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(54) Photographic silver halide material and process.

(57) A photographic recording material is disclosed which contains a coupler capable of releasing a development inhibitor moiety during photographic processing which reduces interlayer interimage effects.

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This invention relates to photographic materials and elements, specifically to materials and elements having a coupler that releases a development inhibitor moiety during photographic processing to provide reduced interlayer interimage effects.

Various compounds, particularly couplers, are known in the photographic art that are capable of releasing a development inhibitor. Such compounds are described in U. S. Patents 3,227,554; 3,384,657; 3,379,529; 3,615,506; 3,617,291; 3,620,746; 3,701,783; 3,733,201; 4,049,455; 4,095,984; 4,248,962; 4,409,323; and 4,962,018, as well as in "Development-Inhibitor-Releasing (DIR) Couplers in Color Photography", C.R. Barr, J.R. Thirtle and P.W. Vittum in Photographic Science and Engineering, Vol. 13, page 174 (1969).

These development inhibitor releasing couplers, known as DIR couplers, are used in silver halide photographic materials to influence many photographic properties. These include but are not limited to the control of intralayer developability (i.e. the control of the gamma of a photographic layer with which they are reactively associated), to the control of interlayer interimage effects (i.e. the control of the developability or gamma of other photographic layers for purposes of influencing, for example color reproduction properties), to the control of granularity and to the control of sharpness.

Silver halide photographic materials comprising thioether assisted DIR compounds which enable low levels of interlayer interimage effects are described in European Patent Application 403,019.

Silver halide photographic materials comprising thioether assisted DIR couplers in combination with bleach accelerator releasing couplers are described in U. S. Patent Application Serial No. 612,341 of R.P. Szajewski filed November 13, 1990.

Silver halide photographic elements comprising "oxidation-reduction" release DIR compounds wherein the released development inhibitor comprises a mercaptothiadiazole moiety are described in U.S. Patent 4,791,049. These "oxidation-reduction" DIR compounds are described as providing extremely high degrees of interlayer interimage effects. Of the 57 "oxidation-reduction" release DIR compounds disclosed, 5 release thioether assisted mercaptothiadiazole development inhibitors. Compound I-23 at column 23, line 1, is an example.

A need has existed in color photographic silver halide materials to provide a combination of (i) localized intralayer development inhibition and (ii) lower interimage effects for the purpose of controlling color reproduction. Such properties are demonstrated by reduced development inhibition in adjacent photographic layers, that is, by extremely low levels of interlayer interimage effects. This combination of properties is extremely difficult to achieve.

It has been found that the described advantages are provided by a photographic material comprising a support bearing at least one photographic silver halide emulsion layer and at least one coupler capable of releasing upon processing a thiadiazole development inhibitor moiety comprising a thioether moiety.

In a preferred embodiment, the present invention provides these improved properties through the use of a photographic material comprising a support bearing at least two photographic silver halide emulsion layers and at least one coupler capable of releasing upon exposure and processing a development inhibitor, wherein the coupler has the structural formula:

$\mathrm{COUP\text{-}(TIME)_n\text{-}INH\text{-}Q}$

wherein:

COUP is a coupler moiety from which $\mathrm{(TIME)_n\text{-}INH\text{-}Q}$ is released during development of the element;

TIME is a timing group;

INH-Q together constitute a development inhibitor moiety;

INH is a mercaptothiadiazole moiety;

Q comprises from 1 to 4 thioether moieties, in each of which the sulfur atom is directly bonded to a saturated carbon atom but is not directly bonded to the INH moiety; and

n is 0, 1 or 2.

Combinations of such couplers are also useful.

A typical development inhibitor releasing coupler as described is represented by the formula:

$\mathrm{COUP\text{-}(TIME)_n\text{-}INH\text{-}Q}$ (I)

wherein COUP, TIME, n, INH and Q are as defined above.

TIME is bonded to the coupling position of COUP. TIME, along with the attached INH-Q moiety, is released from COUP upon exposure and processing of the photographic recording material. The controlled release of INH-Q is advantageous for particular photographic applications.

The coupler and, specifically, the -Q moiety, enables reduced interlayer interimage effect to be observed in a photographic silver halide element because the inhibitor moiety with -Q has reduced transportability in the structure of the photographic element and is more absorbing to silver or silver halide than inhibitors without the -Q group. A highly preferred INH moiety that has the described characteristics is a mercaptothiadiazole moiety. This moiety has highly preferred transportability characteristics and is preferred in combination with a timing group (TIME) that also enables preferred transportability. Such a preferred moiety enables a lower degree of interimage effect and accordingly a lower degree of color correction.

The most effective image is observed when in the coupler, the coupler moiety and the inhibitor moiety are separated by a group that enables timing of release of the inhibitor moiety from the carrier moiety during photographic processing. The reaction of coupler with an oxidized color developing agent cleaves the bond between the carrier moiety and the timing group. Then, the bond between the timing group and the inhibitor moiety is cleaved by means of an intramolecular nucleophilic displacement reaction enabling the development inhibitor moiety to perform its intended function. Bond cleavage between the timing group and the inhibitor moiety does not involve the action of oxidized color developing agent.

A preferred coupler is represented by formula (I) wherein COUP is a coupler moiety. As used herein the terms "coupler" and "coupler compound" refer to the entire compound, including the coupler moiety, the timing group, and the inhibitor moiety, while the term "coupler moiety" refers to the portion of the compound other than the timing group and the inhibitor moiety.

The coupler moiety can be any moiety that will react with oxidized color developing agent to cleave the bond between the timing group and the coupler moiety. It includes coupler moieties employed in conventional color-forming couplers that yield colorless products, as well as coupler moieties that yield colored products on reaction with oxidized color developing agents. Both types of coupler moieties are known to those skilled in the photographic art.

The coupler moiety can be unballasted or ballasted with an oil-soluble or fat-tail group. It can be monomeric, or it can form part of a dimeric, oligomeric or polymeric coupler, in which case more than one INH group can be contained in the coupler, or it can form part of a bis compound in which the timing and inhibitor groups form part of the link between two coupler moieties.

It will be appreciated that, depending upon the particular coupler moiety, the particular color developing agent and the type of processing, the reaction product of the coupler moiety and oxidized color developing agent can be: (1) colored and nondiffusible, in which case it will remain in the location where it is formed; (2) colored and diffusible, in which case it may be removed during processing from the location where it is formed or allowed to migrate to a different location; or (3) colorless and diffusible or nondiffusible, in which case it will not contribute to image density. In cases (2) and (3) the reaction product may be initially colored and/or nondiffusible but converted to colorless and/or diffusible products during the course of processing.

The timing group, TIME, is joined to the coupler moiety at any of the positions from which groups released from couplers by reaction with oxidized color developing agent can be attached. Preferably, the timing group is attached at the coupling position of the coupler moiety so that upon reaction of the coupler with oxidized color developing agent the timing group will be displaced. However, the timing group can be attached to a non-coupling position of the coupler moiety from which it will be displaced as a result of reaction of the coupler with oxidized color developing agent. In the case where the timing group is at a non-coupling position of the coupler moiety, other groups can be in the coupling position, including conventional coupling-off groups or the same or different inhibitor moieties from that contained in the described inhibitor moiety of the invention. Alternatively, the coupler moiety can have a timing and inhibitor group at each of the coupling position and a non-coupling position. Accordingly, couplers of this invention can release more than one mole of inhibitor per mole of coupler. Each of these inhibitors can be the same or different and can be released at the same or different times and rates.

The timing group can be any organic group that will serve to connect COUP to the inhibitor moiety and which, after cleavage from COUP, will cleave from the inhibitor moiety preferably by an intramolecular nucleophilic displacement reaction of the type described in, for example, U.S. Patent 4,248,962 or by electron transfer down a conjugated chain as described in, for example, U.S. Patent 4,409,323, the disclosures of which are incorporated herein by reference. Timing groups utilizing the mechanism in which there is electron transfer down a conjugated chain are especially preferred.

As used herein, the term "intramolecular nucleophilic displacement reaction" refers to a reaction in which a nucleophilic center of a compound reacts directly, or indirectly through an intervening molecule, at another site on the compound, which is an electrophilic center, to effect displacement of a group or atom attached to the electrophilic center. Such compounds have a nucleophilic group and electrophilic group spatially related by the configuration of the molecule to promote reactive proximity. Preferably the nucleophilic group and the electrophilic group are located in the compound so that a cyclic organic ring, or a transient cyclic organic ring, can be easily formed by an intramolecular reaction involving the nucleophilic center and the electrophilic center.

A useful illustrative class of timing group (T) is represented by the structure:

$\{Nu - X - E\}$

wherein:

Nu is a nucleophilic group attached to a position on COUP from which it will be displaced upon reaction of COUP with oxidized color developing agent,

E is an electrophilic group attached to an inhibitor moiety as described and is displaceable therefrom by Nu after Nu is displaced from COUP, and

X is a linking group for spatially relating Nu and E, upon displacement of Nu from COUP, to undergo an intramolecular nucleophilic displacement reaction with the formation of a 3- to 7-membered ring and thereby release INH-Q.

A nucleophilic group (Nu) is understood to be a grouping of atoms one of which is electron rich. This atom is referred to as the nucleophilic center. An electrophilic group (E) is understood to be a grouping of atoms one of which is electron deficient. This atom is referred to as the electrophilic center.

In photographic couplers as described, the timing group can contain a nucleophilic group and an electrophilic group that are spatially related with respect to one another by a linking group (X) so that upon release from the coupler moiety, the nucleophilic center and the electrophilic center will react to effect displacement of the inhibitor moiety from the timing group. The nucleophilic center should be prevented from reacting with the electrophilic center until release from the coupler moiety and the electrophilic center should be resistant to external attack such as hydrolysis. Premature reaction can be prevented by attaching the coupler moiety to the timing group at the nucleophilic center or an atom in conjunction with a nucleophilic center, so that cleavage of the timing group and the inhibitor moiety from the coupler moiety unblocks the nucleophilic center and permits it to react with the electrophilic center, or by positioning the nucleophilic group and the electrophilic group so that they are prevented from coming into reactive proximity until release. The timing group can contain additional substituents, such as additional photographically useful groups (PUG), or precursors thereof, which may remain attached to the timing group or be released.

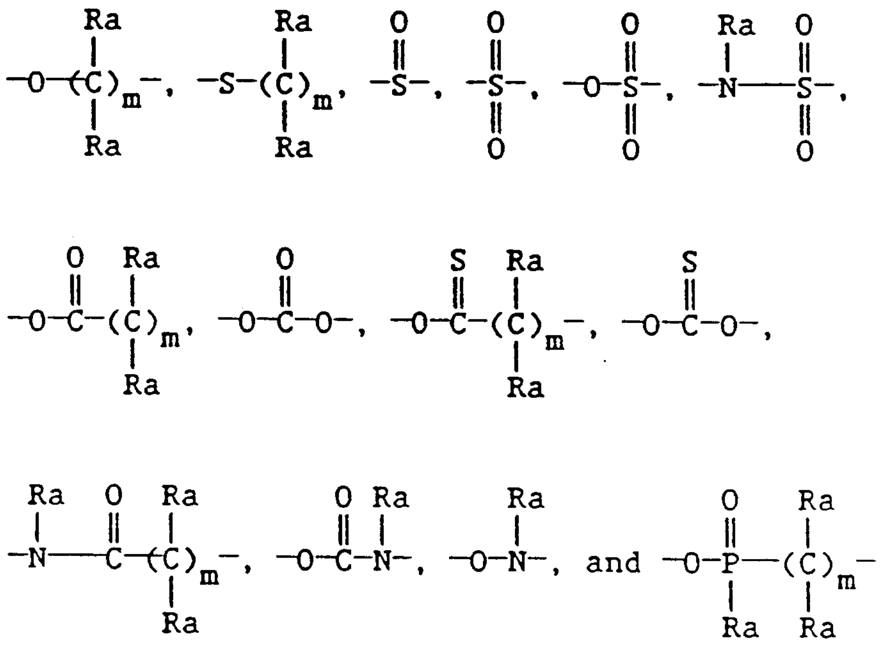
It should be understood that for an intramolecular reaction to occur between the nucleophilic group and the electrophilic group, the groups should be spatially related after cleavage from the coupler, so that they can react with one another. Preferably, the nucleophilic group and the electrophilic group are spatially related within the timing group so that the intramolecular nucleophilic displacement reaction involves the formation of a 3- to 7-membered ring, most preferably a 5- or 6-membered ring.

