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**Photographic element and process having improved response to developer variations.**

(57)

A photographic element comprises at least one light sensitive silver halide layer sensitized to one or more of green, blue, and red light, and having associated therewith a 3-anilino-1-phenyl-5-pyrazolone magenta dye-forming coupler, a two-equivalent trialkylacetylacetanilide yellow dye-forming coupler, and a 2-ureido-5-carbonamidophenol cyan dye-forming coupler.

**EP 0 608 956 A1**

Field of the Invention

This invention relates to photographic elements and processes for developing such elements where the elements contain a combination of dye-forming couplers which render the resulting phototgraphic images less susceptible to variations in the developer solution parameters.

Background of the Invention

There are a variety of photofinishers, minilabs, and microlabs that offer the standard C-41 processing for color negative photographic materials. Analyses of these trade processes for C-41 developer components have indicated that various combinations of CD-4 (color developer) concentration, bromide (Br-) concentration, and developer pH value exist in the photofinishing trade. Ideally, color negative photographic materials would be insensitive to these fluctuations in developer components, such that density levels and color density balance would be consistent lab-to-lab, day-to-day, and film-to-film. However, currently available color negative photographic materials contain imaging chemistries that display an undesirable sensitivity in this respect. In the absence of totally insensitive materials with which to manufacture color photographic materials, emphasis must be placed on reducing individual chemical sensitivity and matching the sensitometric response of the separate color records so that effects on color contrast balance and color density balance are minimized and overall picture quality is not compromised.

Commonly used red light sensitive record image chemicals in current color photographic materials display lower sensitivity to C-41 developer perturbations than materials employed in the green and blue light sensitive records. Accordingly, it has been necessary, in order to achieve matched sensitometric responses of the three color records, to reduce the sensitivity of yellow-dye forming and magenta-dye forming couplers. EP 518,101 describes methodology to lower the sensitivity of yellow dye-forming couplers by the addition of a coupler to the blue light sensitive record that releases 3-thiopropionic acid upon coupling with oxidized developer. This has not proven to be the best solution to the problem.

EP 365,282 discloses the use of certain yellow dye-forming couplers (including 2-pivaloylacetanilides) in a single blue light sensitive layer to improve sensitivity to developer pH variations. Japanese published applications JO 2027-344-A and JO 2039-047 disclose a broad range of magenta, yellow, and cyan couplers for use to impart stability to elements, and in particular to print images. There is no suggestion of the process sensitivity advantages to be obtained using the combination of the invention. US 4,748,107 discloses the combination of 2-pivaloylacetanilides, 3-anilino-1-phenyl-5-pyrazolones, and the different 2-carbonamidophenols as the yellow, magenta, and cyan dye-forming couplers, respectively, for improved color formation and reproducibility and for image stability in color paper products. None of these proposals provide a solution to the developer sensitivity problem.

It is thus a problem to be solved to provide a photographic element and process which will provide an improved response in photographic image properties in spite of variations in developer parameters.

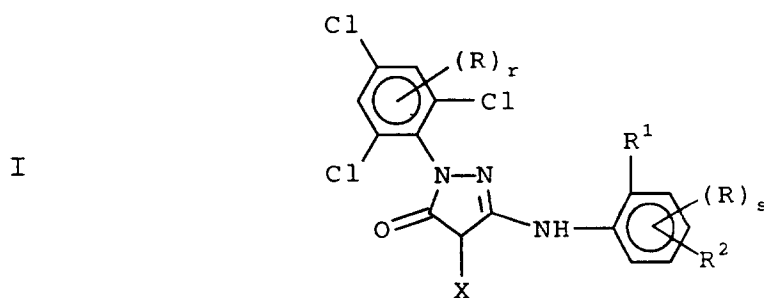
Summary of the Invention

The above problem is solved by providing a photographic element which comprises at least one light sensitive silver halide layer sensitized to one or more of green, blue, and red light, and having associated therewith a 3-anilino-1-phenyl-5-pyrazolone magenta dye-forming coupler, a two-equivalent trialkylacetylacetanilide yellow dye-forming coupler, and a 2-ureido-5-carbonamidophenol cyan dye-forming coupler. The invention also provides a process for forming an image from an exposed element as above described through contact with a color developing agent.

