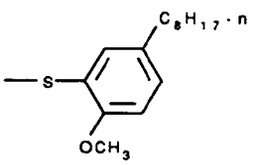


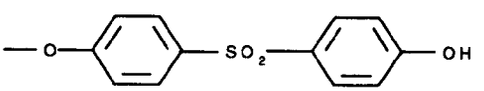


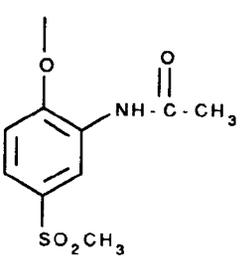










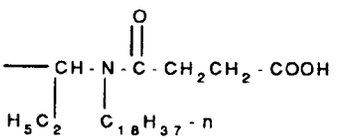


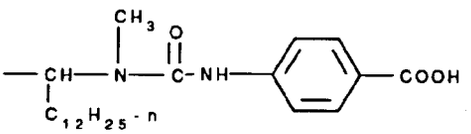
Preferred couplers within the scope of the formula are pyrazolotriazoles, in which X and Z or Y and Z are nitrogen atoms, with the necessary unsaturated bonding being present.

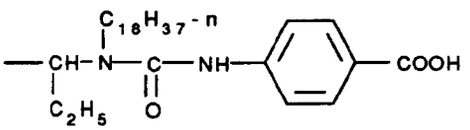
R_1, R_2, and R_3 independently represent a hydrogen, halogen, cyano or substituted or unsubstituted alkyl, aryl, heterocyclic, aliphatic residue, alkoxy, aryloxy, amino, alkylamino, acylamino, anilino, ureido, sulfamoylamino, alkylthio, arylthio, alkoxycarbonylamino, sulfonamido, carbamoyl, sulfamoyl, sulfonyl, heterocyclicoxy, acyloxy, carbamoyloxy, silyloxy, aryloxycarbonylamino, imido, heterocyclicthio, sulfinyl, phosphonyl, aryloxycarbonyl, acyl, or alkoxycarbonyl group; provided that not more than one of R_1, R_2, and R_3 is hydrogen.

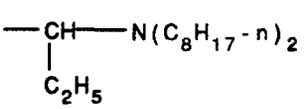
Generally, the substituents have 1 to 30 carbon atoms and typically 1 to 22 carbon atoms.

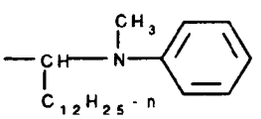
Preferred examples of the selection of R_1, R_2, and R_3 to yield a substituted methylene substituent on the pyrazoloazole ring are as follows:

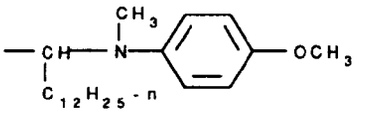


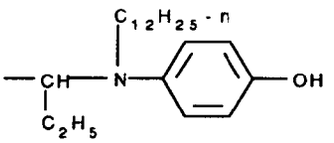


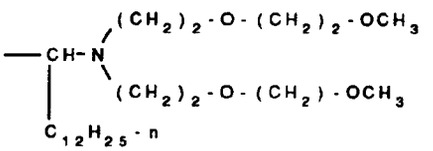


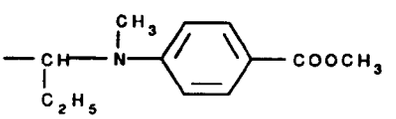


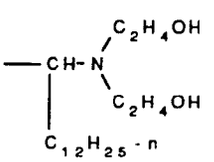


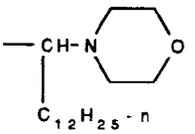


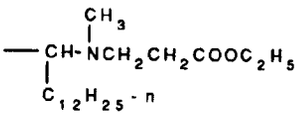


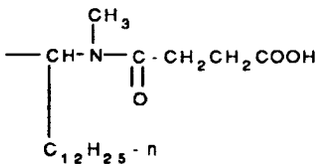


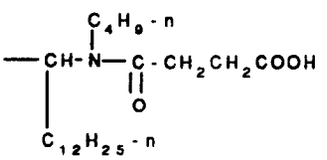


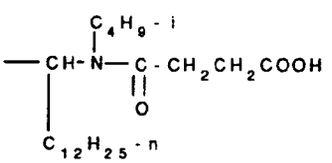


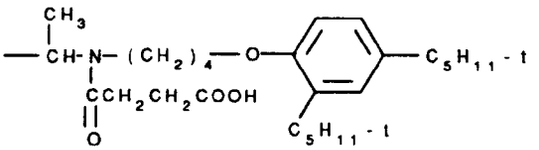


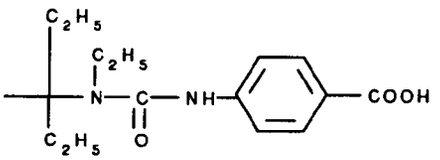


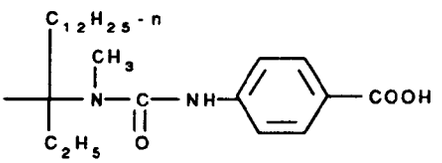


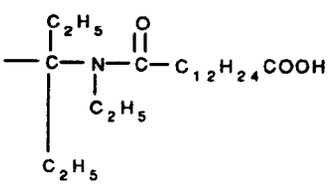


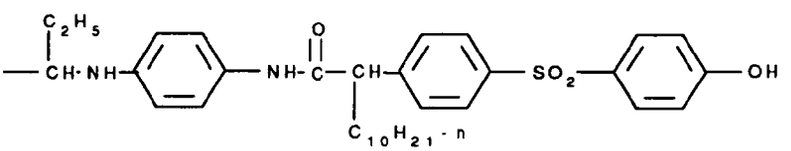


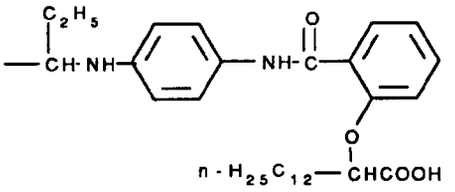


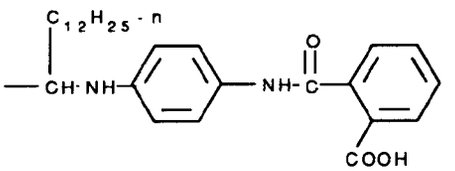


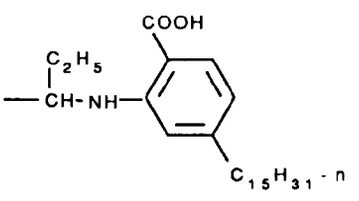


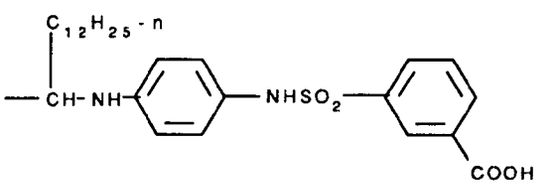


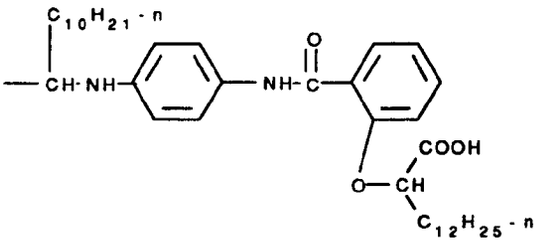


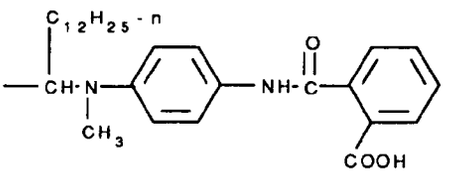


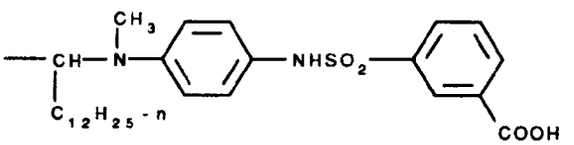


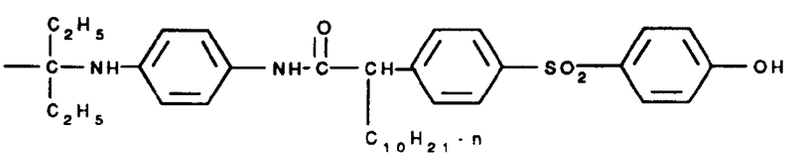


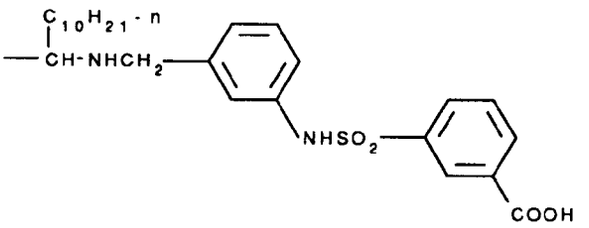


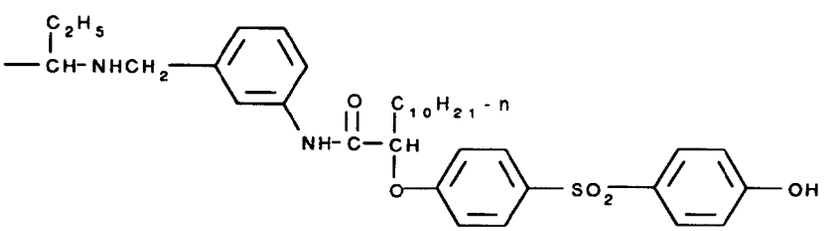


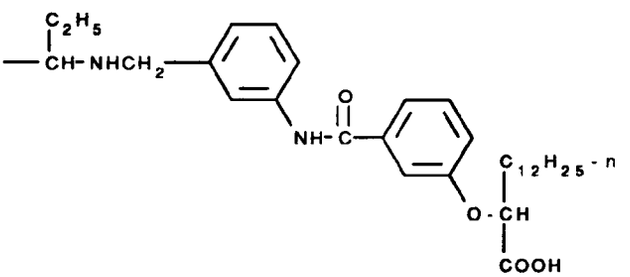


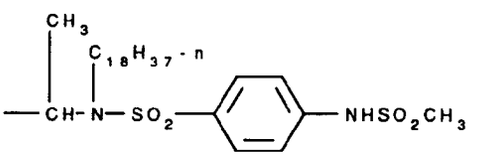


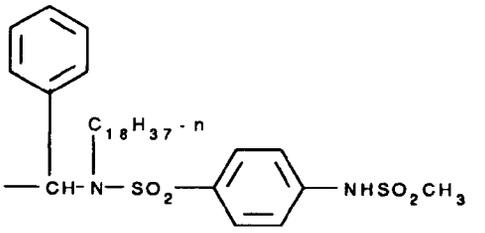


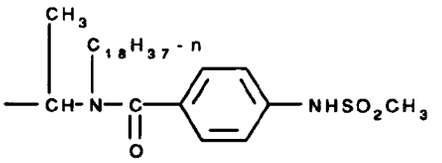


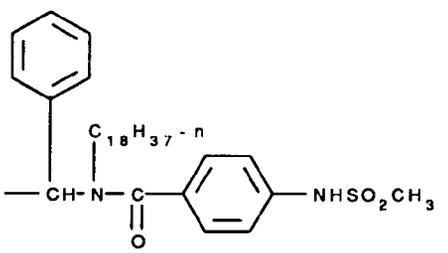


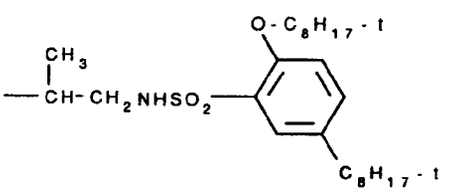


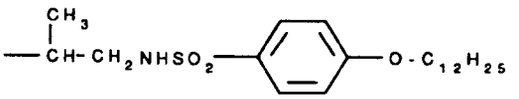


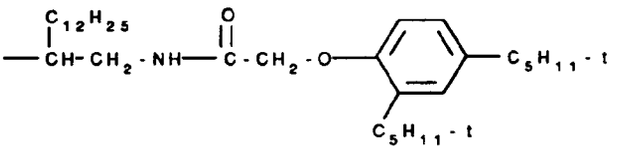


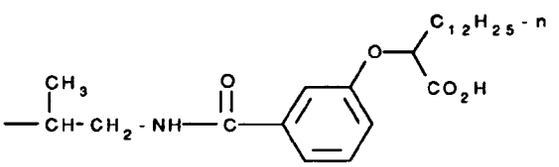


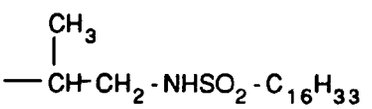


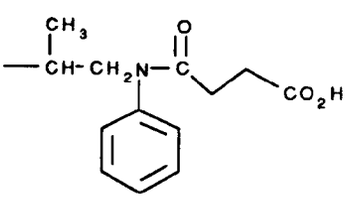


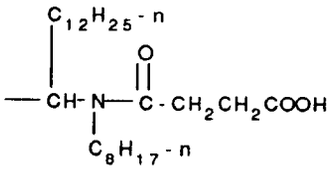


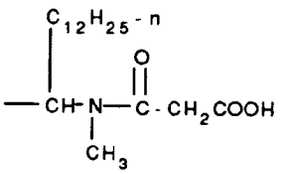


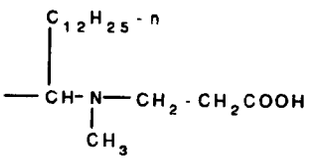


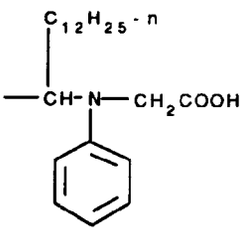


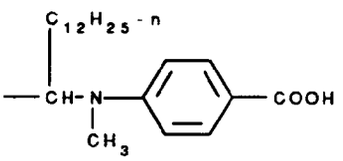






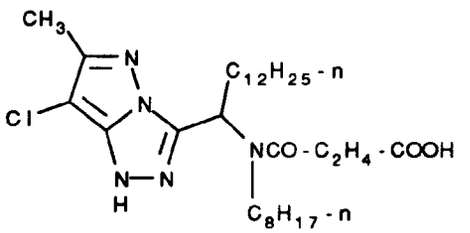




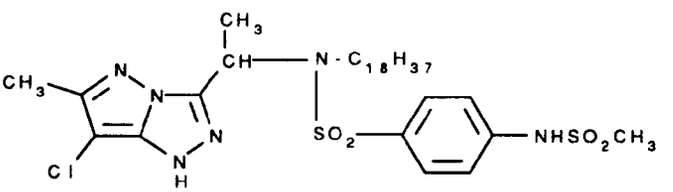


Preferred pyrazolotriazole couplers useful according to the invention are given below, without being limited thereto:

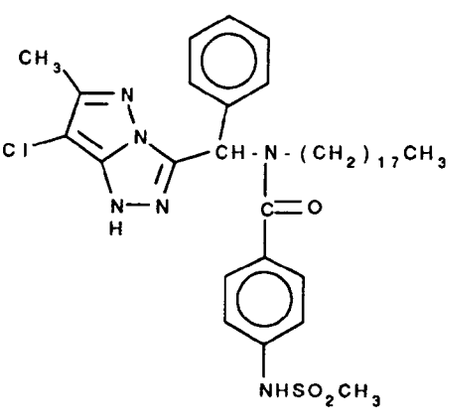
PA-1



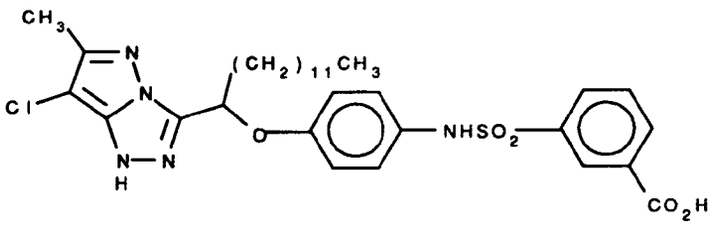
PA-2



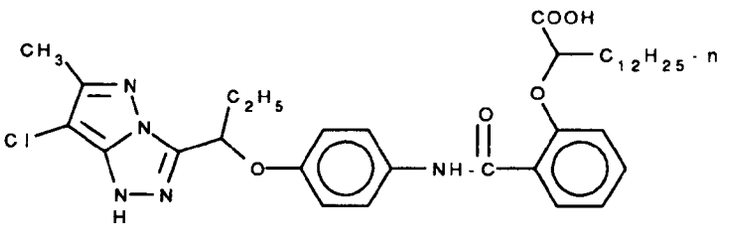
PA-3



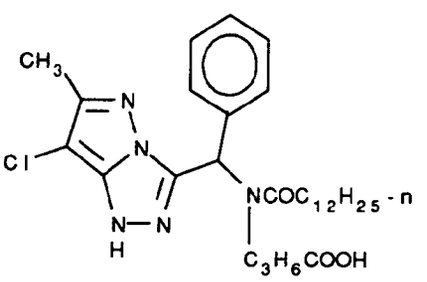
PA-4



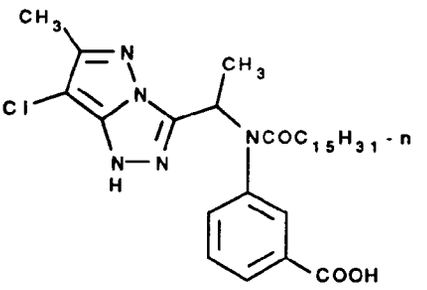
PA-5



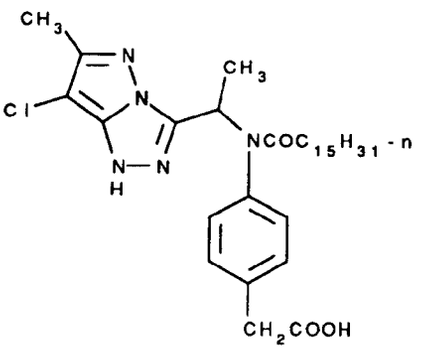
PA-6



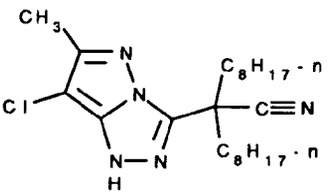
PA-7



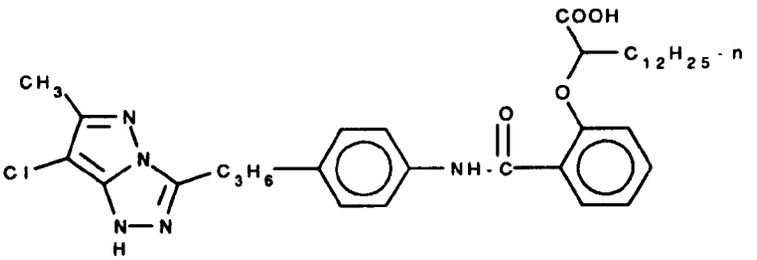
PA-8



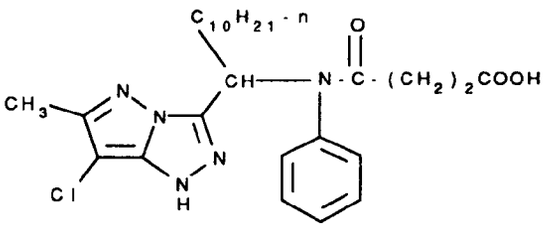
PA-9



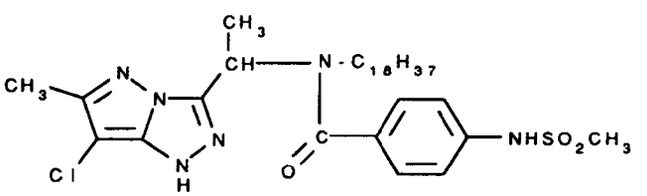
PA-10



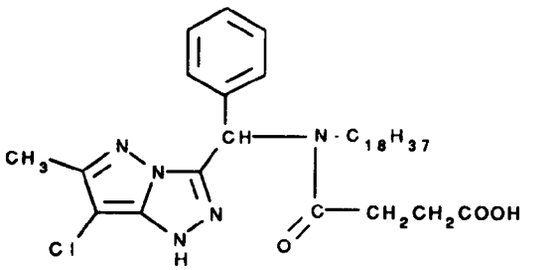
PA-11



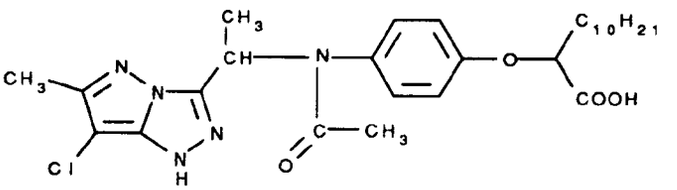
PA-12



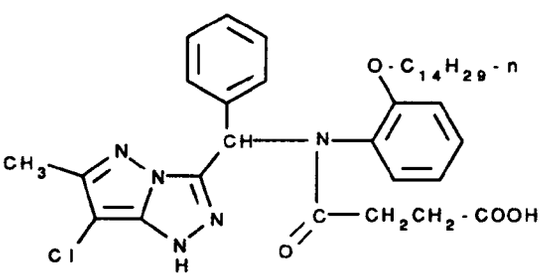
PA-13



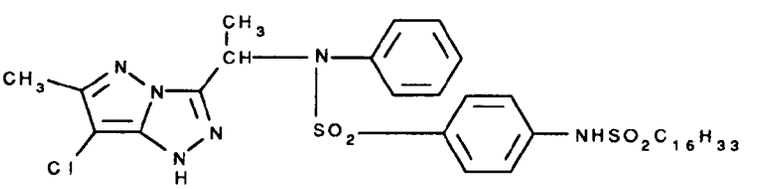
PA-14



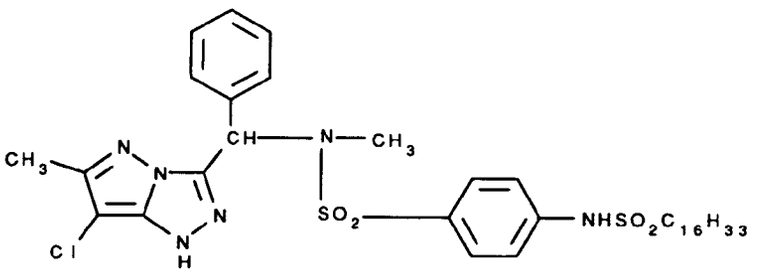
PA-15



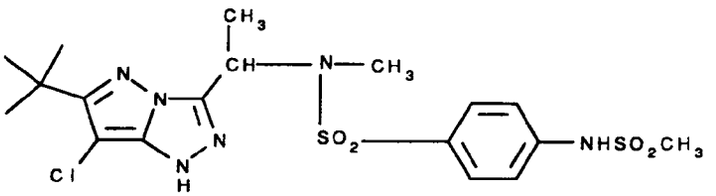
PA-16



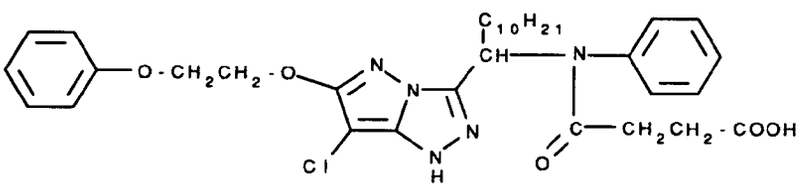
PA-17



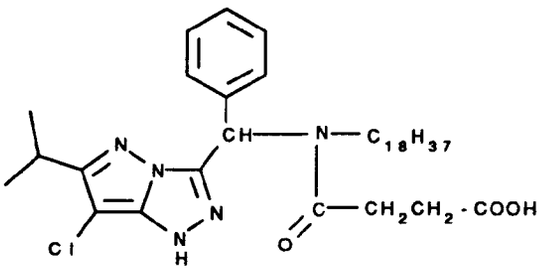
PA-18



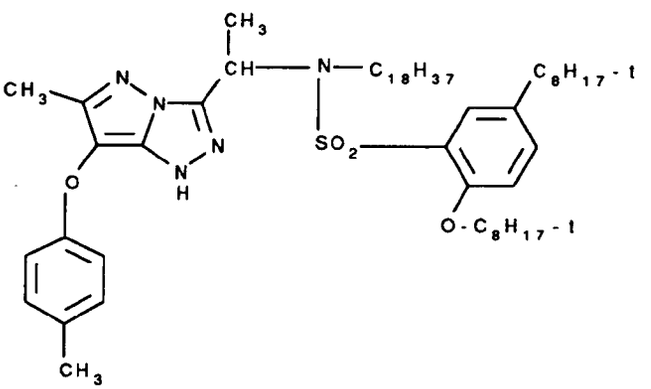
PA-19



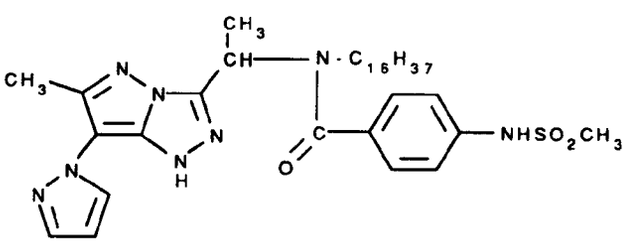
PA-20



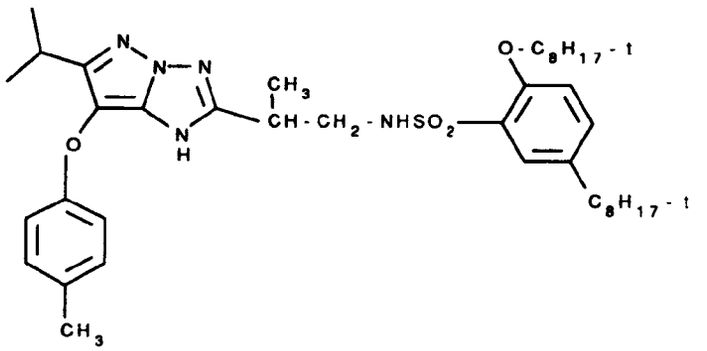
PA-21



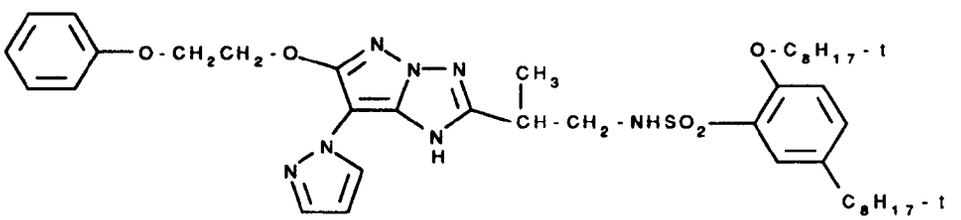
PA-22



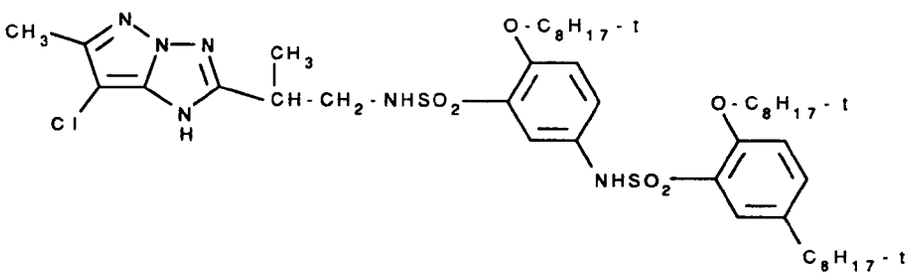
PA-23



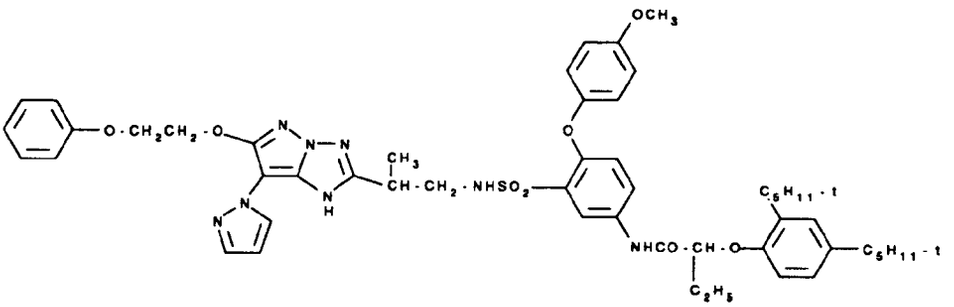
PA-24



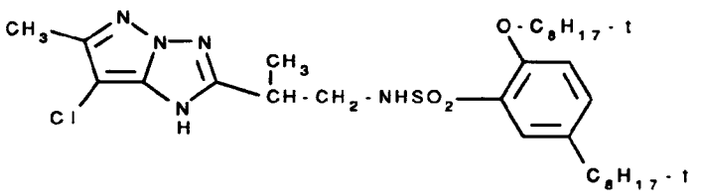
PA-25



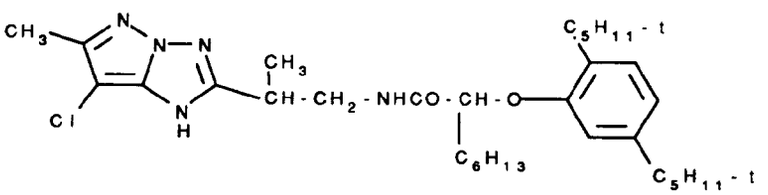
PA-26



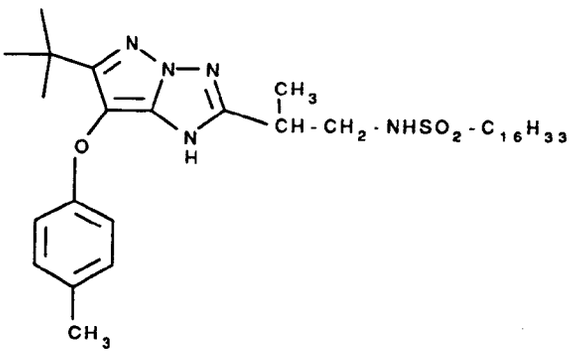
PA-27



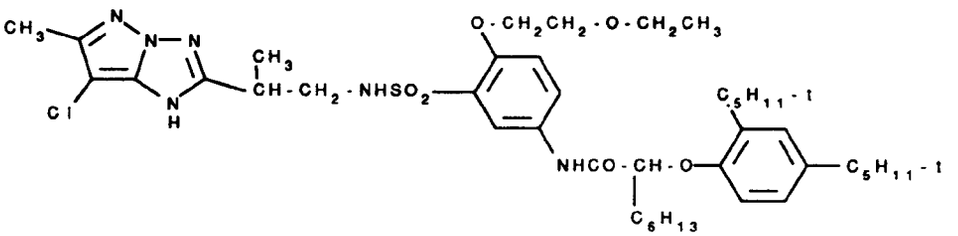
PA-28



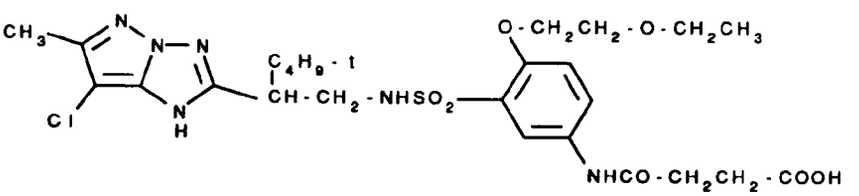
PA-29



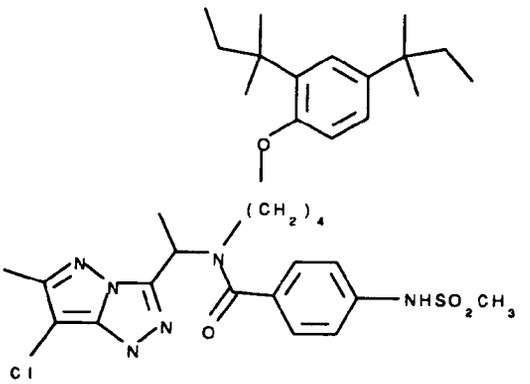
PA-30



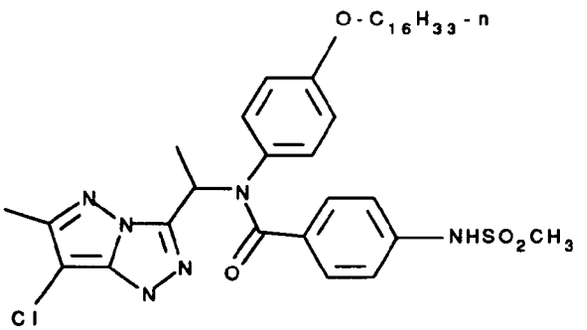
PA-31



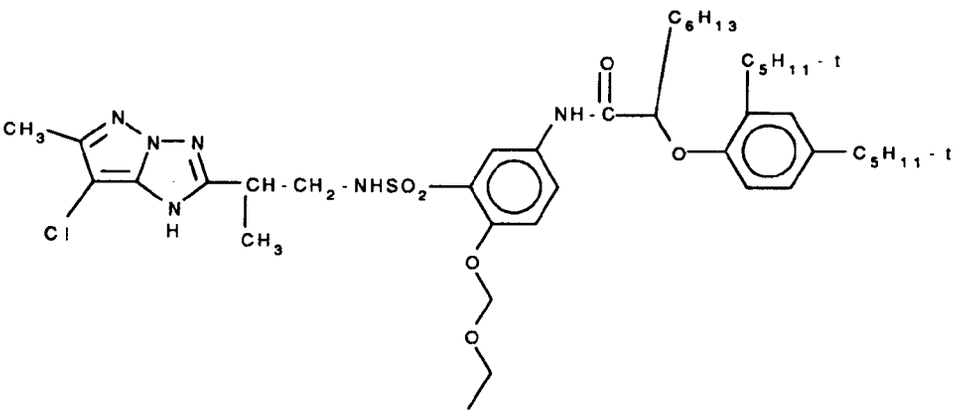
PA-32



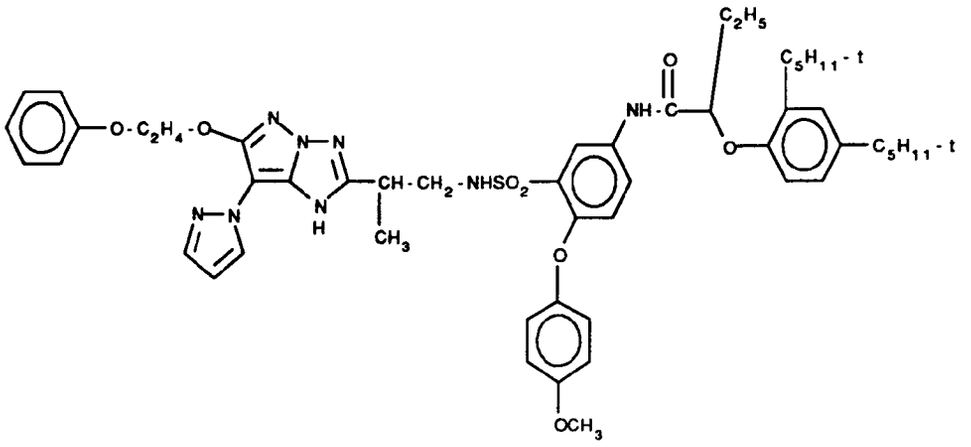
PA-33



PA-34



PA-35

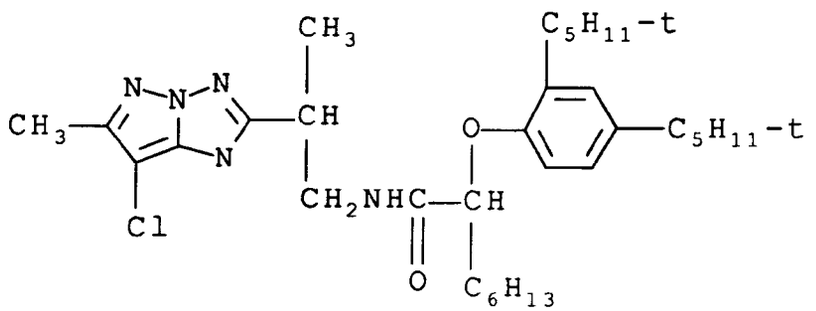


Pyrazoloazole couplers according to the invention are prepared by the general method of synthesis described in Research Disclosure, August 1974, Item No. 12443 published by Kenneth Mason Publications, Ltd., The Old Harbourmaster's, 8 North Street, Emsworth, Hampshire P010 7DD, England, and US-A-4,540,654, EP 0 285 274, EP 0 428 902A1 or EP 0 459 349A1.

Typically R is an organic group having 1-6 carbons such as methyl, ethyl, methoxy, acetamido and phenyl, and R_1, R_2, R_3 are selected from hydrogen, alkyl, phenyl, and substituents linked to the alpha methyl group through nitrogen or oxygen and wherein not more than one of R_1, R_2, R_3 is hydrogen.

Further, R_2 may be selected from methyl and an unsubstituted phenyl group and R_3 may be a substituent linked to the alpha methyl group through nitrogen or oxygen. Further, at least one of the R_1, R_2, R_3 may contain a solubilized ballast-group containing one of carboxylic acid and a sulfamide group.

Such pyrazolotriazole dye-forming couplers have the structure, for example,

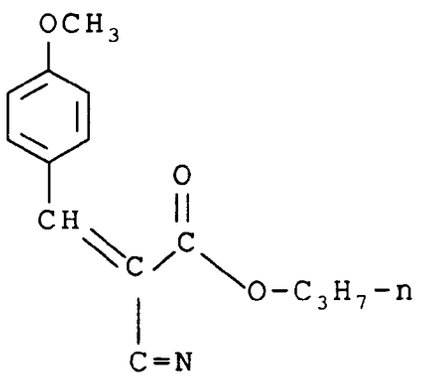


Further, the multilayer color photographic element may comprise a support having coated thereon photographic silver halide emulsion layers, the layers including a unit of at least three green sensitive silver halide emulsion layers having a first green sensitive layer being more sensitive than a second or mid green sensitive layer which is more sensitive than a third green sensitive layer, the green sensitive layers being adjacent and the unit containing a masking coupler. The first green sensitive layer is comprised of at least one magenta image dye-forming coupler (A), a timed development inhibitor