It should be further understood that for an intramolecular reaction to occur in the aqueous alkaline environment encountered during photographic processing, thereby displacing the timing group from the coupler moiety, the thermodynamics should be such and the groups be selected so that the free energy of ring closure plus the bond energy of the bond formed between the nucleophilic group and the electrophilic group is greater than the bond energy between the electrophilic group and other groups. Not all possible combinations of nucleophilic group, linking group, and electrophilic group will yield a thermodynamic relationship favorable to breaking of the bond between the electrophilic group and the inhibitor moiety; however, it is within the skill of the art to select appropriate combinations taking the above energy relationships into account.

Representative Nu groups contain electron rich oxygen, sulfur and nitrogen atoms. Representative E groups contain electron deficient carbonyl, thiocarbonyl, phosphonyl and thiophosphonyl moieties. Other useful Nu and E groups will be apparent to those skilled in the art.

In the following listings of representative Nu and E groups, the groups are oriented so that the lefthand bond of Nu is joined to COUP and the righthand bond of Nu is joined to X, while the lefthand bond of E is joined to X and the righthand bond of E is joined to INH.

Representative Nu groups include:



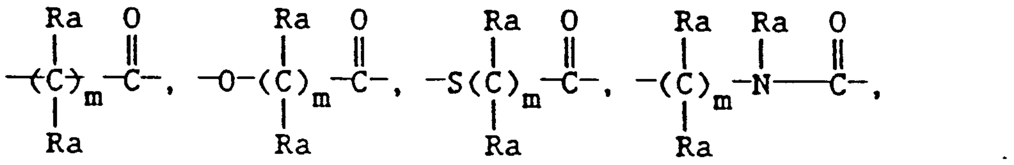
$$-O-\left(\underset{Ra}{\overset{Ra}{C}}\right)_m-,\quad -S-\left(\underset{Ra}{\overset{Ra}{C}}\right)_m,\quad -\overset{O}{\overset{\|}{S}}-,\quad -\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-,\quad -O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-,\quad -\overset{Ra}{N}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-,$$

$$-O-\overset{\overset{O}{\|}}{C}-\left(\underset{Ra}{\overset{Ra}{C}}\right)_m,\quad -O-\overset{\overset{O}{\|}}{C}-O-,\quad -O-\overset{\overset{S}{\|}}{C}-\left(\underset{Ra}{\overset{Ra}{C}}\right)_m-,\quad -O-\overset{\overset{S}{\|}}{C}-O-,$$

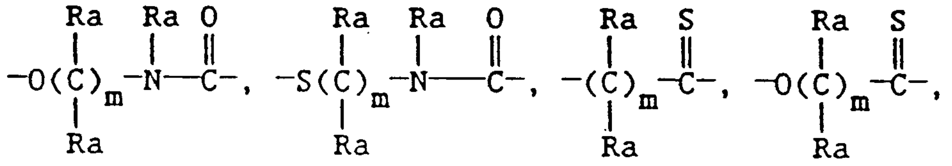
$$-\overset{Ra}{N}-\overset{\overset{O}{\|}}{C}-\left(\underset{Ra}{\overset{Ra}{C}}\right)_m-,\quad -O-\overset{\overset{O}{\|}}{C}-\overset{Ra}{N}-,\quad -O-\overset{Ra}{N}-,\ \text{and}\ -O-\underset{Ra}{\overset{\overset{O}{\|}}{P}}-\left(\underset{Ra}{\overset{Ra}{C}}\right)_m-$$

where each Ra is independently hydrogen, alkyl, such as alkyl of 1 to 20 carbon atoms including substituted alkyl such as methyl, ethyl, propyl, hexyl, decyl, pentadecyl, octadecyl, carboxyethyl, hydroxypropyl, sulfonamidobutyl and the like, or aryl, such as aryl of 6 to 20 carbon atoms including substituted aryl such as phenyl, naphthyl, benzyl, tolyl, t-butylphenyl, carboxyphenyl, chlorophenyl, hydroxyphenyl and the like, and m is an integer from 0 to 4 such that the ring formed by Nu, X and E upon nucleophilic attack of Nu upon the electrophilic center in E contains 3 to 7 ring atoms. Preferably Ra is hydrogen, alkyl of 1 to 4 carbon atoms or aryl of 6 to 10 carbon atoms.

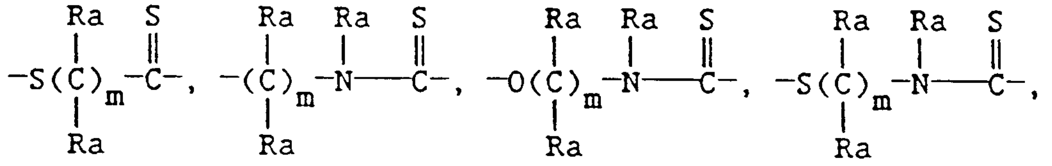
Representative E groups include:



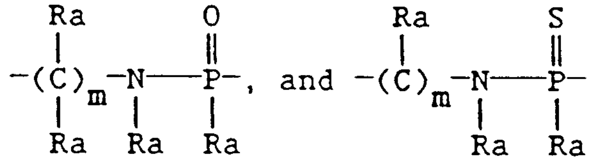
$-(\overset{Ra}{\underset{Ra}{C}})_m-\overset{\overset{O}{\|}}{C}-$, $-O-(\overset{Ra}{\underset{Ra}{C}})_m-\overset{\overset{O}{\|}}{C}-$, $-S(\overset{Ra}{\underset{Ra}{C}})_m-\overset{\overset{O}{\|}}{C}-$, $-(\overset{Ra}{\underset{Ra}{C}})_m-\overset{Ra}{N}-\overset{\overset{O}{\|}}{C}-$,



$-O(\overset{Ra}{\underset{Ra}{C}})_m-\overset{Ra}{N}-\overset{\overset{O}{\|}}{C}-$, $-S(\overset{Ra}{\underset{Ra}{C}})_m-\overset{Ra}{N}-\overset{\overset{O}{\|}}{C}-$, $-(\overset{Ra}{\underset{Ra}{C}})_m-\overset{\overset{S}{\|}}{C}-$, $-O(\overset{Ra}{\underset{Ra}{C}})_m-\overset{\overset{S}{\|}}{C}-$,



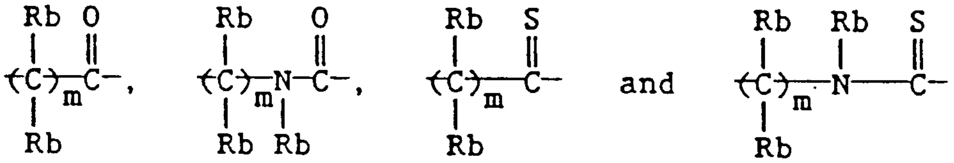
$-S(\overset{Ra}{\underset{Ra}{C}})_m-\overset{\overset{S}{\|}}{C}-$, $-(\overset{Ra}{\underset{Ra}{C}})_m-\overset{Ra}{N}-\overset{\overset{S}{\|}}{C}-$, $-O(\overset{Ra}{\underset{Ra}{C}})_m-\overset{Ra}{N}-\overset{\overset{S}{\|}}{C}-$, $-S(\overset{Ra}{\underset{Ra}{C}})_m-\overset{Ra}{N}-\overset{\overset{S}{\|}}{C}-$,



$-(\overset{Ra}{\underset{Ra}{C}})_m-\underset{Ra}{N}-\overset{\overset{O}{\|}}{\underset{Ra}{P}}-$, and $-(\overset{Ra}{C})_m-\underset{Ra}{N}-\overset{\overset{S}{\|}}{\underset{Ra}{P}}-$

where Ra and m are as defined above.

E is preferably an electrophilic group selected from the group consisting of



$-(\overset{Rb}{\underset{Rb}{C}})_m-\overset{\overset{O}{\|}}{C}-$, $-(\overset{Rb}{\underset{Rb}{C}})_m-\underset{Rb}{N}-\overset{\overset{O}{\|}}{C}-$, $-(\overset{Rb}{\underset{Rb}{C}})_m-\overset{\overset{S}{\|}}{C}-$ and $-(\overset{Rb}{\underset{Rb}{C}})_m-\overset{Rb}{N}-\overset{\overset{S}{\|}}{C}-$

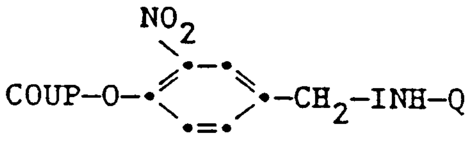
wherein each Rb is independently hydrogen, alkyl, such as alkyl containing 1 to 20 carbon atoms, preferably alkyl containing 1 to 4 carbon atoms, or aryl, such as aryl containing 6 to 20 carbon atoms, preferably aryl containing 6 to 10 carbon atoms; and m is 0 to 4, such that the ring formed upon reaction of the nucleophilic center in Nu with the electrophilic center in E contains 5- or 6-members.

The linking group represented by X can be an acyclic group such as alkylene, for example methylene, ethylene or propylene, or a cyclic group such as an aromatic group, such as phenylene or naphthylene, or a heterocyclic group, such as furan, thiophene, pyridine, quinoline or benzoxazine. Preferably X is alkylene or arylene. The groups Nu and E are attached to X to provide, upon release of Nu from COUP, favorable spatial relationship for nucleophilic attack of the nucleophilic center in Nu on the electrophilic center in E. When X is a cyclic group, Nu and E can be attached to the same or adjacent rings. Aromatic groups in which Nu and E are attached to adjacent ring positions are particularly preferred X groups.

X can be unsubstituted or substituted. The substituents can be those that will modify the rate of reaction, diffusion, or displacement, such as halogen, including fluoro, chloro, bromo, or iodo, nitro, alkyl of 1 to 20 carbon atoms, acyl, such as carboxy, carboxyalkyl, alkoxycarbonyl, alkoxycarbonamido, sulfoalkyl, alkylsulfonamido, and alkylsulfonyl, solubilizing groups, ballast groups and the like, or they can be substituents that are separately useful in the photographic element such as a stabilizer, an antifoggant, a dye (such as a filter dye, a solubilized masking dye) and the like. For example, solubilizing groups will increase the rate of diffusion; ballast groups will decrease the rate of diffusion; electron withdrawing groups will decrease the rate of displacement of the INH group.

As used herein, the term "electron transfer down a conjugated chain" is understood to refer to transfer of an electron along a chain of atoms in which alternate single bonds and double bonds occur. A conjugated chain is understood to have the same meaning as commonly used in organic chemistry. Electron transfer down a conjugated chain is as described in, for example, U.S. Patent 4,409,323.