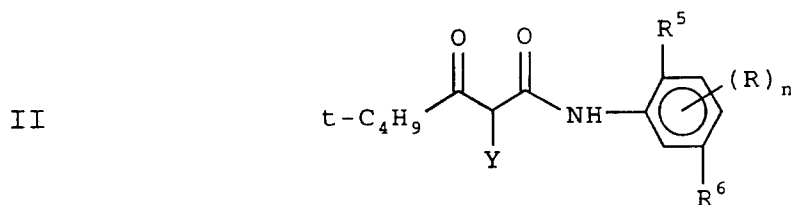
The invention thus provides photographic images which are more consistent for color density balance and contrast balance regardless of developer parameters which therefore enables the photofinisher the opportunity to print the color negative to a correct color balance. This invention also enables photofinishers to maintain the same exposure parameters on automatic printers even as change or variability occurs in the development process due to developer bath variations.

Detailed Description of the Invention

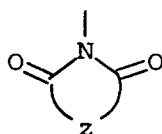
In a preferred embodiment of the invention, the magenta dye-forming coupler is represented by formula I, the yellow dye-forming coupler is represented by formula II, and the cyan dye-forming coupler is represented by formula III:



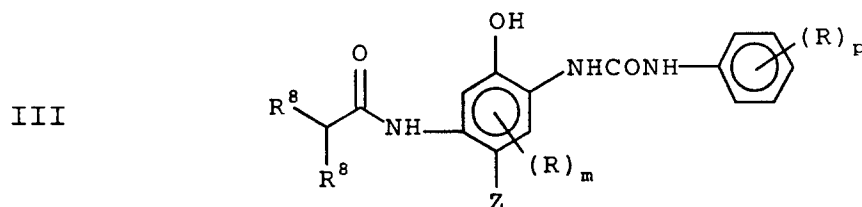
wherein  $R^1$  and  $R^2$  are independently selected from the group consisting of hydrogen, halogen, trifluoromethyl, cyano, nitro, and substituted or unsubstituted alkyl, alkoxy, aryloxy, alkylthio, carbonamido, carbamoyl, sulfonamido, sulfamoyl, alkylsulfonyl, arylsulfonyl, alkoxycarbonyl, acyloxy, and acyl groups; each  $R$  is independently a substituent with  $r$  being 0 to 2 and  $s$  being 0 to 3 and  $X$  is a substituted or unsubstituted arylthio or alkylthio group;



wherein  $R^5$  and  $R^6$  are independently selected from the group consisting of hydrogen, halogen, cyano, nitro, trifluoromethyl, and substituted or unsubstituted alkyl, alkoxy, aryloxy, alkylthio, carbonamido, carbamoyl, sulfonamido, sulfamoyl, alkylsulfonyl, arylsulfonyl, alkoxycarbonyl, acyloxy, and acyl groups; each  $R$  is independently a substituent as hereafter defined with  $n$  being 0 to 3; and  $Y$  is an aryloxy group or is selected from the group consisting of substituted and unsubstituted imidazole, pyrazole, and heterocyclic compounds represented by the formula:



wherein  $z$  represents the atoms necessary to complete a heterocyclic ring; and



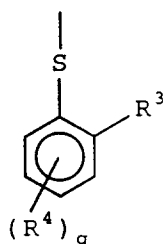
wherein each  $R^8$  is independently selected from the group consisting of substituted and unsubstituted alkyl, alkoxy, aryloxy, alkylthio, carbonamido, aryl, carbamoyl, sulfonamido, sulfamoyl, alkylsulfonyl, arylsulfonyl, acyloxy, acyl, and alkoxycarbonyl groups; each  $R$  is independently a substituent with  $m$  being 0 to 2 and  $p$  being 0 to 5; and  $Z$  is hydrogen or a coupling-off group.