releasing coupler, and preferably a non-timed development inhibitor releasing coupler. The second layer is comprised of at least one first magenta image dye-forming coupler, (A), preferably at least one second magenta image dye-forming coupler, a development inhibitor releasing coupler and preferably a cyan dye-forming coupler. The third layer is comprised of at least one magenta image dye-forming coupler which is also a bleach accelerating releasing coupler. Further, the third layer contains a development inhibitor releasing coupler.

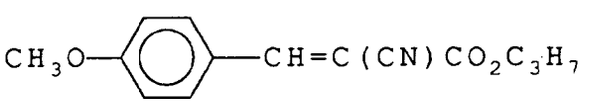
A typical photographic element in accordance with the invention typically comprises the following layer order:

OVERCOAT
UV
MOST SENSITIVE BLUE OR FAST YELLOW
LEAST SENSITIVE BLUE OR SLOW YELLOW
INTERLAYER
MOST SENSITIVE GREEN OR FAST MAGENTA
MID SENSITIVE GREEN OR MID MAGENTA
LEAST SENSITIVE GREEN OR SLOW MAGENTA
INTERLAYER
MOST SENSITIVE RED OR FAST CYAN
LEAST SENSITIVE RED OR SLOW CYAN
INTERLAYER
ANTIHALATION LAYER
SUPPORT

The overcoat layer can be comprised of components known in the photographic art for overcoat layers including UV absorbers, matting agents, surfactants, and like. A UV layer can also be used which contains similar materials. UV absorbing dyes useful in this layer and the antihalation layer have the structure:

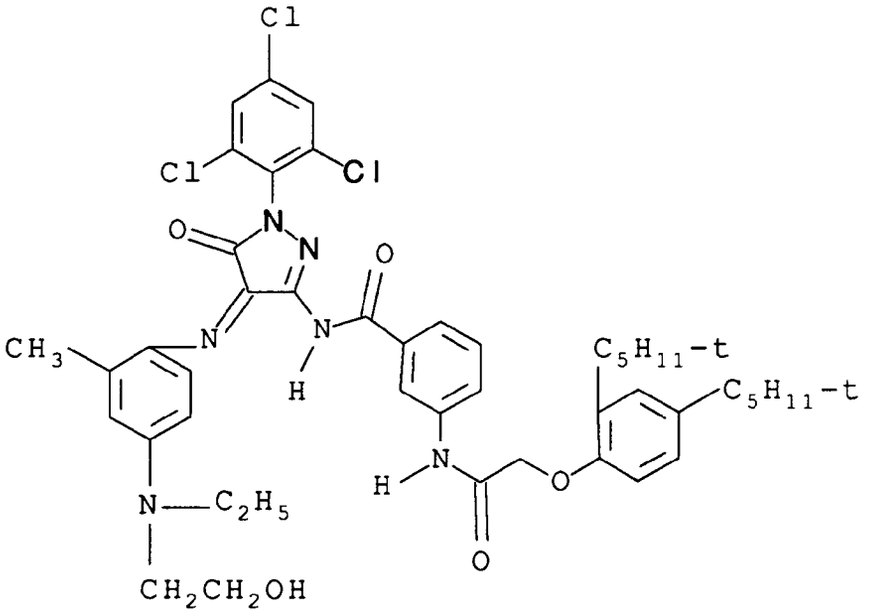


(1)



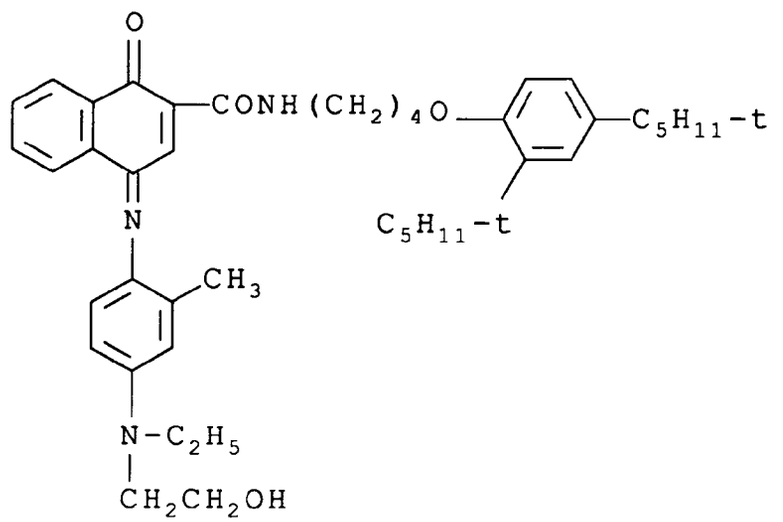
(2)

This layer, for example, also can contain dyes which can help in adjusting the photographic sensitivity of the element. Such dyes can be a green filter dye. A suitable green filter dye has the structure



(10)

A suitable red filter dye has the structure



(20)

Other dyes that may be used include washout dyes of the type referred to herein and filter dyes that decolorize during the photographic process.

IMAGE DYE FORMING COUPLERS

The image dye-forming couplers in the blue-sensitive, green-sensitive and red sensitive layers as described can be any of the image dye-forming couplers known in the photographic art for such layers for forming yellow, magenta and cyan dye images. Such couplers can comprise a coupler moiety (COUP) known in the art and as described. Combinations of the image dye-forming couplers can be useful in the described photographic silver halide emulsion layers.

Couplers that are yellow dye forming couplers are typically acylacetamides, such as benzoylacetanilides and pivalylacetanilides. Such couplers are described in such representative patents and publications as: US-A-2,875,057; 2,407,210; 3,265,506; 2,298,443; 3,048,194; 4,022,620; 4,443,536; 3,447,928 and "Farbkuppler: Eine Literatürbersicht", published in Agfa Mitteilungen, Band III, pages 112-126 (1961).

The couplers that are cyan image dye-forming couplers (C) are typically phenols or naphthols, such as described in the photographic art for forming cyan dyes upon oxidative coupling.

Examples of such couplers (C) that form cyan dyes are typically phenols and naphthols that are described

in such representative patents and publications as: US-A-2,772,162; 3,772,002; 4,526,864; 4,500,635; 4,254,212; 4,296,200; 4,457,559; 2,895,826; 3,002,936; 3,002,836; 3,034,892; 2,474,293; 2,423,730; 2,367,531; 3,041,236; 4,443,536; 4,124,396; 4,775,616; 3,779,763; 4,333,999 and "Farbkuppler: Eine Literaturübersicht", published in Agfa Mitteilungen, Band III, pages 156-175 (1961).