When the timing group TIME is of the type described in above-referenced U.S. Patent 4,409,323, the timing group will be described herein as a "quinone-methide timing group". Examples of useful couplers as described comprising a quinone-methide timing group include: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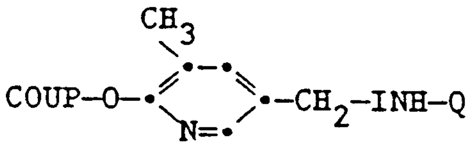
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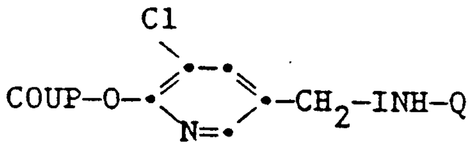
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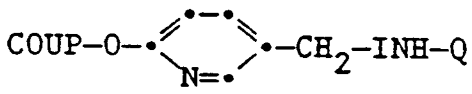
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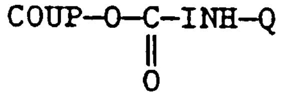
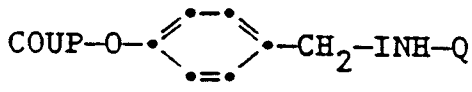

$COUP-O-\underset{\overset{\|}{O}}{C}-INH-Q$;

$COUP-O-CH_2-INH-Q$;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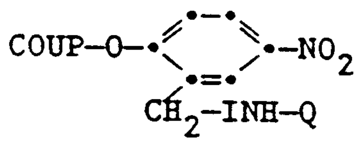
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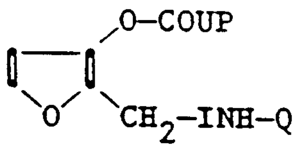
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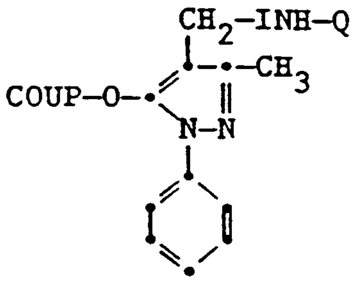

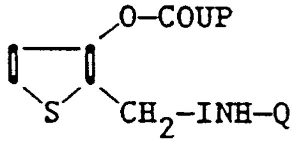

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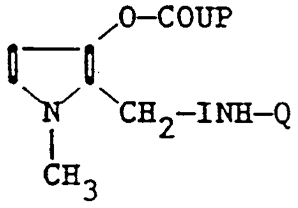

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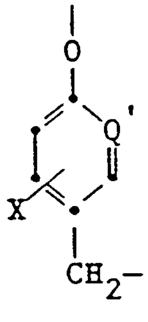
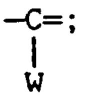
Especially preferred are those timing groups having the structure:



wherein

X is hydrogen and one or more substituents independently selected from hydroxy, cyano, fluoro, chloro, bromo, iodo, nitro, alkyl, alkoxy, aryl, aryloxy, alkoxycarbonyl, aryloxycarbonyl, carbonamido and sulfonamido.

Q' is -N= or



$$-\underset{\displaystyle W}{\overset{|}{C}}=;$$

and

W is a group characterized by a σ_m value greater than 0.0 (σ_m is determined as described in Hansch and Leo, Journal of Medicinal Chemistry, 16, 1207, 1973). Typical W groups are $-NO_2$, $-NHSO_2CH_3$, $-NHSO_2C_{16}H_{33}$, $-NHCOCH_3$, $-NHCOC_{11}H_{23}$, -Cl, -Br, $-OCH_3$, $-OCH_2CH_2OCH_3$, etc.

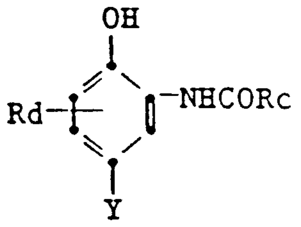
Other useful timing groups are described in U.S. Patents 4,737,451; 4,546,073; 4,564,587; 4,618,571; 4,698,297; 4,818,464; and European Published Patent Applications 167,168A; 255,085A and 362,870A.

There follows a listing of patents and publications that describe representative useful COUP groups. In these structures, Y represents $(TIME)_n$-INH-Q as described. In the case of dye-forming couplers that are useful with a coupler (I), the Y group represents hydrogen or a coupling-off group known in the photographic art.

I. COUP's

A. Couplers that form cyan dyes upon reaction with oxidized color developing agents are described in such representative patents and publications as: U.S. Pat. Nos. 2,772,162, 2,895,826, 3,002,836, 3,034,892, 2,474,293, 2,423,730, 2,367,531, 3,041,236, 4,883,746 and "Farbkuppler-eine Literatureübersicht," published in Agfa Mitteilungen, Band III, pp. 156-175 (1961).

Preferably such couplers are phenols and naphthols that form cyan dyes on reaction with oxidized color developing agent and have the $(TIME)_n$-INH-Q coupling-off group attached at the coupling position, that is the carbon atom in the 4-position. Structures of such coupler moieties include:



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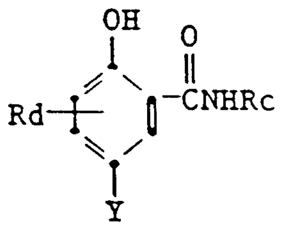
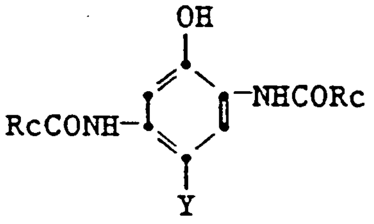
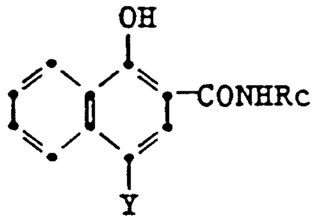


IA-2



IA-3

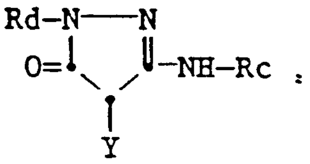


IA-4

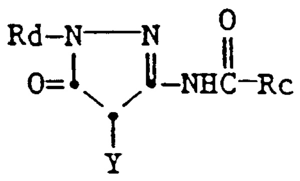
where Rc represents a ballast group, and Rd represents one or more halogen such as chloro or fluoro, lower alkyl containing 1 to 4 carbon atoms, such as methyl, ethyl, or butyl; or alkoxy containing 1 to 4 carbon atoms, such as methoxy, ethoxy, or butoxy groups.

B. Couplers that form magenta dyes upon reaction with oxidized color developing agent are described in such representative patents and publications as: U.S. Pat. Nos. 2,600,788, 2,369,489, 2,343,703, 2,311,082, 3,152,896, 3,519,429, 3,062,653, 2,908,573 and "Farbkuppler-eine Literatureübersicht," published in Agfa Mitteilungen,Band III, pp. 126-156 (1961).

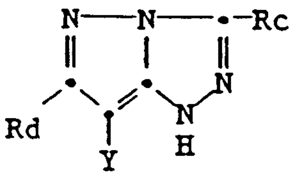
Preferably, such couplers are pyrazolones, pyrazolotriazoles, or pyrazolobenzimidazoles that form magenta dyes upon reaction with oxidized color developing agents and have the Y attached to the coupling position. Structures of preferred such coupler moieties are:



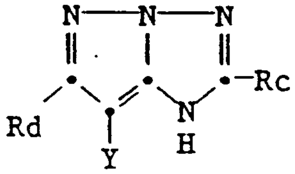
IB-1



IB-2



IB-3



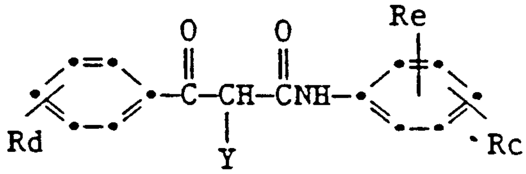
IB-4

where Rc and Rd are chosen independently to be a ballast group, unsubstituted or substituted alkyl, unsubstituted or substituted phenyl.

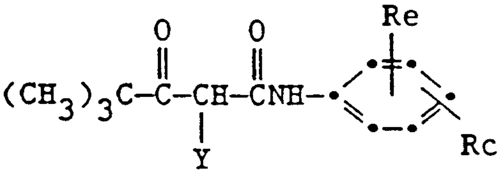
C. Couplers that form yellow dyes upon reaction with oxidized and color developing agent are described in such representative patents and publications as: U.S. Pat. Nos. 2,875,057, 2,407,210, 3,265,506, 2,298,443, 3,048,194, 3,447,928 and "Farbkuppler-eine Literatureübersicht," published in Agfa Mitteilungen, Band III, pp. 112-126 (1961).

Preferably such yellow-dye forming couplers are acylacetamides, such as benzoylacetanilides and have the Y group attached to the coupling position, that is the active methylene carbon atom.

Structures of preferred such coupler moieties are:



IC-1

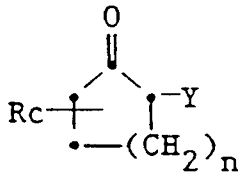


IC-2

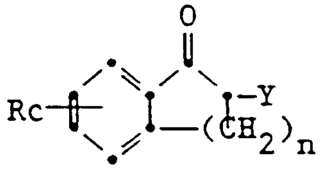
where Rc is as defined above and Rd and Re are hydrogen or one or more halogen, alkyl containing 1 to 4 carbon atoms, such as methyl and ethyl, or ballast groups, such as alkoxy of 16 to 20 carbon atoms.

D. Couplers that form colorless products upon reaction with oxidized color developing agent are described in such representative patents as: U.K. Patent No. 861,138; U.S. Pat. Nos. 3,632,345, 3,928,041, 3,958,993 and 3,961,959. Preferably such couplers are cyclic carbonyl containing compounds that form colorless products on reaction with oxidized color developing agent and have the Y group attached to the carbon atom in the α-position with respect to the carbonyl group.

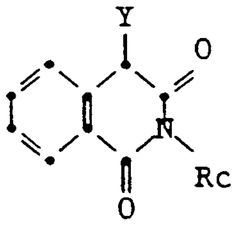
Structures of preferred such coupler moieties are:



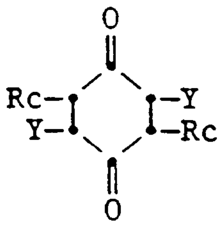
ID-1



ID-2



ID-3



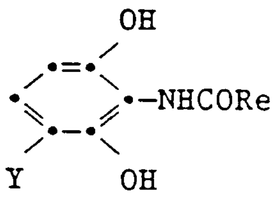
ID-4

where Rc is as defined above and n is 1 or 2.

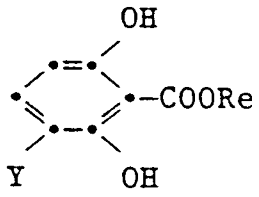
E. Couplers that form black dyes upon reaction with oxidized color developing agent are described in such representative patents as U.S. Pat. Nos. 1,939,231; 2,181,944; 2,333,106; and 4,126,461; German OLS No. 2,644,194 and German OLS No. 2,650,764.

Preferably such couplers are resorcinols or m-aminophenols that form black or neutral products on reaction with oxidized color developing agent and have the Y group para to a hydroxy group.

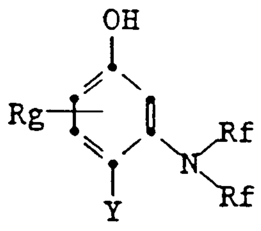
Structures of such preferred coupler moieties are:



IE-1



IE-2

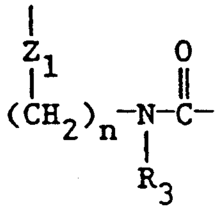


IE-3

where Re is alkyl of 3 to 20 carbon atoms, phenyl or phenyl substituted with hydroxy, halo, amino, alkyl of 1 to 20 carbon atoms or alkoxy of 1 to 20 carbon atoms; each Rf is independently hydrogen, alkyl of 1 to 20 carbon atoms, alkenyl of 1 to 20 carbon atoms, or aryl of 6 to 20 carbon atoms; and Rg is one or more halogen, alkyl of 1 to 20 carbon atoms, alkoxy of 1 to 20 carbon atoms or other monovalent organic groups.