As used herein, the term substituent, unless otherwise specifically stated, has a broad definition. The substituent may be, for example, halogen, such as chlorine, bromine or fluorine; nitro; hydroxyl; cyano; and  $-CO_2H$  and its salts; and groups which may be further substituted, such as alkyl, including straight or

branched chain alkyl, such as methyl, trifluoromethyl, ethyl, *t*-butyl, 3-(2,4-di-*t*-amylphenoxy) propyl, and tetradecyl; alkenyl, such as ethylene, 2-butene; alkoxy, such as methoxy, ethoxy, propoxy, butoxy, 2-methoxyethoxy, *sec*-butoxy, hexyloxy, 2-ethylhexyloxy, tetradecyloxy 2-(2,4-di-*t*-pentylphenoxy)ethoxy, and 2-dodecyloxyethoxy; aryl such as phenyl, 4-*t*-butylphenyl, 2,4,6-trimethylphenyl, naphthyl; aryloxy, such as phenoxy, 2-methylphenoxy, alpha- or beta-naphthyloxy, and 4-tolyloxy; carbonamido, such as acetamido, benzamido, butyramido, tetradecanamido, alpha-(2,4-di-*t*-pentylphenoxy)acetamido, alpha-(2,4-di-*t*-pentylphenoxy)butyramido, alpha-(3-pentadecylphenoxy)hexanamido, alpha-(4-hydroxy-3-*t*-butylphenoxy)-tetradecanamido, 2-oxo-pyrrolidin-1-yl, 2-oxo-5-tetradecylpyrrolin-1-yl, N-methyltetradecanamido, N-succinimido, N-phthalimido, 2,5-dioxo-1-oxazolidinyl, 3-dodecyl-2,5-dioxo-1-imidazolyl, and N-acetyl-N-dodecylamino, ethoxycarbonylamino, phenoxycarbonylamino, benzyloxycarbonylamino, hexadecyloxycarbonylamino, 2,4-di-*t*-butylphenoxycarbonylamino, phenylcarbonylamino, 2,5-(di-*t*-pentylphenyl)-carbonylamino, *p*-dodecylphenylcarbonylamino, *p*-toluylcarbonylamino, N-methylureido, N,N-dimethylureido, N-methyl-N-dodecylureido, N-hexadecylureido, N,N-dioctadecylureido, N,N-dioctyl-N'-ethylureido, N-phenylureido, N,N-diphenylureido, N-phenyl-N-*p*-toluylureido, N-(*m*-hexadecylphenyl)ureido, N,N-(2,5-di-*t*-pentylphenyl)-N'-ethylureido, and *t*-butylcarbonamido; sulfonamido, such as methylsulfonamido, benzenesulfonamido, *p*-toluylsulfonamido, *p*-dodecylbenzenesulfonamido, N-methyltetradecylsulfonamido, N,N-dipropylsulfamoylamino, and hexadecylsulfonamido; sulfamoyl, such as N-methylsulfamoyl, N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-hexadecylsulfamoyl, N,N-dimethylsulfamoyl; N-[3-(dodecyloxy)propyl]-sulfamoyl, N-[4-(2,4-di-*t*-pentylphenoxy)butyl]sulfamoyl, N-methyl-N-tetradecylsulfamoyl, and N-dodecylsulfamoyl; carbamoyl, such as N-methylcarbamoyl, N,N-dibutylcarbamoyl, N-octadecylcarbamoyl, N-[4-(2,4-di-*t*-pentylphenoxy)butyl]carbamoyl, N-methyl-N-tetradecylcarbamoyl, and N,N-dioctylcarbamoyl; acyl, such as acetyl, (2,4-di-*t*-amylphenoxy)acetyl, phenoxycarbonyl, *p*-dodecyloxyphenoxycarbonyl methoxycarbonyl, butoxycarbonyl, tetradecyloxyphenoxycarbonyl, ethoxycarbonyl, benzyloxycarbonyl, 3-pentadecyloxyphenoxycarbonyl, and dodecyloxyphenoxycarbonyl; sulfonyl, such as methoxysulfonyl, octyloxysulfonyl, tetradecyloxysulfonyl, 2-ethylhexyloxysulfonyl, phenoxysulfonyl, 2,4-di-*t*-pentylphenoxysulfonyl, methylsulfonyl, octylsulfonyl, 2-ethylhexylsulfonyl, dodecylsulfonyl, hexadecylsulfonyl, phenylsulfonyl, 4-nonylphenylsulfonyl, and *p*-toluylsulfonyl; sulfonyloxy, such as dodecylsulfonyloxy, and hexadecylsulfonyloxy; sulfinyl, such as methylsulfinyl, octylsulfinyl, 2-ethylhexylsulfinyl, dodecylsulfinyl, hexadecylsulfinyl, phenylsulfinyl, 4-nonylphenylsulfinyl, and *p*-toluylsulfinyl; thio, such as ethylthio, octylthio, benzylthio, tetradecylthio, 2-(2,4-di-*t*-pentylphenoxy)ethylthio, phenylthio, 2-butoxy-5-*t*-octylphenylthio, and *p*-tolylthio; acyloxy, such as acetyloxy, benzoyloxy, octadecanoyloxy, *p*-dodecylamidobenzoyloxy, N-phenylcarbamoyloxy, N-ethylcarbamoyloxy, and cyclohexylcarbamoyloxy; amine, such as phenylanilino, 2-chloroanilino, diethylamine, dodecylamine; imino, such as 1 (N-phenylimido)ethyl, N-succinimido or 3-benzylhydantoinyl; phosphate, such as dimethylphosphate and ethylbutylphosphate; phosphite, such as diethyl and dihexylphosphite; azo, such as phenylazo and naphthylazo; a heterocyclic group, a heterocyclic oxy group or a heterocyclic thio group, each of which may be substituted and which contain a 3 to 7 membered heterocyclic ring composed of carbon atoms and at least one hetero atom selected from the group consisting of oxygen, nitrogen and sulfur, such as 2-furyl, 2-thienyl, 2-benzimidazolyloxy or 2-benzothiazolyloxy; quaternary ammonium, such as triethylammonium; and silyloxy, such as trimethylsilyloxy.