Examples of couplers (A) that form magenta dyes are typically pyrazolones, pyrazolotriazoles and benzimidazoles, such couplers are described in such representative patents and publications as US-A-2,600,788; 2,369,489; 2,343,703; 2,311,082; 3,824,250; 3,615,502; 4,076,533; 3,152,896; 3,519,429; 3,062,653; 2,908,573; 4,540,654; 4,443,536; 3,935,015; 3,451,820; 4,080,211; 4,215,195; 4,518,687; 4,612,278; and European Applications 284,239; 284,240; 240,852; 177,765 and "Farbkuppler: Eine Literaturübersicht", published in Agfa Mitteilungen, Band III, pages 126-156 (1961).

The photographic element may be processed to form a developed image in an exposed color photographic element by developing the element with a color developer.

FAST YELLOW

In the photographic element, the more blue sensitive layer or fast yellow layer contains a timed development inhibitor releasing coupler (DIR). The fast yellow layer is a coupler starved layer. The layer is preferably free of an image dye-forming coupler. As used herein by coupler starved is meant a condition in the layer in which there is less dye-forming coupler than is theoretically capable of reacting with all of the oxidized developing agent generated at maximum exposure. Couplers other than image dye-forming couplers can be present in this layer and such couplers can include, for example, timed development couplers as noted or non-timed DIR couplers and color correcting couplers. These other couplers are typically used at concentrations known in the photographic art and can produce yellow dye typically not more than about 3% of the total density of the yellow record.

Suitable timed DIR couplers used in the fast yellow layer comprise a DIR coupler (E) that is capable of releasing a mercapto-tetrazole development inhibitor comprising a substituent:

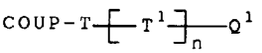
-X-COOR

wherein

X is alkylene of 1 to 3 carbon atoms and R is alkyl of 1 to 4 carbon atoms, and the sum of the carbon atoms X and R is 5 or less. The DIR coupler is typically a pivalylacetanilide coupler, such as described in US-A-4,782,012, the disclosure of which is incorporated herein by reference.

The timed DIR coupler can be any timed DIR coupler useful in the photographic art which will provide a timed development inhibitor release.

That is, a development inhibitor releasing coupler containing at least one timing group (T) that enables timing of release of the development inhibitor group can be any development inhibitor releasing coupler containing at least one timing group known in the photographic art. The development inhibitor releasing coupler containing at least one timing group is represented by the formula:



wherein

COUP is a coupler moiety, as described, typically a cyan, magenta or yellow dye-forming coupler moiety;

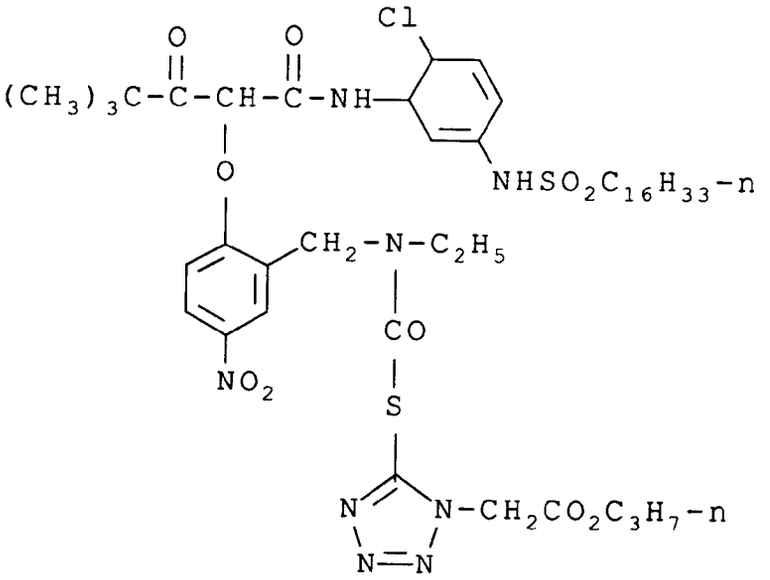
T and T^1 individually are timing groups, typically a timing group as described in US-A-4,248,962 and 4,409,232, the disclosure of which are incorporated herein by reference;

n is 0 or 1; and

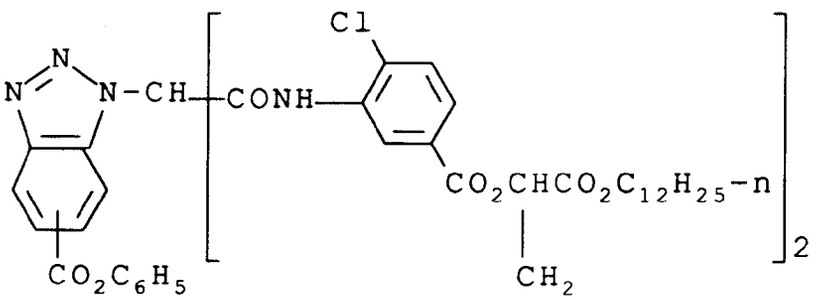
Q^1 is a releasable development inhibitor group known in the photographic art. Q^1 can be selected from the INH group as described.

A preferred coupler of this type is described in US-A-4,248,962.

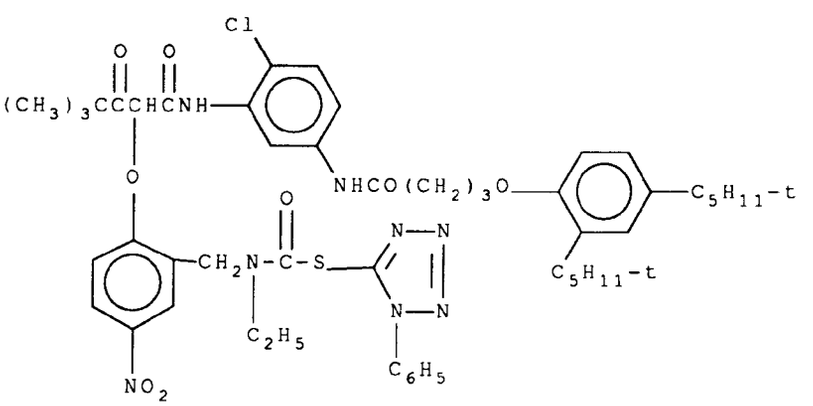
Preferred timed DIR couplers of this type are:



(24)

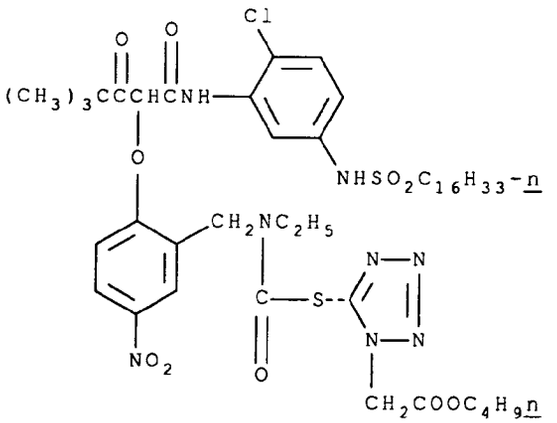


(25)

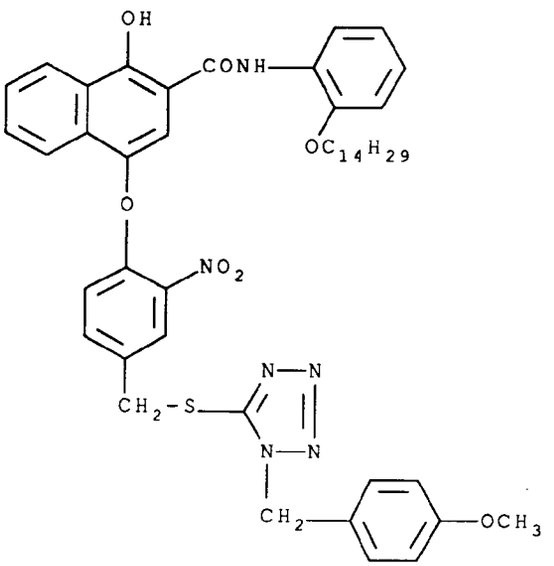


(26)

Highly suitable timed DIR couplers have the structure:

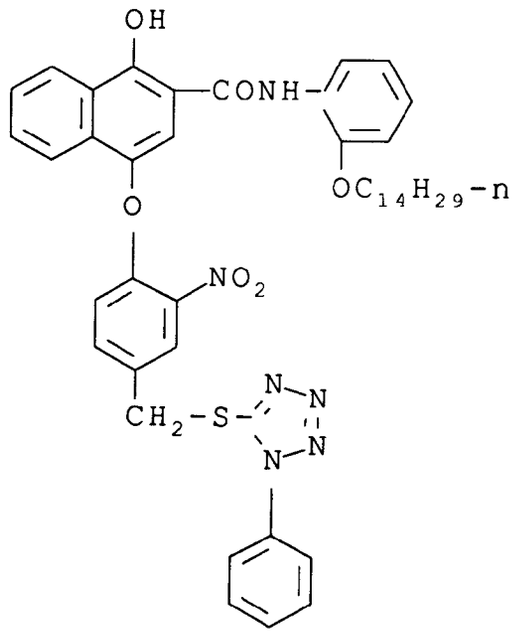


(17)



(27)

(28)



Color from the fast yellow layer is produced mostly as a result of oxidized developer formed in the fast yellow layer migrating to the adjacent slow yellow layer and reacting to form yellow dye.

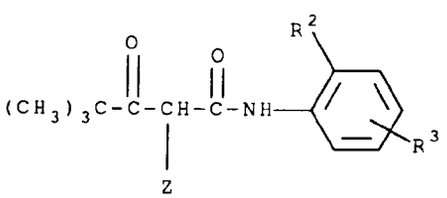
Other couplers that are development inhibitor releasing couplers as described include those described in for example US-A-4,248,962; 3,227,554; 3,384,657; 3,615,506; 3,617,291; 3,733,201; and U.K. 1,450,479. Preferred development inhibitors are heterocyclic compounds, such as mercaptotetrazoles, mercaptotriazoles, mercaptooxadiazoles, selenotetrazoles, mercaptobenzothiazoles, selenobenzothiazoles, mercaptobenzoxazoles, selenobenzoxazoles, mercaptobenzimidazoles, selenobenzimidazoles, benzotriazoles, benzodiazoles and 1,2,4-triazoles, tetrazoles, and imidazoles.

SLOW YELLOW LAYER

In the photographic element, the less blue sensitive layer or slow yellow layer contains a yellow image dye-forming coupler. Such yellow image dye-forming coupler can be any yellow dye-forming coupler useful in the photographic art.

Couplers that are yellow image dye-forming couplers are typically acylacetamides, such as benzoylacetanilides and pivalylacetanilides, such as described in the photographic art for forming yellow dyes upon oxidative coupling.

The yellow dye-forming coupler in the slow yellow layer is typically a pivalylacetanilide coupler containing a hydantoin coupling-off group. Such a coupler is illustrated by the formula:



wherein

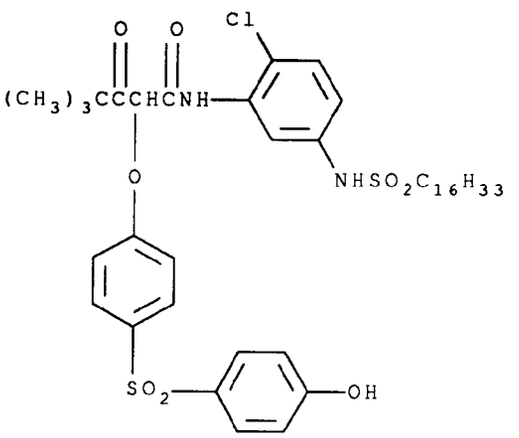
R^2 is chlorine, bromine or alkoxy;

R^3 is a ballast group, such as a sulfonamide or carboxamide ballast group; and

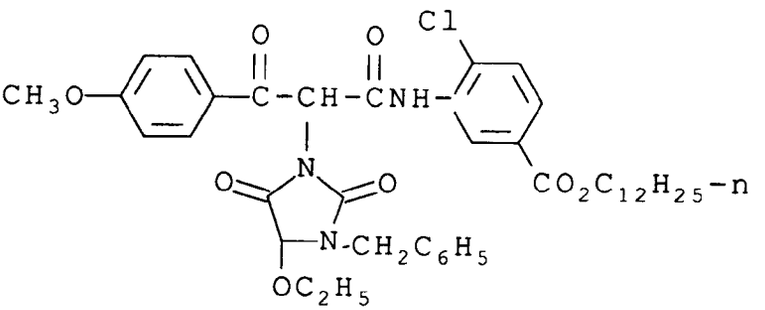
Z is a coupling-off group, preferably a hydantoin coupling off group as described in US-A-4,022,620.

Yellow dye-forming couplers suitable for the slow yellow or less sensitive blue layer are:

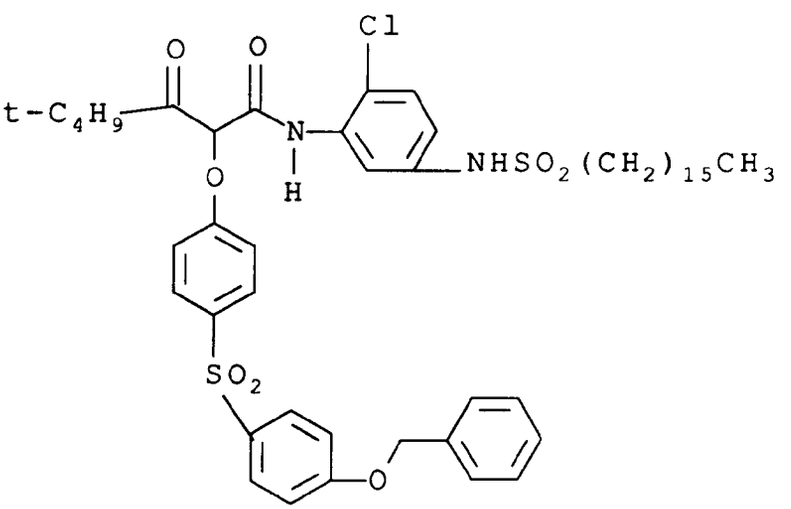
(6)



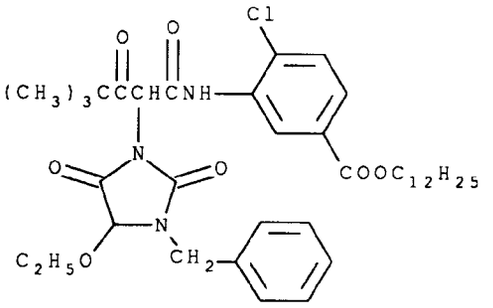
(29)



(30)



A preferred yellow dye-forming coupler for the slow yellow layer has the structure:



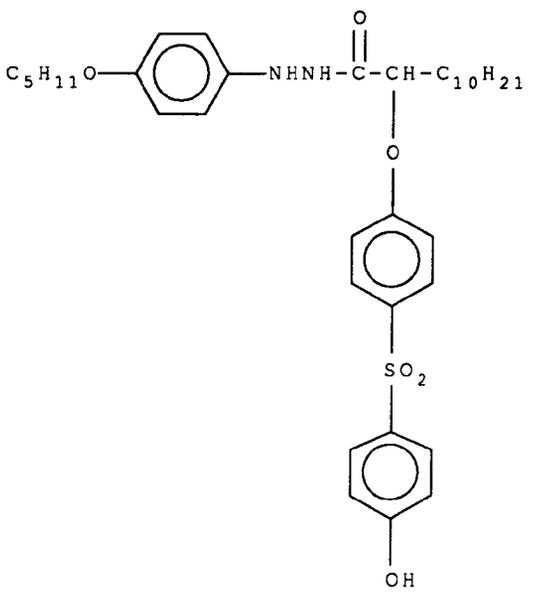
(19)

Timed or non-timed DIR couplers as noted with respect to the fast yellow layer may also be used in the slow yellow lower.