Examples of timing groups that enable an intramolecular nucleophilic displacement reaction are as follows:

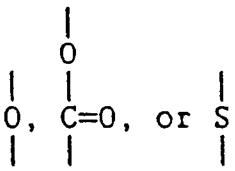
A. Acyclic groups:



$$-Z_1-(CH_2)_n-\underset{\underset{R_3}{|}}{N}-\overset{\overset{O}{\|}}{C}-$$

IIA-1

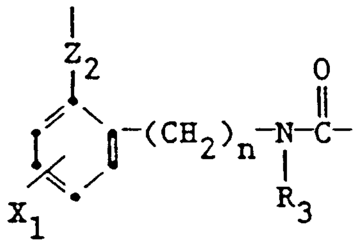
where n is 1-4, preferably 2 or 3, Z_1 is



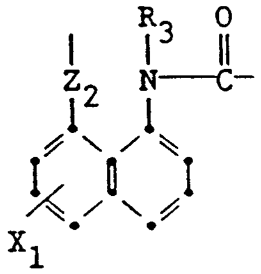
$$-O-,\quad -O-\overset{|}{\underset{|}{C}}=O,\quad \text{or}\quad -S-$$

and R_3 is hydrogen, alkyl, such as alkyl of 1 to 20 carbon atoms, preferably alkyl of 1 to 4 carbon atoms, or aryl, such as aryl of 6 to 20 carbon atoms, preferably aryl of 6 to 10 carbon atoms.

B. Aromatio groups:

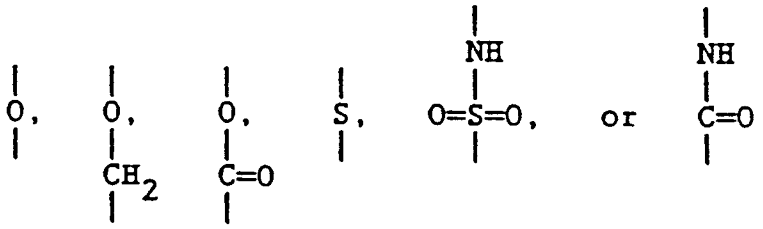


IIB-1



IIB-2

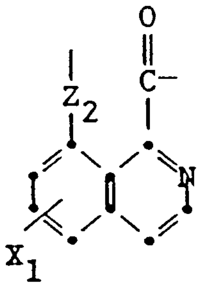
where n is 0 or 1; Z_2 is



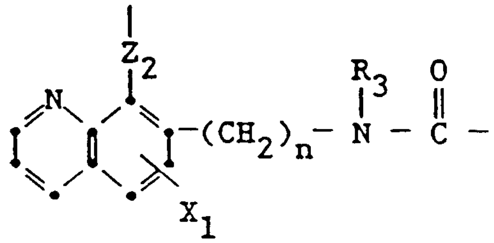
$-O-$, $-O-CH_2-$, $-O-C(=O)-$, $-S-$, $-NH-SO_2-$, or $-NH-C(=O)-$

R_3 is hydrogen, alkyl, such as alkyl containing 1 to 30 carbon atoms, or aryl, such as phenyl and naphthyl; and X_1 is hydrogen or one or more substituent groups independently selected from cyano, fluoro, chloro, bromo, iodo, nitro, alkyl, such as alkyl of 1 to 20 carbon atoms, a dye, $-OR_4$, $-COOR_4$, $-CONHR_4$, $-NHCOR_4$, $NHSO_2R_4$, $-SO_2NHR_4$ of SO_2R_4, where R_4 is hydrogen, alkyl, such as alkyl of 1 to 20 carbon atoms, preferably alkyl of 1 to 4 carbon atoms, or aryl, such as aryl of 6 to 20 carbon atoms, preferably aryl of 6 to 10 carbon atoms.

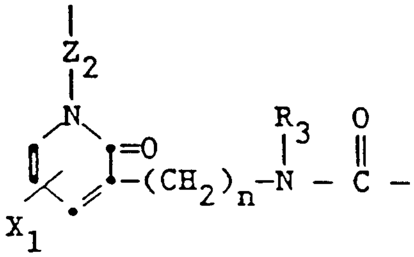
C. Heterocyclic groups:



IIC-1

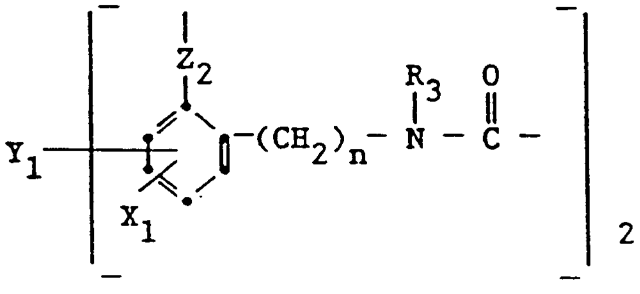


IIC-2



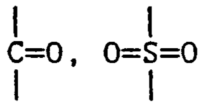
IIC-3

where n is 0 or 1, Z_2, X_1 and R_3 are as defined above.
D. Bis groups:



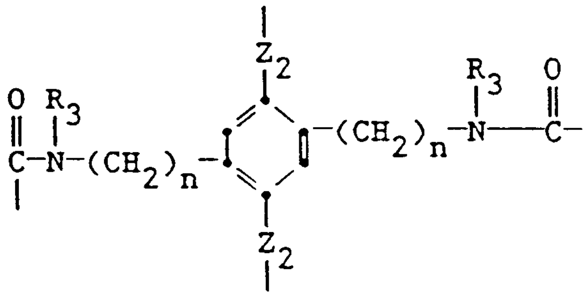
IID-1

where Y_1 is a linking group, such as



$$\overset{|}{\underset{|}{C}}=O, \quad O=\overset{|}{\underset{|}{S}}=O$$

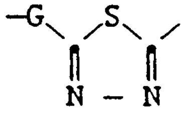
or $-NHSO_2CH_2SO_2NH-$; n is 0 or 1 and X_1, Z_2 and R_3 are as defined above.



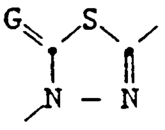
where n is 0 or 1 and Z_2, and R_3 are as defined above.

Such timing groups are described in, for example, U.S. Patent 4,248,962.

INH is a bivalent 2-substituted-1,3,4-thiadiazole moiety, wherein the 2-substituent (shown as -G-) is sulfur, selenium or tellurium, having the structure:

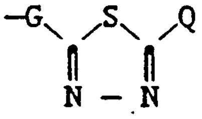


or

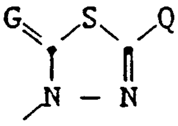


;

and, INH-Q is a monovalent 2-substituted-1,3,4-thiadiazole moiety, wherein the 2-substituent (shown below as -G-) is sulfur, selenium or tellurium, having the structure:

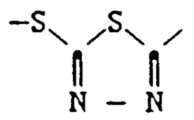


or

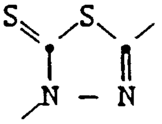


.

In a preferred embodiment, INH is a bivalent 2-mercapto-1,3,4-thiadiazole moiety having the structure:

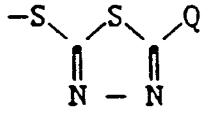


or

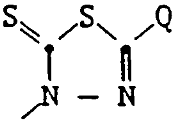


;

and INH-Q is a monovalent 2-mercapto-1,3,4-thiadiazole moiety having the structure:



or



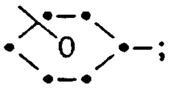
.

The inhibitor moiety can also be substituted with other groups that do not adversely affect the desired properties of INH-Q.

The Q moiety may be unchanged as the result of exposure to photographic processing solution. However, Q may change in structure and effect in the manner disclosed in U.K. Patent No. 2,099,167, European Patent Application 167,168, Japanese Kokai 205150/83 or U.S. Patent 4,782,012 as the result of photographic processing.

Q represents a monovalent group, which can be alkyl, aryl, alkoxy, aryloxy, alkylthio, arylthio, alkylamino, arylamino, carbalkoxy, carbocyclic or heterocyclic. Q comprises from 1 to 4 thioether moieties in each of which the divalent sulfur atom is directly bonded to a saturated carbon atom but is not directly bonded to the INH heterocyclic ring. These groups can be substituted with one or more halogen, nitro, amino, cyano, amido, carbamoyl, sulfonyl, sulfonamido or sulfamoyl substituents. In addition to thioether groups. Q may contain non-thioether sulfur atoms directly bonded to isolated groups C = O, C = S, C = N, or to C = N- which is not incorporated in a heterocyclic ring.

In typical Q groups the thioether sulfur atom can be bonded to -(CH$_2$)$_\ell$-, where ℓ is 1 to 12,



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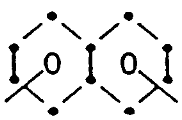
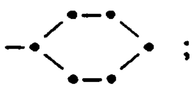


;

-CH$_3$;- CH$_2$CH$_3$; -C$_3$H$_7$; -C$_4$H$_9$; -C$_4$H$_9$-t; -C$_5$H$_{11}$;



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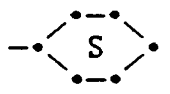
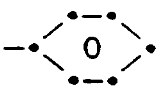


; and



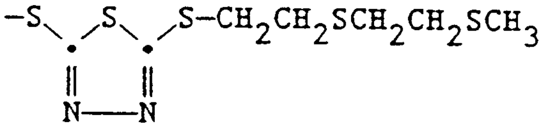
or may form part of a carbocyclic or heterocyclic ring.

The chemistry, characterization and preparation of thioether groups, otherwise known as sulfide groups, is related in Chapter 6 of "The Organic Chemistry of Sulfur", S. Oae Ed., Plenum Press, New York, 1977.

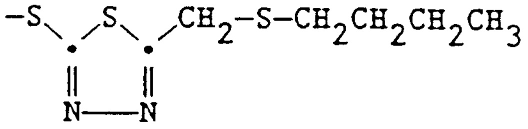
Typical examples of development inhibitor moieties represented by INH-Q include the following:

Compound

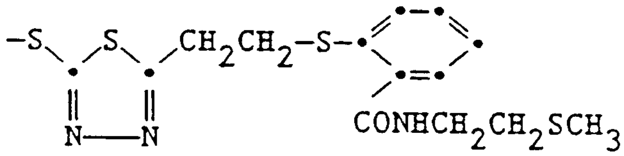
I-1



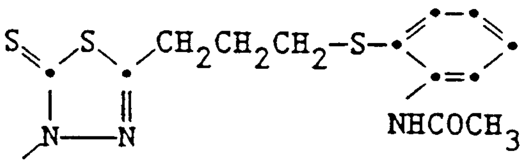
I-2



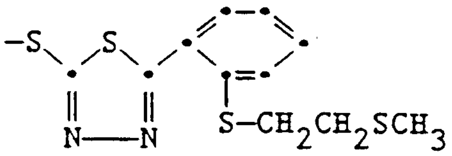
I-3



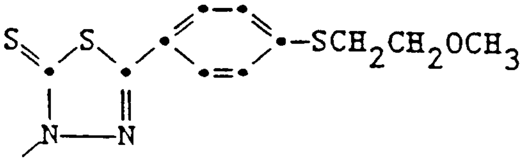
I-4



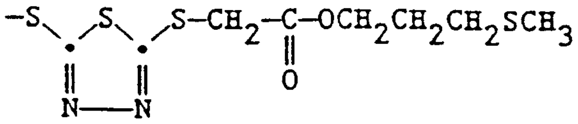
I-5



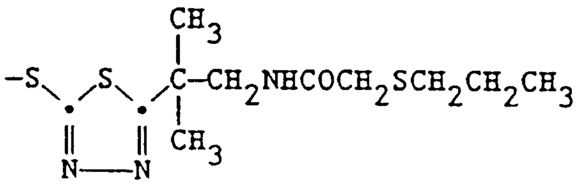
I-6



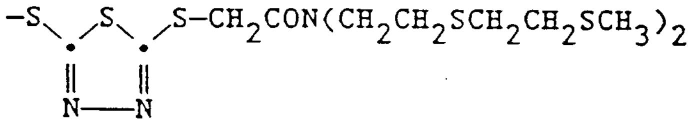
I-7



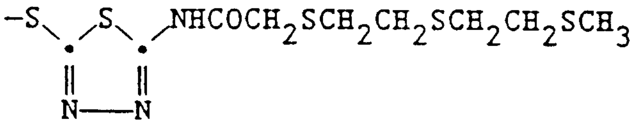
I-8



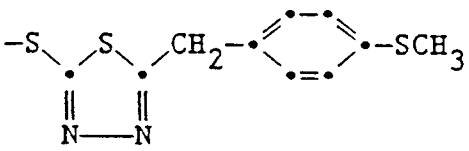
I-9



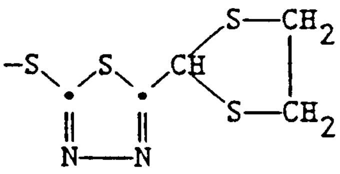
I-10



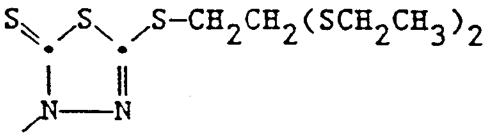
I-11



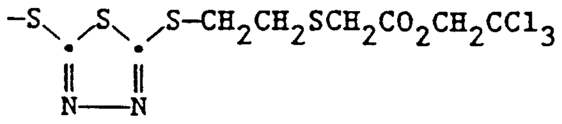
I-12



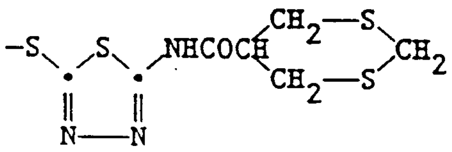
I-13



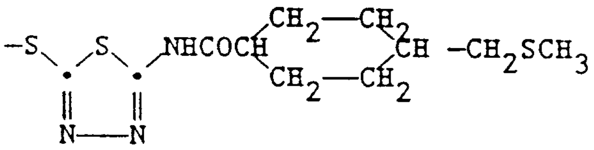
I-14



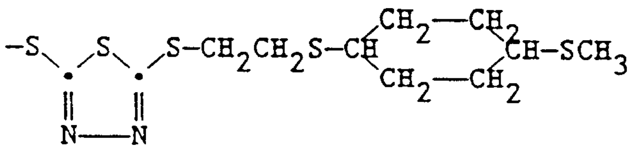
I-15



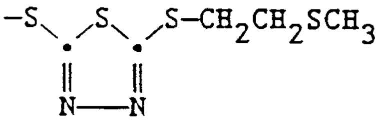
I-16



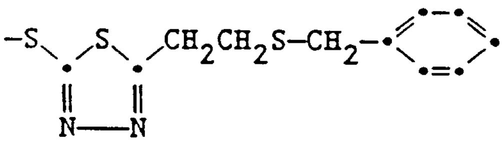
I-17



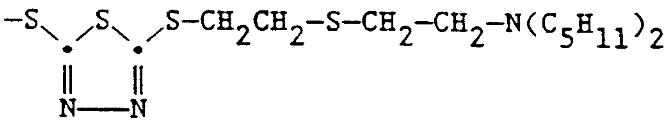
I-18



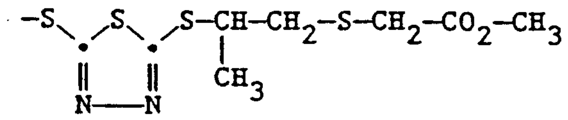
I-19



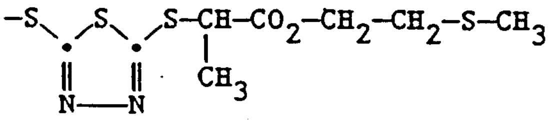
I-20



I-21



I-22



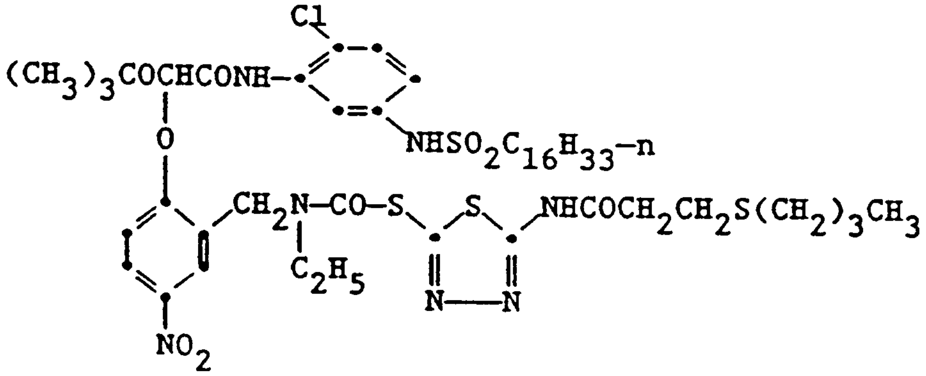
The development inhibitor moieties of the type described above can be prepared by methods already known in the art. One method, useful in the preparation of development inhibitor moiety I-18 is described in Synthesis Example 1 below.

The timing group TIME and INH are selected and prepared to adjust to the activity of the adjoining coupler moiety, and the other groups of the coupler in order to optimize release of the INH-Q for its intended purpose. Accordingly, useful Q groups have differing structural types that enable timing groups having a range of activities. Various properties, such as pKa, are also usefully considered in optimizing the selection of optimum groups for a particular purpose.

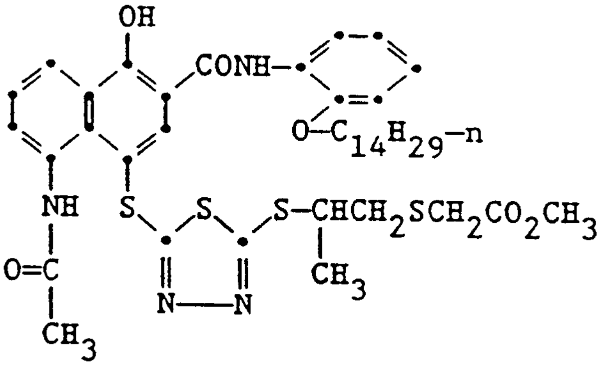
Compounds which contain releasable development inhibitor moieties suitable for use in accordance with this invention can be prepared by first synthesizing the inhibitor fragment and then attaching it to the coupler or to the linking or timing group by well-known methods. Synthesis examples 2 and 3, described below are typical preparations of development inhibitor releasing (DIR) couplers useful in this invention.

Structures of development inhibitor releasing couplers which can be synthesized in accordance with this invention are shown below:

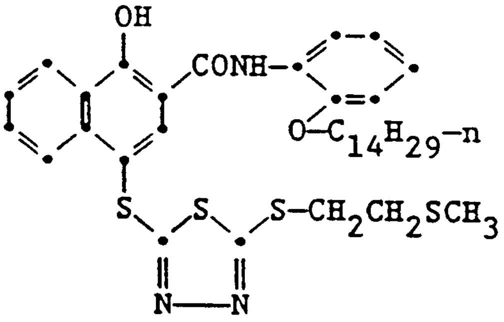
D-1



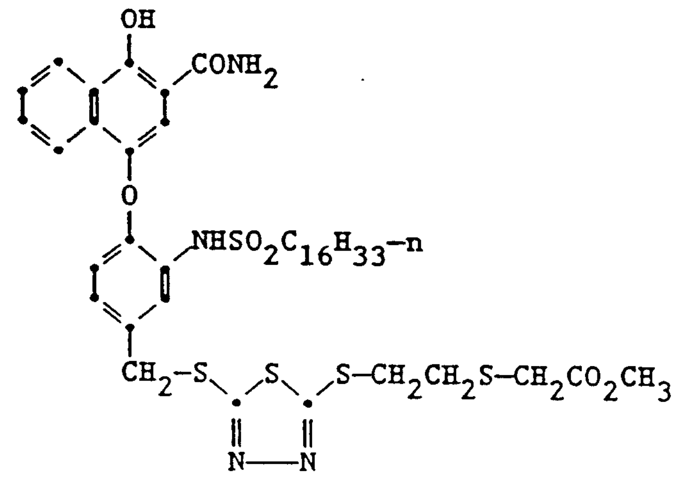
D-2



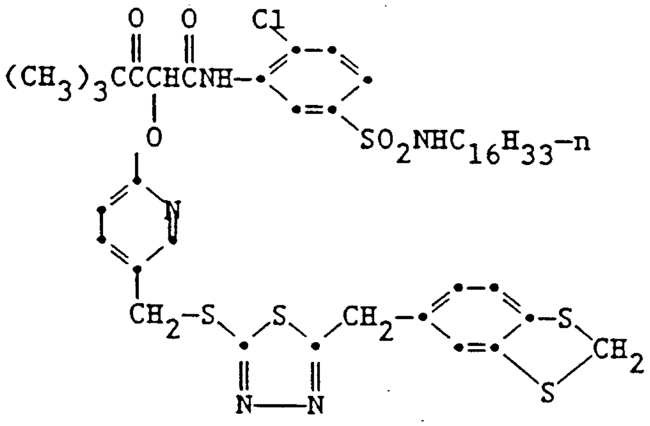
D-3



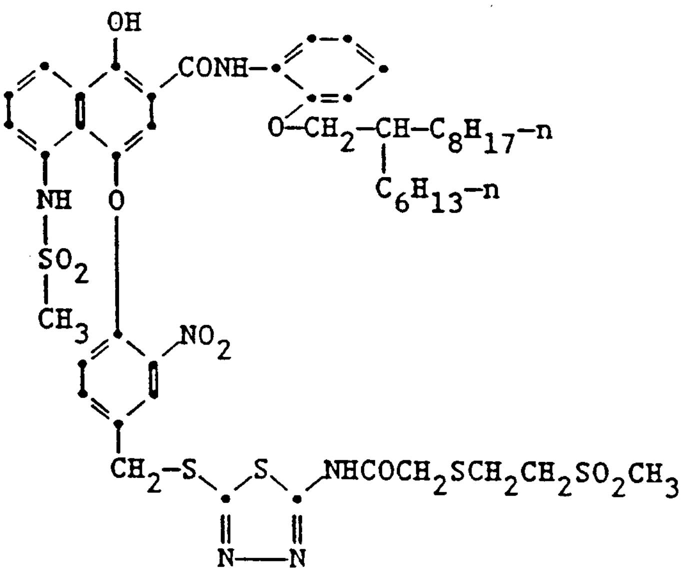
D-4



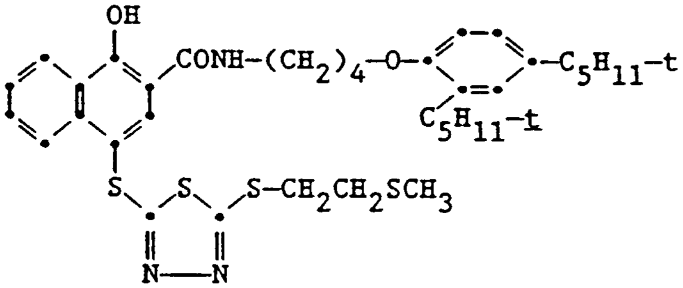
D-5



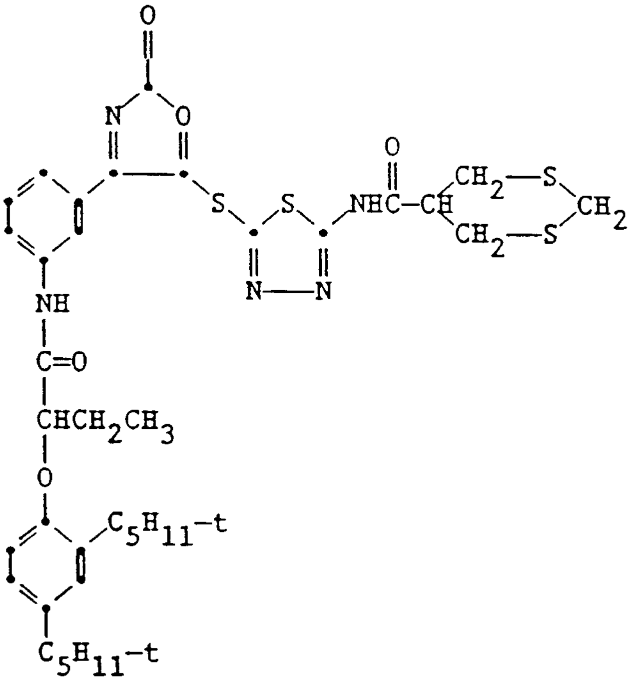
D-6



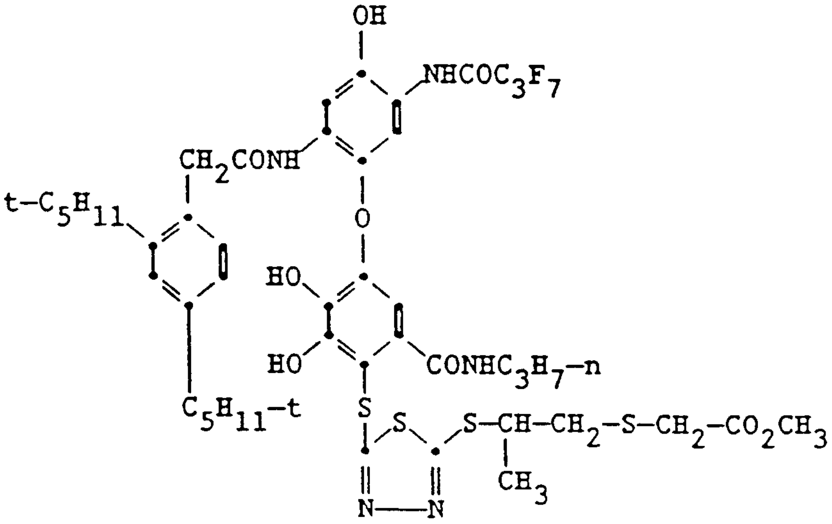
D-7



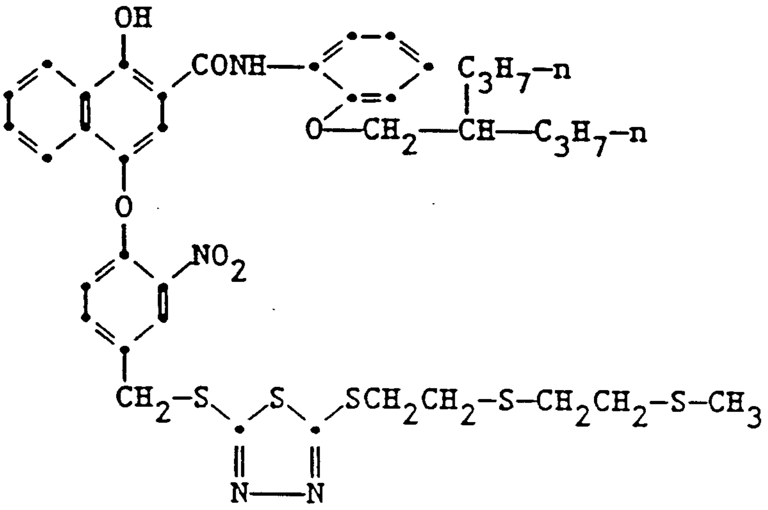
D-8



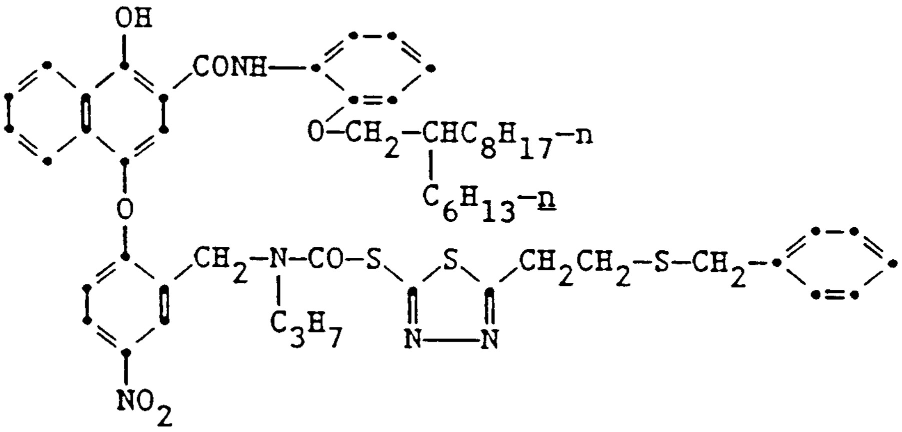
D-9



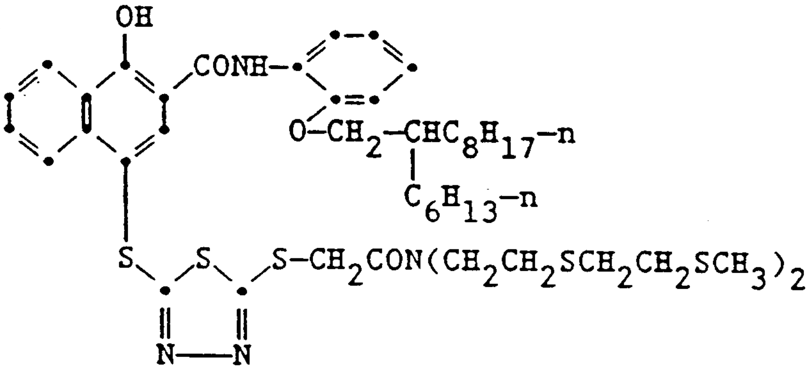
D-10



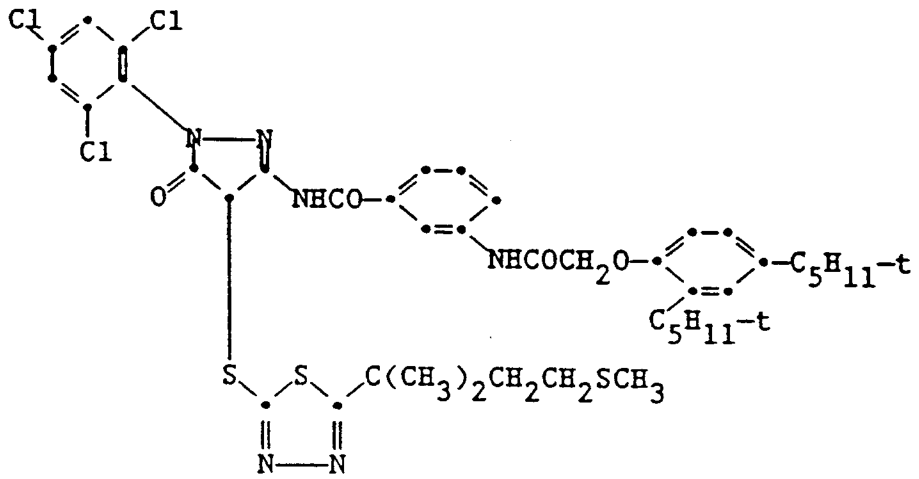
D-11



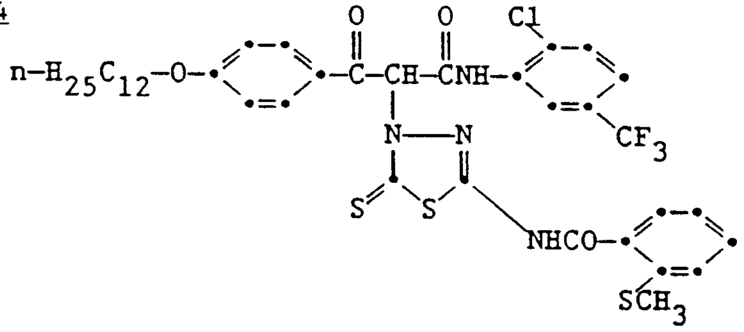
D-12



D-13



D-14



The photographic elements of this invention can be either single or multicolor elements. In a multicolor element, the yellow dye image-forming coupler and a DIR compound are usually associated with a blue-sensitive emulsion, although they could be associated with an unsensitized emulsion or an emulsion sensitized to a different region of the spectrum. Likewise, the magenta dye image-forming coupler and a DIR compound are associated with a green-sensitive emulsion and the cyan dye image-forming image coupler and a DIR compound are associated with a red-sensitive emulsion. The DIR couplers useful in this invention can be incorporated in the same photosensitive emulsion layer on which they act or in a related layer.

It is understood that DIR compounds need not be associated with all color forming photographic layers. It is also understood that the DIR couplers useful in this invention can be employed along with other DIR compounds in the same photographic material.

In an alternative format, the emulsion sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer, e.g. as by the use of microvessels as described in U.S. Patent No. 4,362,806.

Multicolor elements contain dye image-forming units sensitive to each of the three primary regions of the spectrum. Each unit can be comprised of a single emulsion layer or of multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art.

A typical multicolor photographic element comprises a support bearing a cyan dye image-forming unit comprising at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler. The element can contain additional layers, such as filter layers, interlayers, overcoat layers, subbing layers, and the like. The element typically will have a total thickness (excluding the support) of from 5 to 30 microns.

In the following discussion of suitable materials for use in the elements of this invention, reference will be made to Research Disclosure, December 1978, Item 17643, and December 1989, Item No. 308119 published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire PO10 7DQ, ENGLAND, the disclosures of which are incorporated herein by reference. This publication will be identified hereafter by the term "Research Disclosure." The elements of the invention can comprise emulsions and addenda described in these publications and publications referenced in these publications.

The silver halide emulsions employed in the elements of this invention can be comprised of silver bromide, silver chloride, silver iodide, silver chlorobromide, silver chloroiodide, silver bromoiodide, silver chlorobromoiodide or mixtures thereof. The emulsions can include silver halide grains of any conventional shape or size. Specifically, the emulsions can include coarse, medium or fine silver halide grains. High aspect ratio tabular grain emulsions are specifically contemplated, such as those disclosed by U.S. Patents 4,434,226, 4,424,310, 4,399,215, 4,433,048, 4,386,156, 4,504,570, 4,400,463, 4,414,306, 4,435,501, 4,414,966, 4,672,027 and 4,693,964. Also specifically contemplated are those silver bromoiodide grains with a higher molar proportion of iodide in the core of the grain than in the periphery of the grain, such as those described in GB 1.027,146; JA 54/48,521; U.S. Patents 4,379,837; 4,444,877; 4,665,012; 4,686,178; 4,565,778; 4,728,602; 4,668,614 and 4,636,461; and in EP 264,954. The silver halide emulsions can be either monodisperse or polydisperse as precipitated. The grain size distribution of the emulsions can be controlled by silver halide grain separation techniques or by blending silver halide emulsions of differing grain sizes.

Sensitizing compounds, such as compounds of copper, thallium, lead, bismuth, cadmium and Group VIII noble metals, can be present during precipitation of the silver halide emulsion.

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

The silver halide emulsions can be surface sensitized, noble metal (e.g., gold), middle chalcogen (e.g., sulfur, selenium, or tellurium), and reduction sensitizers, employed individually or in combination, are specifically contemplated. Typical chemical sensitizers are listed in Research Disclosure, Item 17643, cited above, Section III.

The silver halide emulsions can be spectrally sensitized with dyes from a variety of classes, including the polymethine dye class, which includes the cyanines, merocyanines, complex cyanines and merocyanines (i.e., tri-, tetra-, and polynuclear cyanines and merocyanines), oxonols, hemioxonols, styryls, merostyryls, and streptocyanines. Illustrative spectral sensitizing dyes are disclosed in Research Disclosure, Item 17643, cited above, Section IV.

Suitable vehicles for the emulsion layers and other layers of elements of this invention are described in Research Disclosure Item 17643, Section IX and the publications cited therein.

In addition to the couplers described herein the elements of this invention can include additional couplers as described in Research Disclosure Section VII, paragraphs D, E, F and G and the publications cited therein. These additional couplers can be incorporated as described in Research Disclosure Section VII, paragraph C and the publications cited therein. The coupler combinations of this invention can be used with colored masking couplers as described in U.S. Patent 4,883,746.

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

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.