INTERLAYER

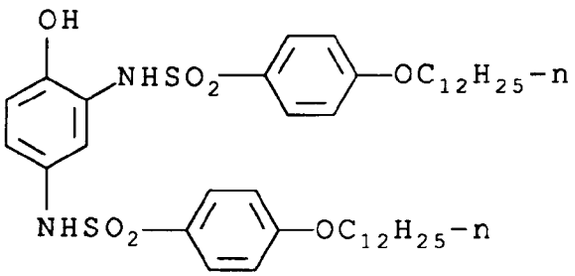
In the photographic element a yellow filter layer is provided between the slow yellow and the fast magenta. This layer can comprise Carey Lea silver (CLS), bleach accelerating silver salts, any oxidized developer scavenger known in the photographic art, such as described in US-A-4,923,787, and a dye to enable improved image sharpness or to tailor photographic sensitivity of the element. A preferred oxidized developer scavenger is:

(3)

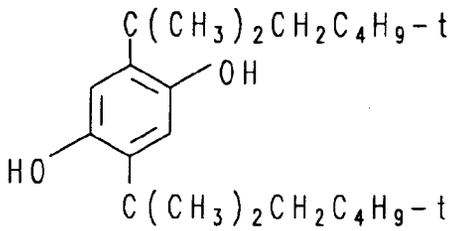


Other oxidized developer scavenger useful in the invention include:

(31)



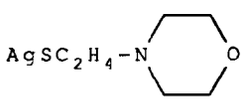
(32)

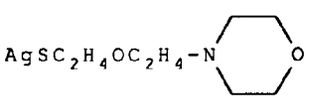


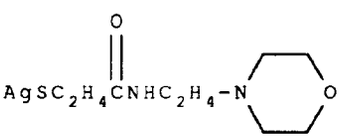
When finely divided silver such as Carey Lea silver is used in the yellow filter layer, then preferably an interlayer is provided between the yellow filter and any other layer in the photographic element containing a bleach accelerating releasing coupler (BARC). If a bleach accelerating silver salt (BASS) is used, preferably in the yellow filter layer, then it is preferred to provide an interlayer to isolate the BASS containing layer from the remainder of the film. This interlayer may contain the oxidized developer scavenger noted above. Further, the interlayer may be contiguous with the yellow filter layer and may be disposed on both sides of the yellow filter layer. Representative bleach accelerating silver salts are disclosed in US-A-4,865,965; 4,923,784; 4,163,669. The bleach accelerating silver salts can comprise silver salts of mercapto proprionic acid.

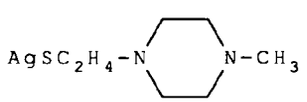
BARC and BASS compounds may be used in combination in the element.

Other representative bleach accelerating silver salts which may be used in the interlayer are structurally shown as follows:



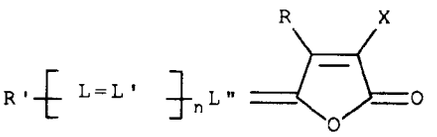






$AgSC_2H_4OC_2H_4N(CH_3)_2$
$AgSC_2H_4N(C_2H_4OCH_3)_2$

Instead of using finely divided silver in the yellow filter layer, filter dyes may be used. When filter dyes are used, then the interlayer contiguous or adjacent the yellow filter layer may be omitted. Oxidized developer scavenger as referred to above may be used in the yellow filter layer with the filter dye. Examples of filter dyes such as washout or decolorizing dyes useful in the present invention are described in US-A-4,923,788 incorporated herein by reference. Such filter dyes have the formula:



wherein R is substituted or unsubstituted alkyl or aryl, X is an electron withdrawing group, R' is substituted or unsubstituted aryl or a substituted or unsubstituted aromatic heterocyclic nucleus, and L, L', and L" are each independently a substituted or unsubstituted methine group, and n is 0 to 6.

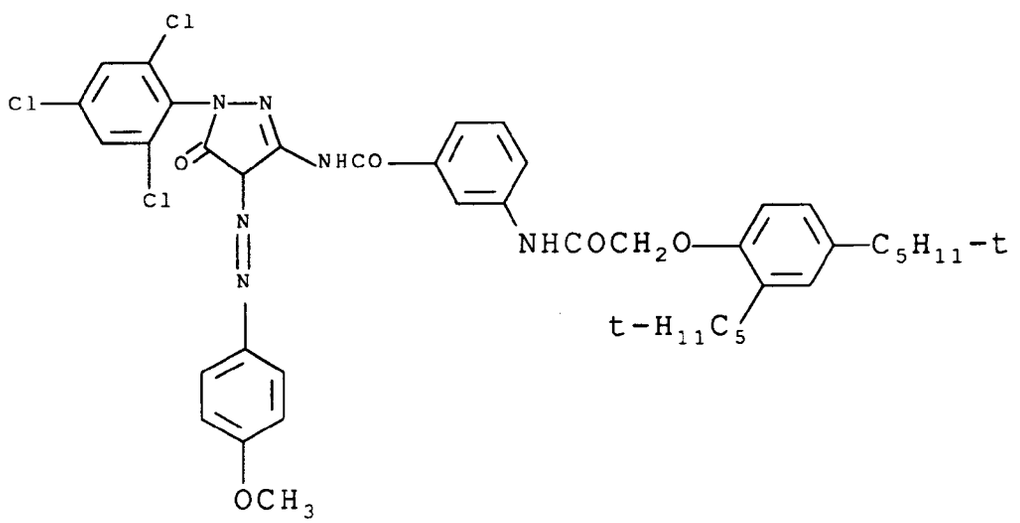
Preferred alkyl groups include alkyl of from 1 to 20 carbon atoms, including straight chain alkyls such as methyl, ethyl, propyl, butyl, pentyl, decyl, dodecyl, and so on, branched alkyl groups such as isopropyl, isobutyl, t-butyl, and the like. These alkyl groups may be substituted with any of a number of known substituents, such as sulfo, sulfato, sulfonamide, amido, amino, carboxyl, halogen, alkoxy, hydroxy, phenyl, and the like. The substituents may be located essentially anywhere on the alkyl group. The possible substituents are not limited to those exemplified, and one skilled in the art could easily choose from a number of substituted alkyl groups that would provide useful compounds according to the formula.

Preferred aryl groups for R include aryl of from 6 to 10 carbon atoms (e.g., phenyl, naphthyl), which may be substituted. Useful substituents for the aryl group include any of a number of known substituents for aryl groups, such as sulfo, sulfato, sulfonamido (e.g., butane-sulfonamido), amido, amino, carboxyl, halogen, alkoxy, hydroxy, acyl, phenyl, alkyl, and the like.

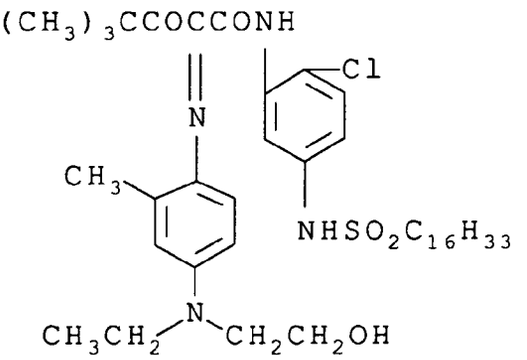
The filter dyes may be used in combination with the finely divided silver.

It will be appreciated that permanent yellow filter dyes can be used instead of CLS or washout-filter dyes, such permanent dyes, for example, have structures:

(33)

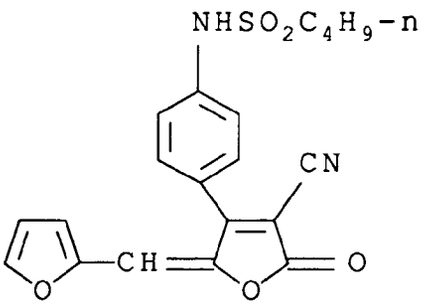


(11)



A microcrystalline dye useful in the invention has the structure:

(18)



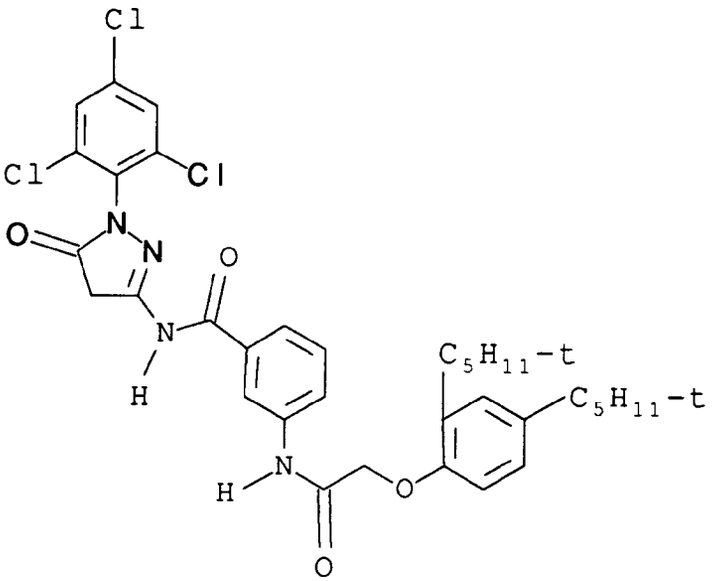
FAST MAGENTA LAYER

The most green sensitive layer or fast magenta layer comprises a magenta image dye-forming coupler (A), a timed development inhibitor releasing coupler (DIR), preferably a non-timed DIR coupler and preferably a masking coupler.

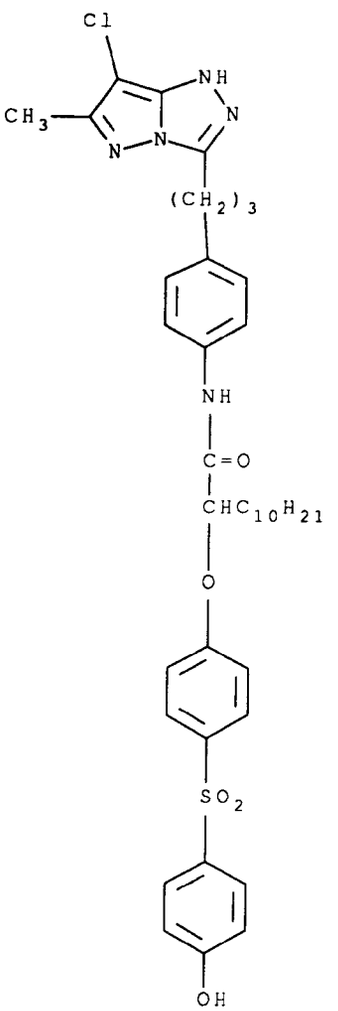
The magenta image dye-forming coupler (A) can be any image forming coupler dye useful in the photographic art.

A typical magenta image dye-forming coupler is a pyrazolotriazole. Suitable couplers that form magenta dyes include:

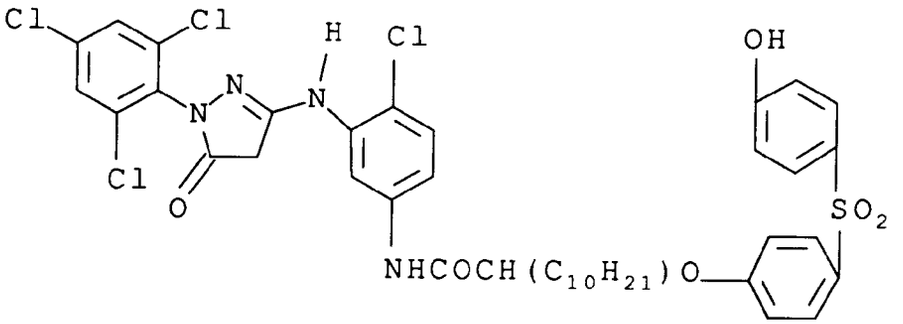
(34)



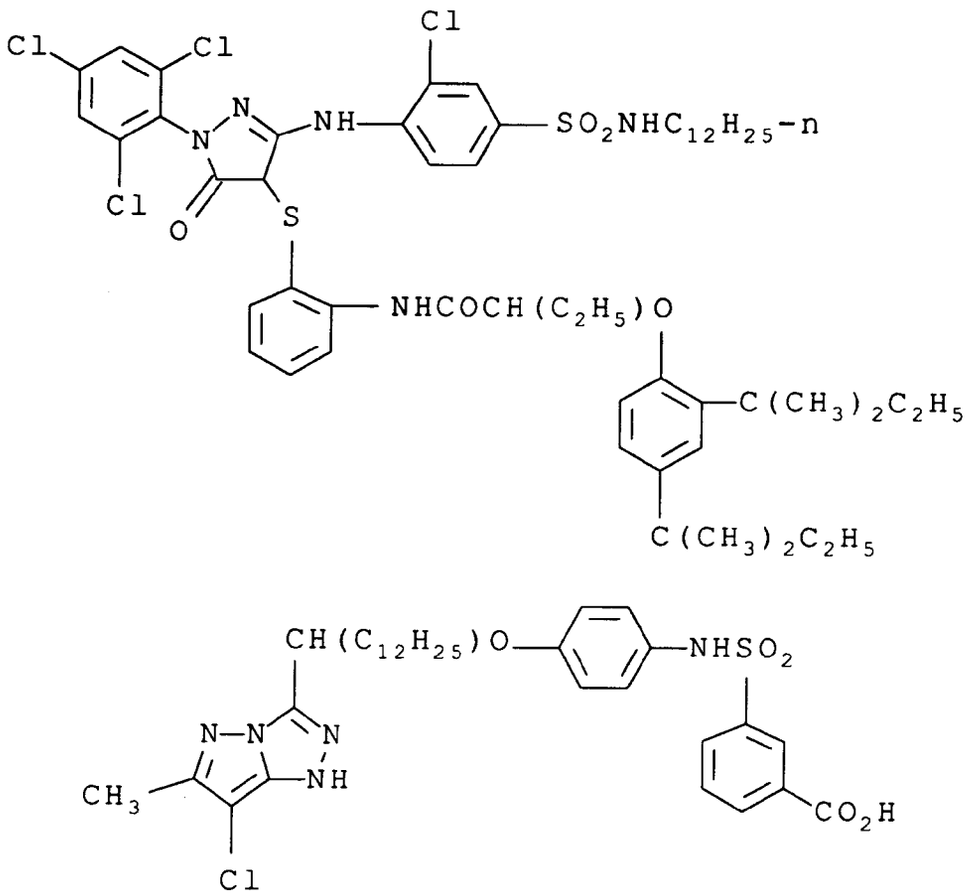
(14)