Preferred color developing agents are p-phenylenediamines. Especially preferred are 4-amino-3-methyl-

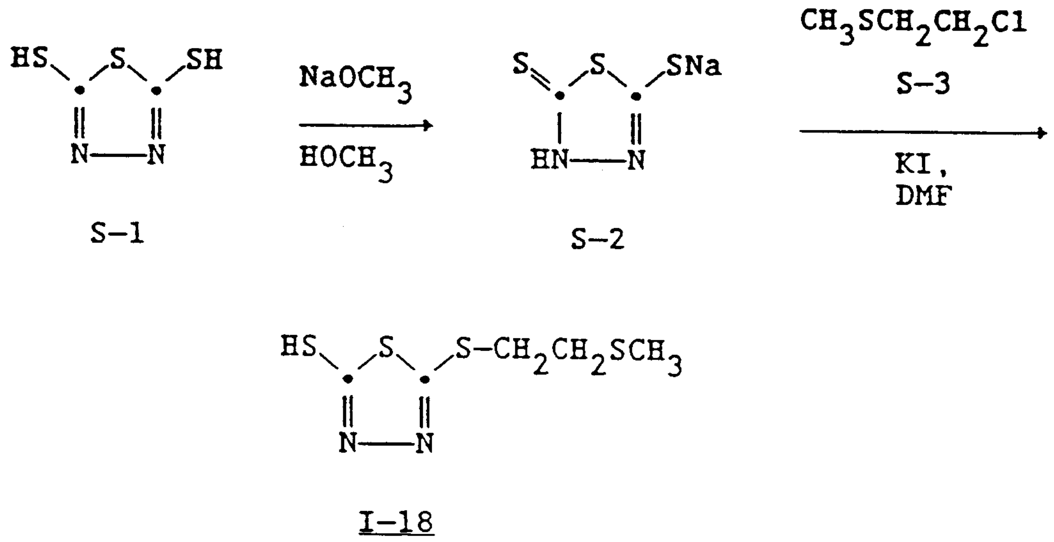
N,N-diethylaniline hydrochloride, 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)-ethylaniline sulfate hydrate, 4-amino-3-methyl-N-ethyl-N-β-hydroxyethylaniline sulfate, 4-amino-3-β-(methanesulfonamido)ethyl-N,N-diethylaniline hydrochloride and 4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluenesulfonic acid.

With negative-working silver halide, the processing step described above provides a negative image. The described elements are preferably processed in the known C-41 color process as described in, for example, the British Journal of Photography Annual of 1988, pages 196-198. To provide a positive (or reversal) image, the color development step can be preceded by development with a non-chromogenic developing agent to develop exposed silver halide, but not form dye, and then uniformly fogging the element to render unexposed silver halide developable. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

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

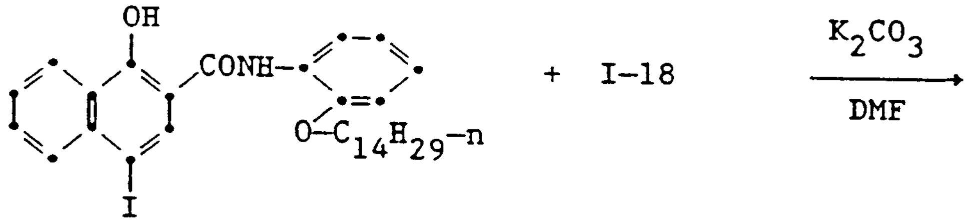
The following examples further illustrate the invention.

Synthesis Example 1 - Preparation of Development Inhibitor Moiety I-18

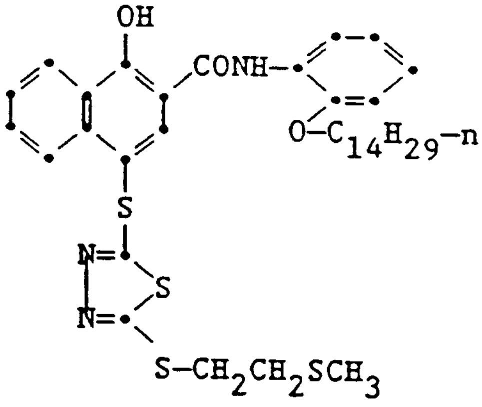


To a solution of 27.2 g (0.18 mol) of 2,5-dimercapto-1,3,4-thiadiazole (S-1) in 100 ml of methanol under a nitrogen atmosphere was dropwise added over a period of 15 minutes, 41.4 ml of a 25% solution of sodium methoxide (0.18 mol) in methanol. The mixture was stirred at room temperature for 2 hours and the methanol evaporated to leave a solid residue (S-2). This residue (S-2) was dissolved, under a nitrogen atmosphere, in 200 ml of dry dimethylformamide (DMF). To this solution was dropwise added 20.0 g (0.18 mol) of 1-thiomethyl-2-chloroethane (S-3) followed by 2 g of solid potassium iodide. This mixture was stirred under a nitrogen atmosphere for 16 hours at room temperature. After this time, the mixture was poured into a 1:1:1 mixture of ice : 10% hydrochloric acid : ethyl acetate. The ethyl acetate phase was separated and then washed sequentially in a separatory funnel with equal volumes of water (two times) and saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered through silica and evaporated to yield 43.3 g of a yellow oil. This oil was dissolved in 60 ml of hot acetonitrile and the resultant solution cooled to 0 ° C. The crystals formed were collected by filtration, washed with cold acetonitrile, and air dried to yield 11 g of inhibitor I-18 showing mp 66-68 ° C.

Synthesis Example 2 - Preparation of DIR Coupler D-3



S-4



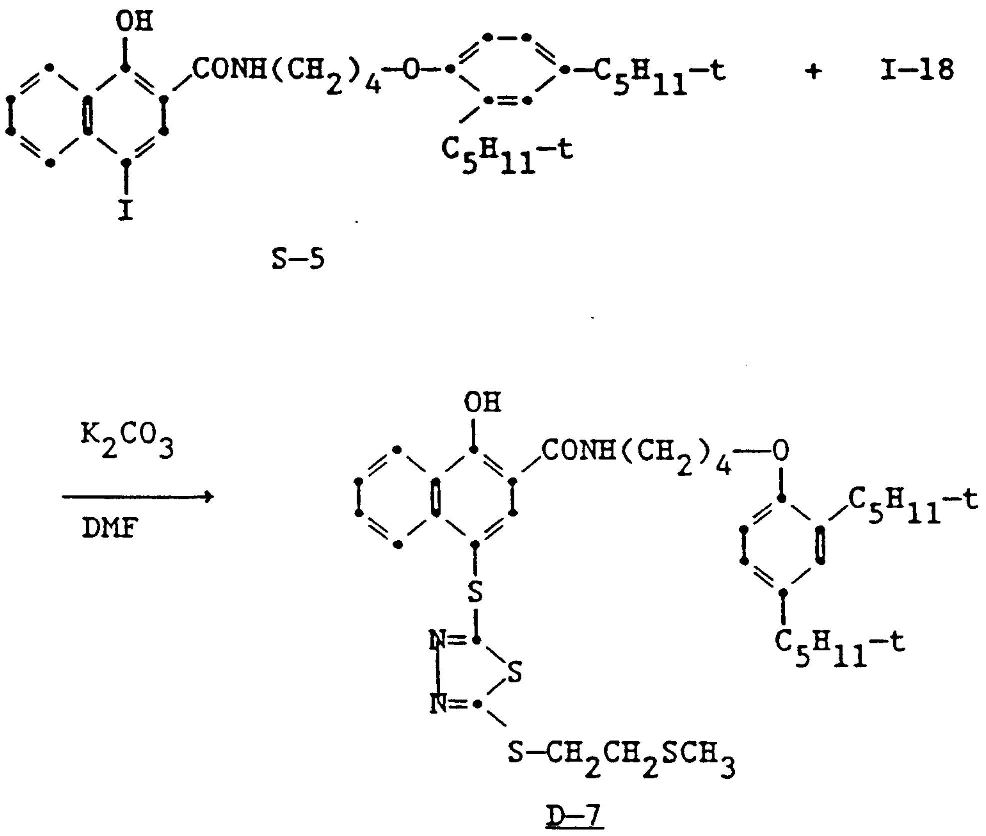
D-3

Coupler S-4 (12.0 g, 0.02 mol) and inhibitor I-18 (4.5 g, 0.02 mol) were combined under nitrogen in 140 ml of dimethylformamide and the mixture slowly warmed to 90 ° C. To this mixture was added, in portions, 5.5 g (0.04 mol) of potassium carbonate and the mixture stirred at 90 ° C under a nitrogen atmosphere for 3 hours. This mixture was then added to a 1:1:1 mixture of ice water : 10% hydrochloric acid : ethyl acetate. The ethyl acetate phase was separated using a separatory funnel, washed sequentially with equal volumes of water (two times), saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered and evaporated to yield a yellow-brown glass.

This glass was dissolved in 40 ml of ethyl acetate eluted from a 2 L silica gel column with 10% ethyl acetate in heptane. The eluted fractions containing the desired material were combined and evaporated to a volume of about 150 ml at which time crystals were formed. These crystals were collected by filtration, washed with ethyl acetate : heptane (1:1) and air dried. The resultant solid was dissolved in 150 ml of hot acetonitrile, decanted from a heavy brown residue, cooled to room temperature and stirred for 16 hours. The white crystalline solid formed was collected by filtration, washed with cold acetonitrile and air dried to yield 4.3 g of coupler D-3, mp 90-91 ° C.

Elemental Analysis:			
Calculated:	61.94% (C);	6.79% (H);	6.02% (N)
Found:	62.11% (C);	6.59% (H);	6.08% (N)

Synthesis Example 3 - Preparation of DIR Coupler D-7



S-5

D-7

Coupler S-5 (8.0 g, 0.013 mol) and inhibitor I-18 (2.8 g, 0.0126 mol) were combined under nitrogen in 90 ml of dimethylformamide and the mixture heated at 90 ° C. To this mixture was added, in portions, 3 g (0.022 mol) of potassium carbonate and the mixture stirred at 90 ° C under a nitrogen atmosphere for 2 hours. This mixture was then added to a 1:1:1 mixture of ice water : 10% hydrochloric acid : ethyl acetate to give a slightly tan solid precipitate.. This solid was collected by filtration and washed with water. It was then taken up in ethyl acetate and the ethyl acetate solution was dried over anhydrous magnesium sulfate, filtered and evaporated.

This product was dissolved in ethyl acetate eluted from a 2 L silica gel column with 10% ethyl acetate in heptane, graduated to 15% ethyl acetate in heptane. The eluted fractions containing the desired material were combined and concentrated by evaporation at which time a white solid wag formed. The solid was collected by filtration, washed with 10% ethyl acetate in heptane and air dried. The resultant crystals were recrystallized from 20 ml of hot ethyl acetate in two crops to form a white crystalline solid. The white crystalline solids formed were collected by filtration, washed with cold ethyl acetate : heptane (1:1) and air dried to give a combined yield 4.45 g of coupler D-7, mp 120-121 ° C.

Elemental Analysis:			
Calculated:	61.94% (C);	6.79% (H);	6.02% (N)
Found:	62.21% (C);	6.82% (H);	5.94% (N)

PHOTOGRAPHIC EXAMPLES

A series of photographic elements were prepared having the following structure and composition. Unless otherwise indicated, the numbers following a component represent the amount of the component in the element, expresses in grams per square meter.

Element 1 was prepared by sequentially applying the following layers to a clear support:

Antihalation Layer (layer 1):

gelatin at 2.45 g, grey colloidal silver at 0.33 g; 2,5-didodecylhydroquinone at 0.12 g.

Photographic Layer (layer 2):

gelatin at 2.4 g, red sensitized silver iodobromide emulsion (6.4 mol % I, 0.53 microns equivalent circular diameter) at 1.6 g, yellow dye forming coupler Ya at 1.3 g.

Interlayer (layer 3):

gelatin at 0.86 g and 2,5-didodecylhydroquinone at 0.12 g.

Photographic Layer (layer 4):

gelatin at 2.7 g, green sensitized silver iodobromide emulsion (6.4 mol % I, 0.53 microns equivalent circular diameter) at 1.6 g, cyan dye-forming coupler Ca at 0.75 g. Inventive and comparative DIR compounds were added to this layer as indicated in Table I.