(35)

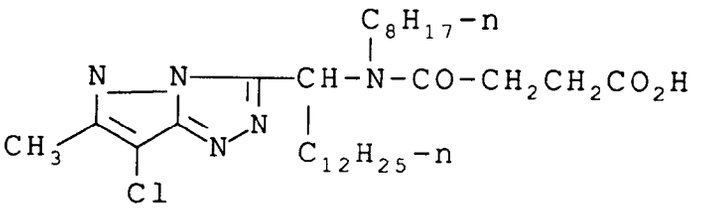


(36)



A preferred magenta image dye-forming coupler has the structure:

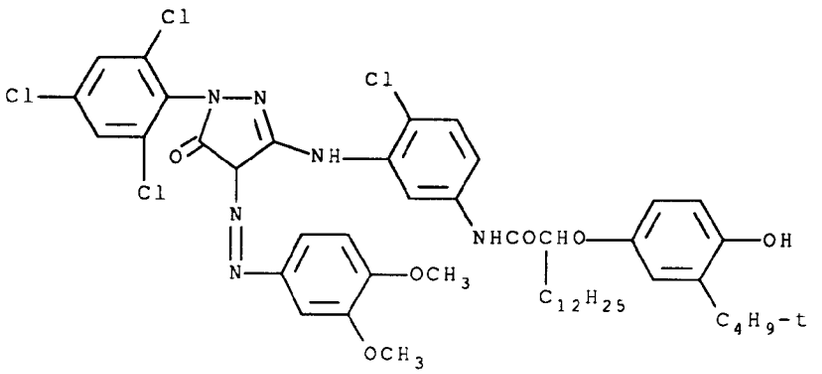
(15)



Suitable timed DIR couplers comprise a DIR coupler (E) that is capable of releasing a mercaptotetrazole development inhibitor as noted with respect to the fast yellow layer.

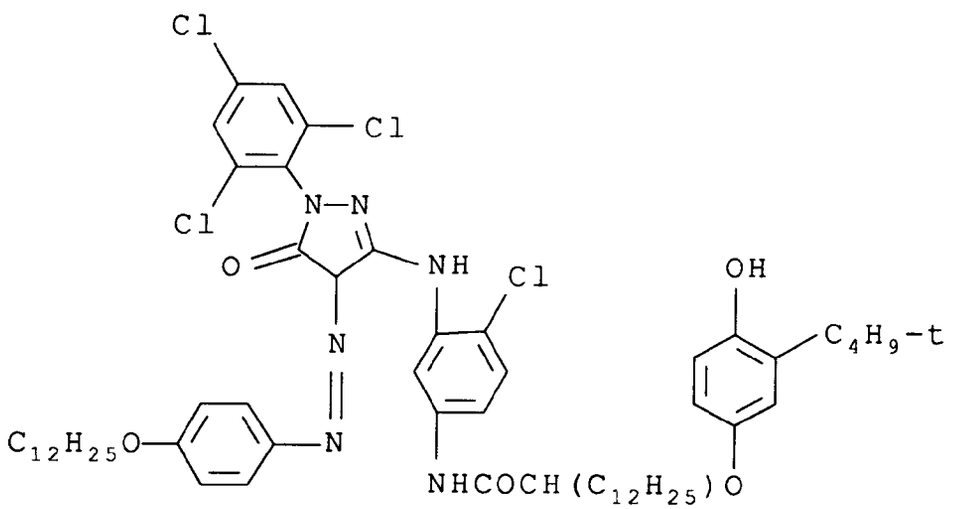
The masking coupler can be any masking coupler suitable for use in a photographic element. Preferably the masking coupler has structure:

(16)



or

(22)

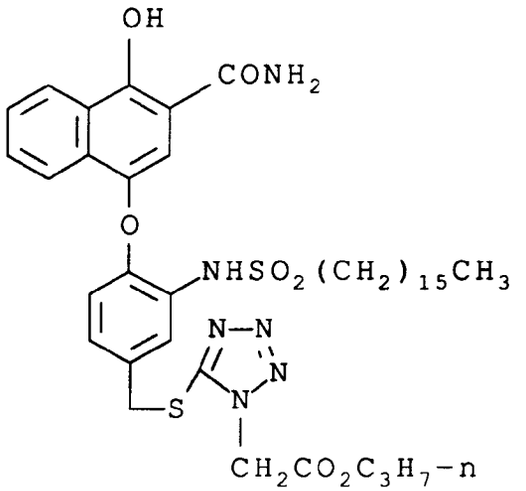


The masking coupler can be placed in any of the three magenta imaging layers.

The non-timed DIR coupler (B) used in the fast magenta layer can be any non-timed DIR coupler known in the photographic art. Examples of such non-timed DIR couplers are disclosed in US-A-3,227,554.

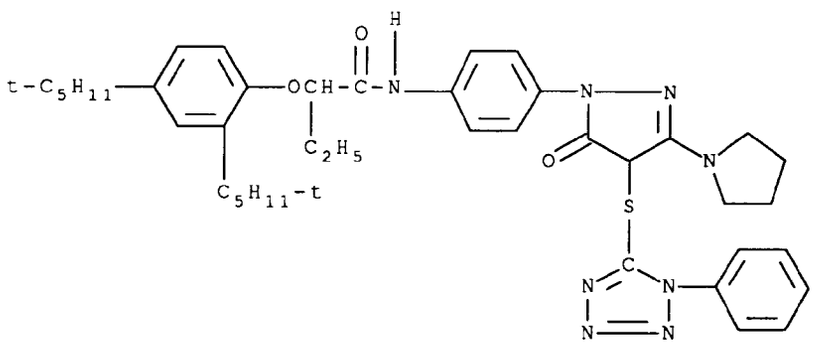
Preferred non-timed DIR couplers (B) have the structure:

(37)



(B)

(13)



MID MAGENTA LAYER

The mid-magenta or mid green sensitive layer comprises at least one first magenta image dye-forming coupler, and preferably at least one second magenta image dye-forming coupler, preferably a non-timed DIR coupler and preferably a cyan dye-forming coupler (C).

The first magenta image dye-forming coupler can be coupler (A) referred to in the fast magenta layer.

The second magenta image dye-forming coupler can be any image forming coupler dye useful in the photographic art and can include the magenta image dye-forming coupler (A) referred to in the fast magenta layer.

A typical magenta image dye-forming coupler is a pyrazolotriazole. A preferred second image dye-forming coupler is coupler (34).

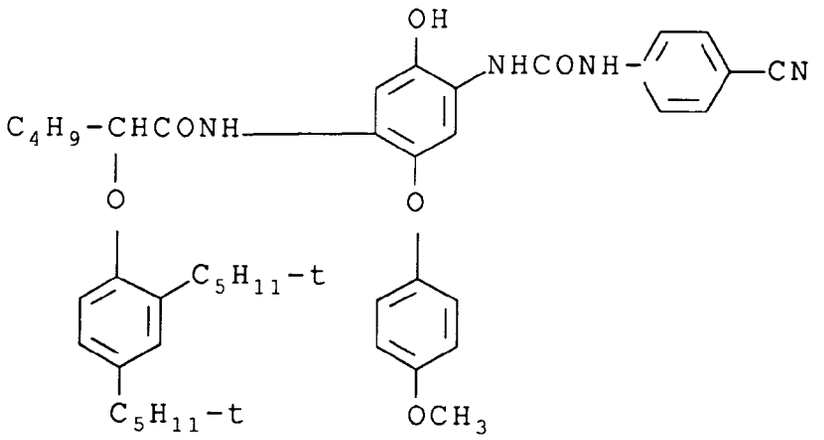
Coupler (14) is another preferred second magenta image dye forming coupler.

Suitable non-timed DIR couplers useful in the mid magenta layer are as described for the fast magenta layer and can be preferred coupler (B), for example.

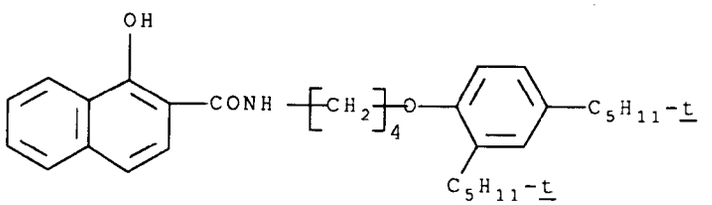
The described cyan image dye-forming coupler (C) can be any cyan image dye-forming coupler known in the photographic art with its use in the magenta record herein referred to as a color correcting coupler. The cyan image dye-forming coupler is typically a phenol or naphthol coupler described in such representative patents and publications as noted herein.

Preferred cyan image dye-forming couplers (C) for the mid magenta layer have the structures:

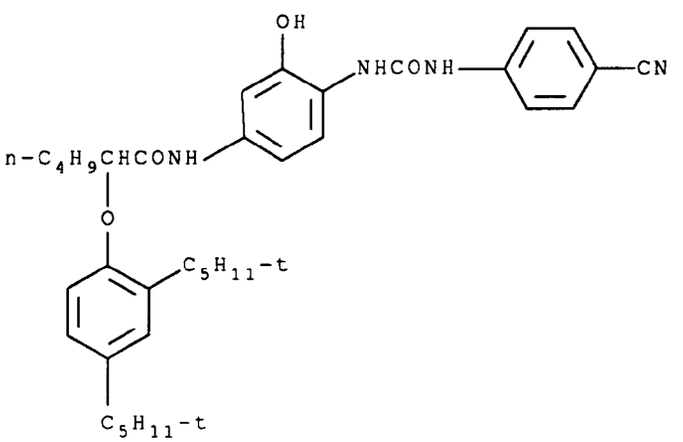
(38)



(39)



(4)



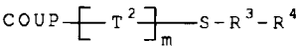
Coupler (21) may also be used in the mid magenta layer.

SLOW MAGENTA LAYER

The slow magenta layer contains at least one magenta image dye-forming coupler which is preferably a bleach accelerating releasing coupler (BARC). The slow magenta layer also contains a development inhibiting releasing coupler (DIR) preferably a non-timed DIR.

The bleach accelerator releasing coupler can be any bleach accelerator releasing coupler known in the photographic art. Combinations of such couplers are also useful. The bleach accelerator releasing coupler can

be represented by the formula:



wherein

COUP is a coupler moiety as described, typically a cyan, magenta or yellow dye-forming coupler moiety;

T^2 is a timing group known in the photographic art, typically a timing group as described in US-A-2,962 and 4,409,323;

m is 0 or 1;

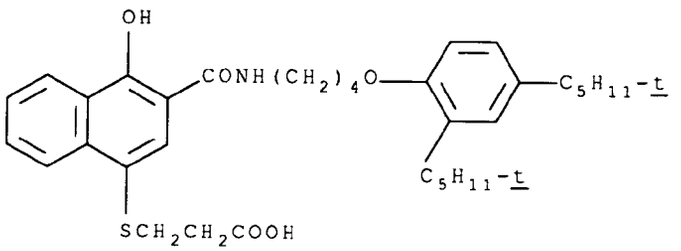
R^3 is an alkylene group, especially a branched or straight chain alkylene group, containing 1 to 8 carbon atoms; and

R^4 is a water-solubilizing group, preferably a carboxy group.

Typical bleach accelerator releasing couplers are described in, for example, European Patent 193,389, the disclosure of which is incorporated herein by reference.

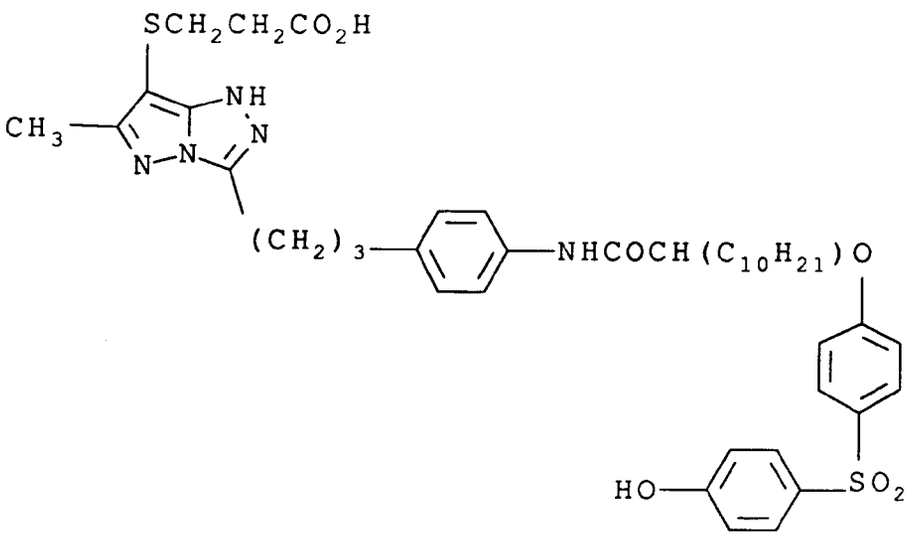
A suitable bleach accelerator releasing coupler has the structure:

(21)



A preferred bleach accelerator releasing coupler has the structure:

(12)



Combinations of bleach accelerating couplers may be used the bleach accelerating coupler can be used in the other imaging layer including the magenta imaging layers.

The DIR coupler for the slow magenta layer can be the same coupler (B) used for the fast magenta or mid magenta layer.

An interlayer may be added between the fast and mid or mid and slow magenta layers.

Cyan dye-forming coupler (C) may be used in the slow magenta layer as in the mid magenta layer.

INTERLAYER

The interlayer between the slow magenta and the fast cyan layers can contain an oxidized developer scavenger or dyes that are added to adjust photographic speed or density of the film. A preferred oxidized developer scavenger is as described for the yellow filter layer. The dyes can be the same as for the UV layer and an additional dye which is useful in this layer can include coupler (11).

FAST CYAN LAYER

The fast cyan or most red sensitive layer contains a cyan image dye-forming coupler (C), a first non-timed DIR coupler, preferably a second non-timed DIR coupler, a masking coupler and a yellow image dye-forming correcting coupler.

The cyan image dye-forming coupler (C) useful in the fast cyan layer is as described for the mid magenta layer. The preferred cyan image dye-forming coupler is the same preferred coupler (C) as for the mid magenta layer.

The first and second non-timed DIR couplers in the fast cyan layer or most red sensitive layer can be any development inhibitor releasing coupler known in the photographic art. Typical DIR couplers are described in, for example, US-A-3,227,554; 3,384,657; 3,615,506; 3,617,291; 3,733,201 and U.K. 1,450,479. Such DIR couplers upon oxidative coupling preferably do not contain a group that times or delays release of the development inhibitor group. The DIR coupler is typically represented by the formula:

COUP-INH

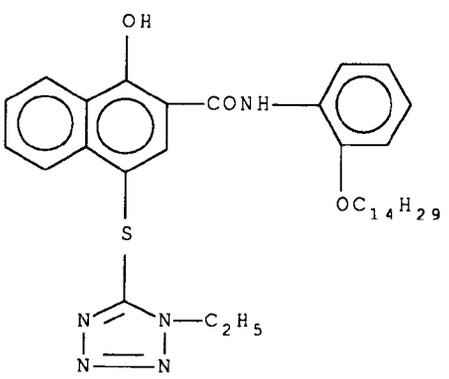
wherein COUP is a coupler moiety and INH is a releasable development inhibitor group that is bonded to the coupler moiety at a coupling position. The coupler moiety COUP can be any coupler moiety that is capable of releasing the INH group upon oxidative coupling.

The coupler moiety (COUP) is, for example, a cyan, magenta or yellow forming coupler known in the photographic art. The COUP can be ballasted with a ballast group known in the photographic art. The COUP can also be monomeric, or it can form part of a dimeric, oligomeric or polymeric coupler, in which case more than one inhibitor group can be contained in the DIR coupler.

The releasable development inhibitor group (INH) can be any development inhibitor group known in the photographic art. Illustrative INH groups are mercaptotetrazoles, selenotetrazoles, mercaptobenzothiazoles, selenobenzothiazoles, mercaptobenzimidazoles, selenobenzimidazoles, mercaptobenzoxazoles, selenobenzoxazoles, mercaptooxadiazoles, mercaptothiadiazoles, benzotriazoles, and benzodiazoles. Preferred inhibitor groups are mercaptotetrazoles and benzotriazoles. Particularly preferred inhibitor groups are described in for example US-A-4,477,563 and 4,782,012.

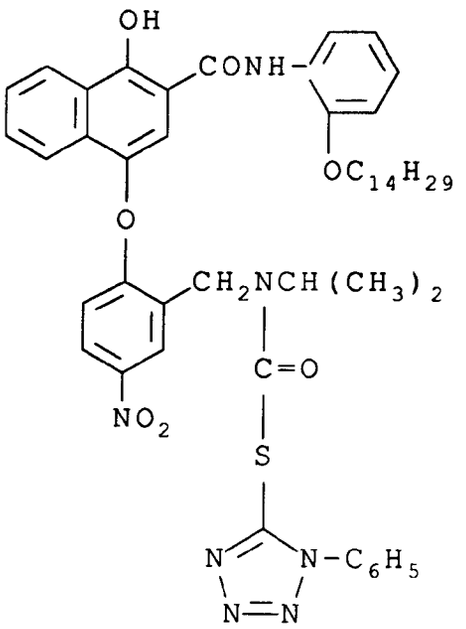
Preferred DIR couplers within COUP-INH are coupler (37) and:

(9)



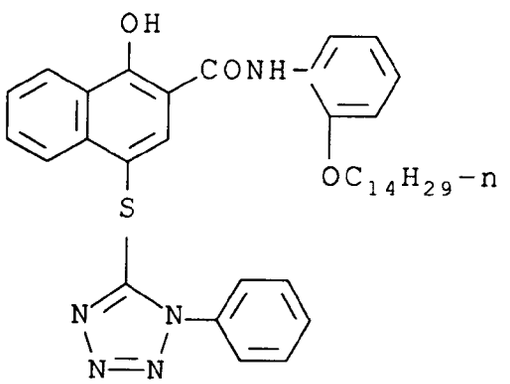
Timed DIR couplers which may be used in this layer have the structures of couplers (24), (27) and (28) and

(5)



The second non-timed DIR coupler which may be used in the fast cyan layer has the structure

(8)

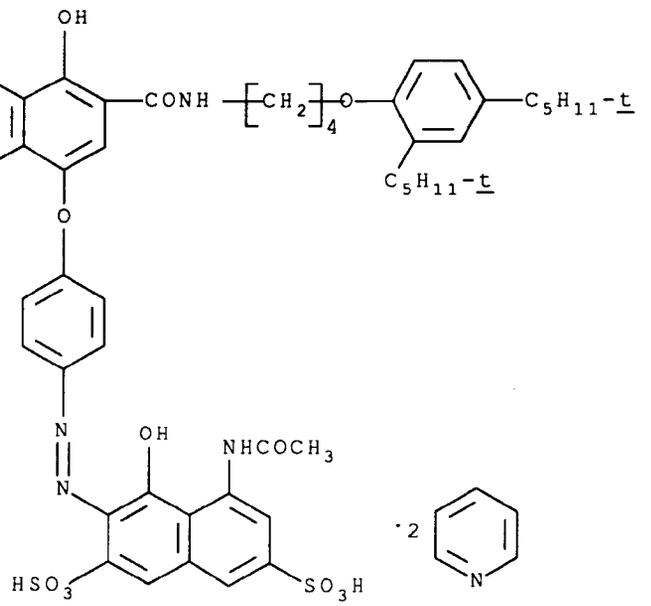


A further second non-timed DIR coupler which may be used in the fast cyan layer has the structure of coupler (37).

The masking coupler in the most red sensitive layer is typically a cyan dye-forming masking coupler, such as a naphthol cyan dye-forming masking coupler.

A preferred cyan dye-forming masking coupler for the cyan dye-forming layers of the photographic element is:

(7)



The yellow image dye-forming coupler can be any such coupler useful in the photographic art with its use in the cyan record sometimes referred to as a color correcting coupler. Couplers that are yellow dye forming couplers are typically acylacetamides, such as benzoylacetanilides and pivalylacetanilides as noted. Such couplers are described in such representative patents and publications as noted earlier.

The yellow dye-forming coupler is preferably a pivalylacetanilide comprising a phenoxy coupling off group. Such yellow dye-forming couplers have the same structures as used in the slow yellow layer and the preferred coupler is coupler (6).

SLOW CYAN LAYER

The slow cyan or less sensitive red layer contains a cyan image dye-forming coupler (C), a timed DIR coupler or development inhibitor anchimeric releasing coupler (DIAR), a non-timed DIR coupler, and a yellow image dye-forming correcting coupler.

The cyan image dye-forming coupler can be the same cyan image dye-forming coupler (C) as used in the fast cyan layer. Also, the yellow image dye-forming correcting coupler can be the same yellow image dye-forming coupler as used in the fast cyan layer.

An illustrative development inhibitor releasing coupler containing at least one timing group (T) that enables timing of release of the development inhibitor group preferably has the structure of coupler (5).

The non-timed DIR coupler can be the same as for the fast cyan layer.

INTERLAYER

An interlayer is provided between the slow cyan layer and the antihalation layer. The interlayer can contain an oxidized developer scavenger. A preferred oxidized developer scavenger is as described for the yellow filter layer. This interlayer solves a problem of increased fog resulting from interaction of bleach accelerating releasing coupler with silver in the antihalation layer. Thus, providing this interlayer between a BARC containing layer anywhere in the element and the antihalation layer so as to isolate the antihalation layer from layers containing dye-forming couplers, permits the advantageous use of a BARC for good silver bleaching without increasing fog or Dmin with respect to the antihalation layer, for example, while maintaining desired acutance.

ANTIHALATION LAYER

The antihalation layer can contain very fine gray or black silver filamentary or colloidal silver, e.g. CLS, and preferably a UV absorbing dyes, gelatin and colored dyes such as coupler (11) to provide density to the film.

While the antihalation layer has been described with respect to silver, other materials can be substituted for or used in conjunction with the silver. That is, instead of using finely divided silver in the antihalation layer, filter dyes such as washout-dyes or decolorizing dyes of the type referred to herein may be used. When filter dyes are used in the antihalation layer, the interlayer adjacent the antihalation layer may be omitted. Oxidized developer scavenger may be omitted from the antihalation layer when filter dyes are used. Examples of dyes which may be used in the antihalation layer are described in US-A-4,923,788 as noted earlier.

Bleach accelerating silver salts as described with respect to the yellow filter layer may be used in the antihalation layer in conjunction with the finely divided silver. When bleach accelerating silver salts are used in antihalation it is preferred to use the interlayer over the antihalation layer as noted to minimize fog or Dmin..

In the following discussion of suitable materials for use in the emulsions and elements of this invention, reference will be made to Research Disclosure, December 1989, Item 308119, published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire P010 7DQ, ENGLAND, the disclosures of which are incorporated herein by reference. This publication will be identified hereafter by the term "Research Disclosure".

The silver halide emulsions employed in the elements of this invention can be negative-working. Suitable emulsions and their preparation are described in Research Disclosure Sections I and II and the publications cited therein. Suitable vehicles for the emulsion layers and other layers of elements of this invention are described in Research Disclosure Section IX and the publications cited therein.

In addition to the couplers generally described above, the elements of the invention can include additional couplers as described in Research Disclosure Section VII, paragraphs D, E, F and G and the publications cited therein. These couplers can be incorporated in the elements and emulsions as described in Research Disclosure Section VII, paragraph C and the publications cited therein.

The photographic elements of this invention or individual layers thereof, can contain brighteners (see Research Disclosure Section V), antifoggants and stabilizers (See Research Disclosure Section VI), antistain agents and image dye stabilizers (see Research Disclosure Section VII, paragraphs I and J), light absorbing and scattering materials (see Research Disclosure Section VIII), hardeners (see Research Disclosure Section IX), plasticizers and lubricants (See Research Disclosure Section XII), antistatic agents (see Research Disclosure Section XIII), matting agents (see Research Disclosure Section XVI) development modifiers (see Research Disclosure Section XXI) surfactants and coating aids.

The photographic elements can be coated on a variety of supports as described in Research Disclosure Section XVII and the references described therein.

Photographic elements can be exposed to actinic radiation, typically in the visible region of the spectrum, to form a latent image as described in Research Disclosure Section XVIII and then processed to form a visible dye image as described in Research Disclosure Section XIX. 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.

With negative working silver halide, the processing step described above gives a negative image.

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

EXAMPLE I

A three color photographic film was prepared as follows using conventional surfactants, antifoggants and the materials indicated. After providing a developable image and then processing in accordance with the Kodak C-41 process (British Journal of Photographic, pp. 196-198 (1988)) excellent results e.g. improved color, sharpness, granularity and neutral scale, were obtained. All silver halide emulsions were stabilized with 1.75 gm 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene per mole of silver. All silver halide emulsions were sensitized with the appropriate spectral red, green and blue sensitizing dyes.

Support	mg/m^2	mg/ft^2	
Layer 1			
Antihalation Layer	215	20	Black colloidal silver
	91	8.5	UV absorbing dye coupler (1)
	91	8.5	UV absorbing dye coupler (2)
	14.3	13	Blue filter dye (11)
	2422	225	Gelatin
Layer 2			
Interlayer	54	5.0	D-Ox scavenging coupler (3)
	861	80.0	Gelatin
Layer 3			
Least Red Sensitive Layer	915	85	Red sensitized silver iodobromide emulsion (4.5% iodide, tabular grains with average grain diameter 1.1 micron and average grain thickness 0.1 micron),
	1238	115	Red sensitized silver iodobromide emulsion (0.5% iodide, cubic grains with average edge length 0.21 microns)
	603	56	Cyan dye forming image coupler (4)

	36	3.3	Cyan dye forming development inhibitor release (DIR) coupler (5)
	86	8.0	Yellow dye-forming image coupler (6)
	3078	286	Gelatin
Layer 4			
Most Red-Sensitive Layer	1291	120	Red sensitized silver iodobromide emulsion (3% iodide, octahedral grains with average grain diameter 0.90 micron)
	54	5.0	Cyan dye-forming image coupler (4)
	32.3	3	Cyan dye-forming masking coupler (7)
	50	4.6	Cyan dye-forming DIR coupler (9)
	11	1.0	Yellow dye-forming image coupler (6)
	2368	220	Gelatin
	4.3	0.4	Cyan dye-forming DIR coupler (8)
Layer 5			
Interlayer	129	12	Oxidized development scavenger coupler (3)
	861	80	Gelatin
	11	1	Green filter dye (10)
	49	4	Blue filter dye (11)
Layer 6			

Least Green-Sensitive Layer	124	15	Green sensitized silver iodobromide emulsion (3% iodide, tabular grains with average grain diameter 0.8 micron, and average grain thickness 0.1 micron)
	592	55.0	Green sensitized silver iodobromide emulsion (0.5% iodide, tabular gains with average grain diameter 0.5 and average grain thickness 0.1 micron)
	161	15.0	Magenta dye-forming image coupler that releases a bleach accelerating fragment (12)
	12	1.1	Magenta dye-forming DIR coupler (13)
	1507	140	Gelatin
Layer 7			
Mid Green-Sensitive Layer	969	90.0	Green sensitized silver iodobromide emulsion (3% iodide, tabular grains with average grain diameter 0.8 micron and average grain thickness 0.1 micron)
	75.0	7.0	Magenta dye-forming image coupler (14)
	54.0	5.0	Magenta dye-forming image coupler (15)

	9.0	0.8	Magenta dye-forming DIR coupler (13)
	11.0	1.0	Cyan dye forming, image coupler (4)
	1238	115.0	Gelatin
Layer 8			
Most Green-Sensitive Layer	753.0	70.0	Green sensitized silver iodobromide emulsion (6% iodide, tabular grains with average grain diameter 1.0 micron and average grain thickness 0.1 micron)
	22.0	2.0	Magenta dye-forming image coupler (15)
	13.0	1.2	Magenta dye-forming DIR coupler (13)
	65.0	6.0	Magenta dye-forming development masking coupler (16)
	26.0	2.4	Yellow dye-forming DIR coupler (17)
	969	90.0	Gelatin
Layer 9			
Interlayer	75.0	7.0	D-Ox scavenging coupler (3)
	194.0	18.0	Developer bleachable yellow filter dye (18)
	861.0	80.0	Gelatin
Layer 10			

Least Blue-Sensitive Layer	215.0	20.0	Blue sensitized silver iodobromide emulsion (6% iodide, octahedral grains with average grain diameter of 0.65 micron)
	129.0	12.0	Blue sensitized silver iodobromide emulsion (5% iodide, octahedral grains with average grain diameter of 0.40 micron)
	258.0	24.0	Blue sensitized silver iodobromide emulsion (5% iodide, octahedral grains with average grain diameter of 0.23 micron)
	11.0	97.0	Yellow dye-forming image coupler (19)
	1420	132.0	Gelatin
Layer 11			
Most Blue-Sensitive Layer	377.0	35.0	Blue sensitized silver iodobromide emulsion(6% iodide, octahedral grains with average grain diameter of 1.0 micron)
	11.0	1.0	Yellow dye-forming DIR coupler (17)
	1076	100.0	Gelatin

Layer 12			
First Protective Layer	215.0	20.0	Unsensitized silver bromide Lippman emulsion (0.04 microns)
	108.0	10.0	UV absorbing dye (1)
	129.0	12.0	UV absorbing dye (2)
	753.0	70.0	Tricresyl phosphate
	1345	125.0	Gelatin
	40	0.4	Green absorbing dye (10)
	20	0.2	Red absorbing dye (20)
Layer 13			
Second Protective Layer	44.0	4.1	Matte polyvinyltoluene beads
	883.0	82.0	Gelatin

EXAMPLE II

A three color photographic film was prepared as follow using conventional surfactants, antifoggants and the materials indicated to illustrate the improvement in fog reduction using interlayers in conjunction with the finely divided silver layer, e.g. antihalation layer. After providing a developable image and the element was processed in accordance with the Kodak C-41 process (British Journal of Photographic, pp. 196-198 (1988).