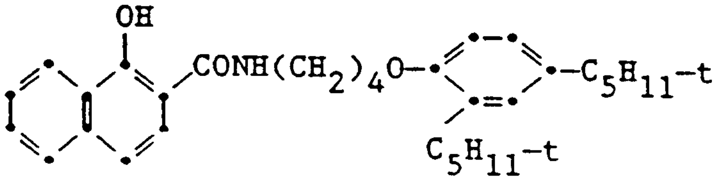
Protective Overcoat (layer 5):

gelatin at 5.4 g and bisvinylsulfonylmethyl ether as gelatin hardener at 2% by weight to total gelatin.

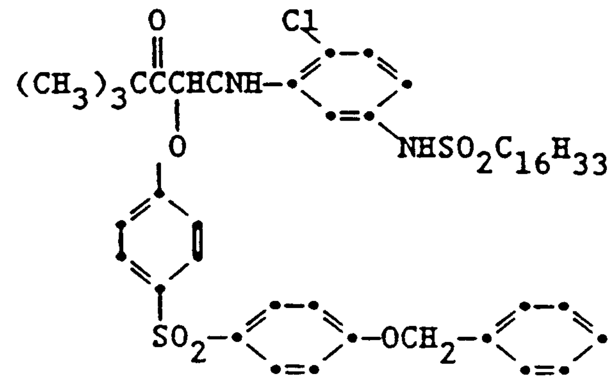
Elements 2 through 5 were prepared in a manner analogous to Element 1, the control sample which contains no release compound, by adding the comparison or DIR compound to photographic layer 4 at the level indicated in Table I.

The dye-forming couplers for the photographic layers were each dispersed in half their weight of di-n-butyl phthalate, while the DIR couplers were each dispersed in twice their weight of diethyl lauramide.

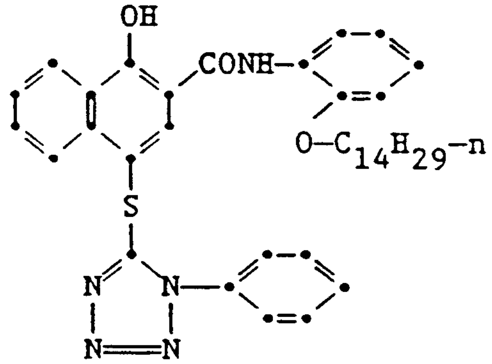
Cyan Dye-Forming Coupler Ca:



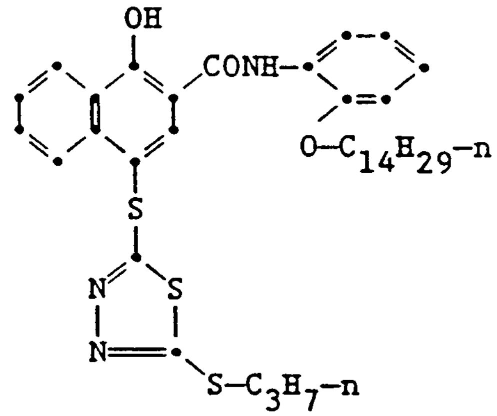
Yellow Dye-Forming Coupler Ya:



Comparative Coupler A:



Comparative Coupler B:



For interimage evaluation, the elements were exposed through a graduated density test object and a KOKAK Wratten 12 (minus blue) filter (KODAK is a trademark of the Eastman Kodak Company, U.S.A.). This procedure exposed both layers 2 and 4. These elements were then developed using a color negative process, the KODAK C-41 process, as described in The British Journal of Photography Annual of 1988, pages 196-198.

The oxidized color developing agent generated by development of exposed silver reacts with adjacent dye image-forming compounds and the DIR coupler, if present, to form dyes and to release inhibitor or inhibitor precursor in photographic layer 4. The intralayer development inhibiting effects of inhibitor released from the DIR coupler were assessed by monitoring the gamma of photographic layer 4. The interlayer development inhibiting effects of inhibitor released from the DIR coupler were assessed by monitoring the gamma of photographic layer 2. The interimage effects of the inhibitor released from the DIR compound were assessed by monitoring the ratio of the gamma of photographic layer 4 (causer of interimage) and photographic layer 2 (receiver of interimage). The smaller the gamma ratio, the smaller the interimage effect (degree of color correction) in the element. Table I shows the identity and quantity of DIR compound coated (in grams per m^2), the gamma of photographic layers 2 and 4 and the degree of interimage effect (color correction) of photographic layer 4 onto photographic layer 2 ((gamma of layer 4)/(gamma of layer 2)).

TABLE I

Interimage Comparisons

Element	DIR Comp. Added to Layer 4		Gammas		
	Identity	Quantity	Layer 4	Layer 2	IIE*
1 (Control)	None	0	1.97	1.16	1.46
2 (Comparison)	A	0.0175	1.76	1.17	1.50
3 (Comparison)	B	0.0179	1.66	1.15	1.44
4 (Invention)	D-3	0.0751	1.78	1.29	1.38
5 (Invention)	D-3	0.1503	1.78	1.35	1.32

*IIE (Interlayer Interimage Effect) is determined as:

$$\frac{\text{(gamma layer 4)}}{\text{(gamma layer 2)}}$$

As can be readily appreciated, the inventive elements (Elements 4 and 5) show surprisingly low levels of interlayer interimage effect when compared to the control element (Element 1) or the comparison elements (Elements 2 and 3).

It is noteworthy that inventive coupler D-3 (incorporated in inventive Elements 4 and 5) enables a lower degree of interlayer interimage effect than does comparative coupler A (incorporated in comparative Element 2).

This result is especially surprising since it is reported at U.S. 4,791,049 that release of phenylmercaptotetrazole (the same development inhibitor that is released by DIR coupler A) by an "oxidation-reduction" DIR compound results in lower interlayer interimage effects than are enabled by release of substituted mercaptothiadiazole development inhibitors from "oxidation-reduction" DIR compounds. Inventive DIR coupler, D-3, releases an inhibitor fragment that is identical to the one released by "oxidation-reduction" DIR compond I-23 of U.S. 4,791,049 which is said to enable extremely high degrees of interlayer interimage effect.

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

Claims

1. A photographic material comprising a support bearing at least two photographic silver halide emulsion layers and at least one coupler capable of releasing upon exposure and processing a development inhibitor, wherein the coupler has the structural formula:

COUP-$(\text{TIME})_n$-INH-Q

wherein

COUP is a coupler moiety from which $(TIME)_n$-INH-Q is released during development of the element;

TIME is a timing group;

INH-Q together constitute a development inhibitor moiety;

INH is a mercaptothiadiazole inhibitor moiety;

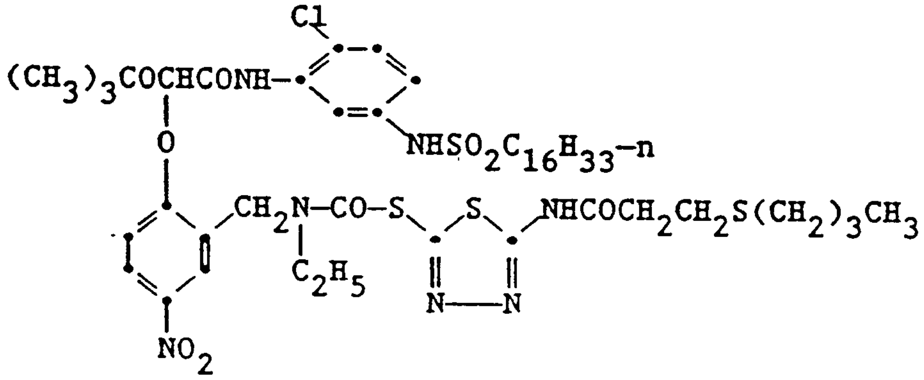
Q comprises from 1 to 4 thioether moieties, in each of which the sulfur atom is directly bonded to a saturated carbon atom but is not directly bonded to an INH moiety; and

n is 0, 1, or 2

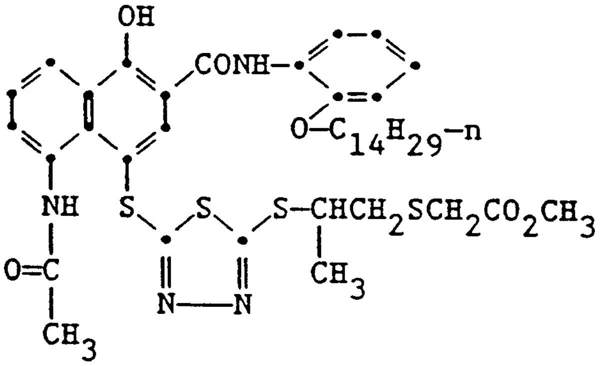
2. The recording material according to claim 1 wherein the thioether moieties comprise an alkyl, aryl, alkoxy, aryloxy, alkylthio, arylthio, alkylamino, arylamino, carbalkoxy, carboxylic or a heterocyclic group.

3. The recording material of claim 1 wherein the compound capable of releasing the development inhibitor is represented by the structure:

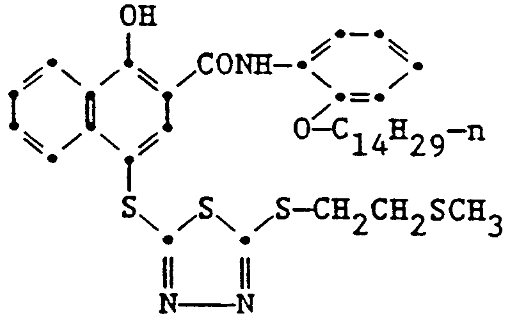
D-1



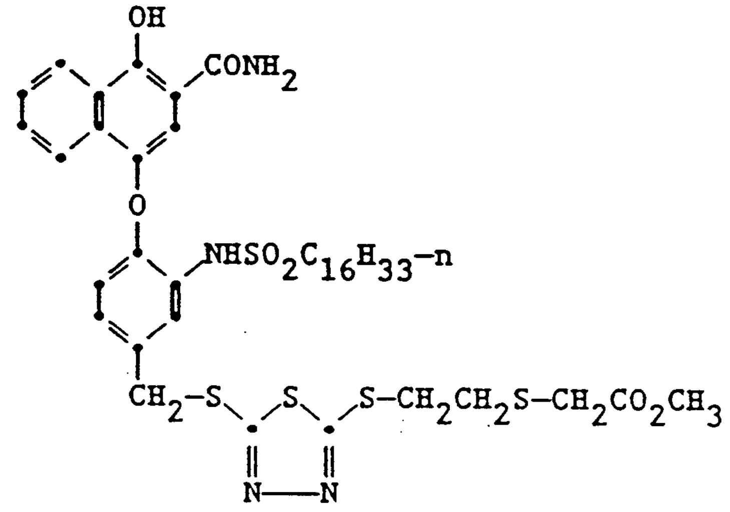
D-2



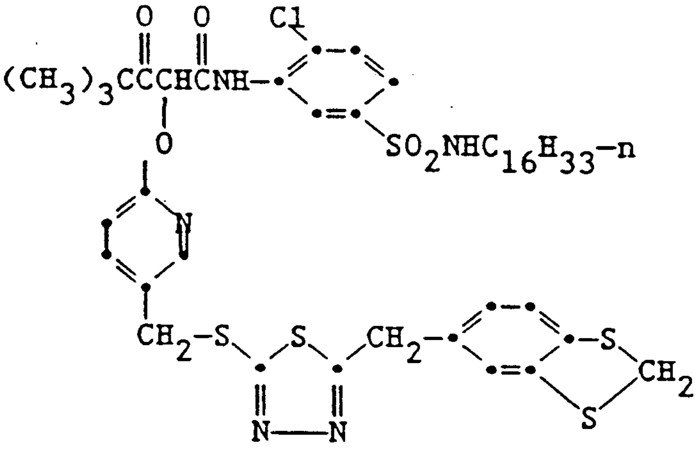
D-3



D-4



D-5



D-7