Support	mg/m^2	mg/ft^2	
Layer 1			
Antihalation Layer	183	17	Black colloidal silver
	91	8.5	UV absorbing dye coupler (1)
	2422	225	Gelatin
	140	13	Blue absorbing dye (11)
Layer 2			
Interlayer	161	15	D-Ox scavenging coupler (3)
	861	80.0	Gelatin
Layer 3			
Least Red Sensitive Layer	570	53	Red sensitized silver iodobromide emulsion (4.5% iodide, tabular grains with average grain diameter 1.1 micron and average grain thickness 0.1 micron)
	2013	187	Red sensitized silver iodobromide emulsion (0.5% iodide, cubic grains with average edge length 0.21 microns)
	54	5.0	Cyan dye forming DIR coupler (8)
	430	40	Cyan dye-forming image coupler (4)

	97	9.0	Cyan dye-forming coupler that releases a bleach accelerating fragment(21)
	2691	250	Gelatin
Layer 4			
Most Red-Sensitive Layer	1291	120	Red sensitized silver iodobromide emulsion (3% iodide, octahedral grains with average grain diameter 0.90 micron)
	38	3.5	Cyan dye-forming DIR coupler (9)
	4	0.4	Cyan dye-forming DIR coupler (8)
	32	3.0	Cyan dye-forming masking coupler (7)
	102	9.5	Cyan dye-forming image coupler (4)
	2368	220	Gelatin
Layer 5			
Interlayer	43	4	Oxidized development scavenger coupler (3)
	861	80	Gelatin
			Green filter dye (10)
			Blue filter dye (11)

Layer 6			
Least Green-Sensitive Layer	926	86	Green sensitized silver iodobromide emulsion (3% iodide, tabular grains with average grain diameter 0.8 micron, and average grain thickness 0.1 micron)
	538	50	Green sensitized silver iodobromide emulsion (0.5% iodide, tabular gains with average grain diameter 0.5 and average grain thickness 0.1 micron)
	22	2	Magenta dye-forming masking coupler (22)
	4.3	0.4	Magenta dye-forming DIR coupler (13)
	2422	225	Gelatin
	678	63	Magenta dye-forming image coupler (14)
Layer 7			
Most Green-Sensitive Layer	1345	125	Green sensitized silver iodobromide emulsion (6% iodide, tabular grains with average grain diameter 1.0 micron and average grain thickness 0.1 micron)
	113	10.5	Magenta dye-forming image coupler (15)

	4.3	0.4	Magenta dye-forming DIR coupler (13)
	43	4.0	Magenta dye-forming masking coupler (22)
	73	7.0	Yellow dye-forming DIR coupler (17)
	1722	160	Gelatin
Layer 8			
Interlayer	75.0	7.0	D-Ox scavenging coupler (3)
	194.0	18.0	Developer bleachable yellow filter dye (18)
	861.0	80.0	Gelatin
Layer 9			
Least Blue-Sensitive Layer	280	26	Blue sensitized silver iodobromide emulsion (6% iodide, octahedral grains with average grain diameter of 0.65 micron)
	387	36	Blue sensitized silver iodobromide emulsion (5% iodide, octahedral grains with average grain diameter of 0.40 micron)
	1238	115	Yellow dye-forming image coupler (19)
	1420	132.0	Gelatin
Layer 10			

Most Blue-Sensitive Layer	430	40	Blue sensitized silver iodobromide emulsion(6% iodide, octahedral grains with average grain diameter of .90 micron)
	24	2.2	Yellow dye-forming DIR coupler (17)
	1076	100.0	Gelatin
	54	5	Yellow dye-forming image coupler (19)
Layer 11			
First Protective Layer	215.0	20.0	Unsensitized silver bromide Lippman emulsion (0.04 microns)
	108.0	10.0	UV absorbing dye (1)
	10.8	10.0	UV absorbing dye (2)
	108	100	Tricresyl phosphate
	1345	125.0	Gelatin
Layer 12			
Second Protective Layer	44.0	4.1	Matte polyvinyltoluene beads
	883.0	82.0	Gelatin

The following tests were run to illustrate the advantage of an interlayer using the layer structure of Example II.

Table I

Specimen	AHU (mg/ft2) Gray Silver	AHU**/SC* interlayer	BARC location above AHU (coupler)	Red Dmin
1	0	none	none	0.166
2	17	none	none	0.215
3	0	none	9mg in (21) SC*	0.209
4	17	none	9mg (21) in SC*	0.381
5	17	none	12mg (21) in SC*	0.412
6	17+15mg coupler (9)	none	9mg (21) in SC*	0.326
7	17	80gel+15 coupler (9)	9mg (21) in SC*	0.202
8	17	none	12mg (12) in SM***	0.226

* Slow cyan layer

** Antihalation layer

***Slow magenta layer

It will be seen from Table I that the addition of an interlayer between the antihalation layer (AHU) and the slow cyan layer when it contained a bleach accelerating releasing coupler (BARC) lowered the red Dmin significantly.

EXAMPLE III

Photographic elements having the layer structure as shown in Example II were prepared to illustrate the improvement in red Dmin when the photographic element was prepared using bleach accelerating silver salts (BASS) in accordance with the invention.

Table II

Bleach Accelerator	Interlayer between SC/AHU	Actual Red Dmin	Normalized Red Dmin
5-7 None	None	0.407	0 (check)
5-4 Coupler (21) (BARC in SC)	None	0.464	+0.054
5-8 Ag-MPA (BASS in AHU)	None	0.500	0.093
4-2 None	Yes	0.153	0 (check)
Ag-MPA (BASS in AHU)	Yes	0.162	+0.009

As will be seen from Table II, in one example (5-7), the element was prepared without a bleach accelerator releasing coupler and without an interlayer to isolate the antihalation layer containing finely divided silver. Table II shows that the normalized red Dmin is zero (0).

In the second example (5-4), the element was prepared and a bleach accelerating releasing coupler was used in the slow cyan (SC) layer. However, no interlayer was used between the antihalation layer and the remainder of the element. It will be noted that the normalized red Dmin increases to 0.054.

In a third example (5-8), a silver salt of mercapto proprionic acid ($AgSCH_2CH_2COOH$) was used in the antihalation and no interlayer was used between the antihalation layer and the remainder of the element. The normalized red Dmin increased to 0.093.

In a fourth example (4-2), no bleach accelerating releasing coupler was used in the element and an interlayer was positioned between the antihalation layer and the remainder of the element. The normalized red Dmin was zero (0).

Lastly, in this example (4-4), silver salt of mercapto proprionic acid was used in the antihalation layer and an interlayer was positioned between antihalation layer and the remainder of the element. The amount of normalized red Dmin was reduced to a level of 0.009.

Thus, when bleach accelerating silver salts are used in an antihalation layer containing finely divided silver, surprisingly the interlayer provided between the antihalation layer and the remainder of the element has the effect of markedly reducing the red Dmin.

EXAMPLE IV

This example was prepared to illustrate the advantage of reduced fog when providing an interlayer between a filter layer containing finely divided silver and a bleach accelerating releasing coupler. The photographic element used was substantially the same as in Example I except finely divided silver was used in the yellow filter layer, an interlayer was provided above and below the finely divided silver layer, and bleach accelerating releasing couplers were provided in the slow yellow, fast magenta, and the mid magenta illustrated as follows:

SOC

UV

FY

SY +/-BARC

+/-IL

CLS

+/-IL

FM +/-BARC

MM +/-BARC

SM

IL

FC

SC

IL

AHU

///////

The data provided in Table III show the results of incorporating the finely divided silver layer (CLS layer) with an interlayer below and/or above the CLS layer.

Table III

#	mg/ft2 BARC (location)	Interlayers Above CLS	Interlayers Below CLS	B Dmin*	G Dmin*
11	None	None	None	Check (0)	Check (0)
12	5mg (21) in SY**	None	None	+ 0.070	+ 0.168
3	5mg (21) in SY**	None	Yes	+ 0.031	- 0.013
2	5 (21) in SY**	Yes	Yes	- 0.209	- 0.108
9	5 (21) in FM***	None	None	+ 0.096	+ 0.150
6	5mg (21) in FM***	None	Yes	+ 0.033	- 0.073
10	12mg (12) in MM****	None	None	- 0.020	- 0.025
5	12mg (12) in MM****	None	Yes	- 0.023	- 0.120

* Normalized

** Slow yellow

*** Fast magenta

****Mid magenta

From Table III it will be seen that the addition of BARC compounds to a film element containing colloidal silver (CLS) in a non-imaging layer caused significant Dmin increase in layers that contain dye forming couplers adjacent the CLS layer. Addition of interlayers to isolate the CLS layer from layers containing dye forming couplers significantly reduced the Dmin resulting from the use of BARC compounds in the presence of the CLS layer.

EXAMPLE V

For purposes of illustrating lowered fog in a photographic element using an active magenta coupler, e.g. coupler (15) the following coatings were made using the photographic element of Example I. Coating 1 was

the same as Example I. Finely divided silver (CLS) was used in the yellow filter layer of coatings 2 and 3, instead of dye coupler (18). Further, coupler (14), a less active coupler, was used in place of coupler (15) as follows:

Coating	Coupler in fast magenta record (coupler)	Yellow filter material (dye)
1	(15)	(18)
2	(15)	CLS
3	(14)	CLS
4	(14)	(18)

Table IV

Coating	Yellow Filter	Fast Magenta Image Coupler	Green Minimum Density	Green Relative Log Sensitivity
1	194 mg/m2 (18)	27 mg/m2 (15)	0.60	+0.07
2	59 mg/m2 CLS	27 mg/m2 (15)	0.75	-0.19
3	59 mg/m2 CLS	54 mg/m2 (14)	0.66	-0.15
4	194 mg/m2 (18)	54 mg/m2 (14)	0.59	0.00

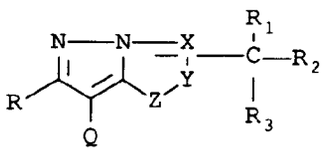
From Table IV it will be seen that there was a green speed loss in coatings 2 and 3 and there was an increase in green speed (coating 1) using dye (18) and coupler (15) in accordance with the invention. Further, coatings 2 and 3 had an increased green minimum density (fog) compared to the coating of the invention.

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

Claims

1. An improved multilayered color photographic element having lowered levels of fog comprising a support having coated thereon photographic silver halide emulsion layers, the layers including a unit of at least one green sensitive silver halide emulsion layer and a yellow filter layer adjacent said green sensitive layer,

(a) the green sensitive layer comprising a pyrazolotriazole dye-forming coupler, the coupler having the structure



where

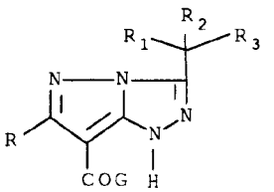
R is a substituent which does not adversely affect the desired properties of the coupler,

R_1, R_2, R_3 are linked to the alpha carbon and are selected from the group consisting of hydrogen, halogen, cyano or substituted or unsubstituted alkyl, aryl, heterocyclic, aliphatic residue, alkoxy, aryloxy, amino, alkylamino, acylamino, anilino, ureido, sulfamoylamino, alkylthio, arylthio, alkoxycarbonylamino, sulfonamido, carbamoyl, sulfamoyl, sulfonyl, heterocyclicoxy, acyloxy, carbamoyloxy, silyloxy, aryloxycarbonylamino, imido, heterocyclicthio, sulfinyl, phosphonyl, aryloxycarbonyl, acyl, or alkoxycarbonyl group wherein not more than one of R_1, R_2, R_3 is hydrogen,

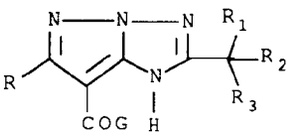
Q is hydrogen or a coupling-off group (COG), X, Y, Z are individually carbon or nitrogen atoms necessary to complete an azole ring, with unsaturated bonding being present in the ring as needed, and

(b) the yellow filter layer comprising a dye.

2. The element as in Claim 1 characterized in that the coupler has the formula:



or



wherein R is an organic group having 1-30 carbons,

COG is a coupling off group, and

R_1, R_2, R_3 are selected from hydrogen, alkyl, aryl, and substituents linked to the alpha carbon by nitrogen or oxygen and wherein not more than one of R_1, R_2, R_3 is hydrogen.

3. The element as in any one of the preceding claims characterized in that R is selected from methyl, ethyl, methoxy, acetamido and phenyl.

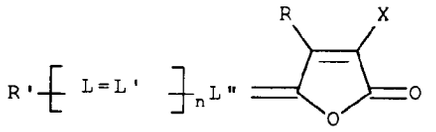
4. The photographic element as in in any one of the preceding claims characterized in that R_1 is hydrogen, R_2 is selected from alkyl and phenyl, and R_3 is selected from those substituents linked to the central methlene by an atom of nitrogen or oxygen.

5. The photographic element as in in any one of the preceding claims characterized in that R_2 is selected from methyl and unsubstituted phenyl group.

6. The photographic element as in in any one of the preceding claims characterized in that R_3 is selected from those substituents linked to the alpha carbon by an atom of nitrogen.

7. The photographic element as in in any one of the preceding claims characterized in that at least one of R_1, R_2, R_3 contains a solubilized ballast group containing a group selected from carboxylic acid and sulfonamide group.

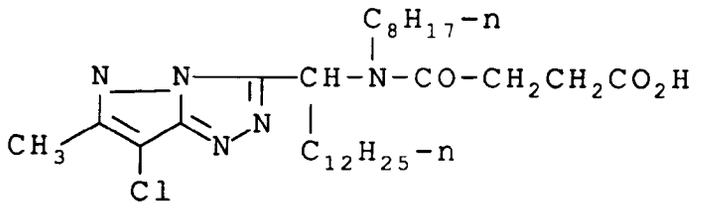
8. The element as in in any one of the preceding claims characterized in that the yellow filter layer comprises a microcrystalline dye of the formula:



wherein R is substituted or unsubstituted alkyl or aryl, X is an electron withdrawing group, R' is substituted or unsubstituted aryl or a substituted or unsubstituted aromatic heterocyclic nucleus, and L, L', and L" are each independently a substituted or unsubstituted methine group, and n is 0 to 6..

9. The element as in in any one of the preceding claims characterized in that the coupler has one of the structures identified as PA-1 to PA-35.

10. The element as in in any one of the preceding claims characterized in that the coupler has the formula:



and the yellow filter layer comprises a microcrystalline dye having the structure