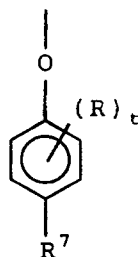
The particular substituents used may be selected to attain the desired photographic properties for a specific application and can include, for example, hydrophobic groups, solubilizing groups, blocking groups, etc. Generally, the above groups and substituents thereof may typically include those having 1 to 30 carbon atoms and usually less than 24 carbon atoms, but greater numbers are possible depending on the particular substituents selected. Moreover, as indicated, the substituents may themselves be suitably substituted with any of the above groups.

In the magenta dye-forming coupler there are certain preferred embodiments. The R<sup>1</sup> group is preferably chlorine or alkoxy of up to 8 carbon atoms. R<sup>2</sup> is preferably carbonamido, sulfamoyl or sulfonamido. Typically, the coupling-off group X is an alkylthio or arylthio group. In the latter case, the coupling-off group can suitably have the formula:



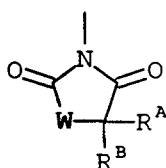
wherein  $R^3$  and  $R^4$  are individually selected from the group consisting of hydrogen, halogen, carboxyl, and substituted or unsubstituted alkyl, alkoxy, aryloxy, carbonamido, ureido, carbamate, sulfonamido, carbamoyl, sulfamoyl, acyloxy, alkoxycarbonyl, aryloxycarbonyl, and amino groups;  $q$  is 0 to 4; and  $R^4$  may be para and/or meta to the sulfur atom. It is preferred that  $R^3$  have at least one carbon atom and that the total number of carbon atoms in  $R^3$  and  $R^4$  together be from 4 to 25.

The yellow dye-forming coupler II also has certain preferred embodiments. The  $R^5$  substituent is typically chlorine or alkoxy of up to 8 carbon atoms. The  $R^6$  substituent is preferably carbonamido, sulfamoyl, or sulfonamido.  $Y$  is suitably an aryloxy coupling-off group. One example would have the formula:



wherein  $R^7$  is selected from the group consisting of hydrogen, halogen, cyano, nitro, trifluoromethyl and substituted or unsubstituted alkyl, alkoxy, alkylthio, carbonamido, carbamoyl, sulfonamido, sulfamoyl, alkylsulfonyl, arylsulfonyl, alkoxycarbonyl, acyloxy, and acyl groups and each  $R_t$  is independently a substituent with  $t$  being 0 to 4. Preferably,  $R^7$  is arylsulfonyl.

In another specific embodiment,  $Y$  may be represented by the formula:

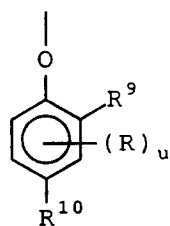


wherein  $W$  is  $-O-$ ,  $-S-$ ,  $-N(R^C)-$ , or  $-C(R^D)(R^E)-$ ;  $R^A$  is H, or substituted or unsubstituted alkyl, alkoxy, phenyl, or phenoxy;  $R^B$  and  $R^E$  are independently H or substituted or unsubstituted alkyl;  $R^C$  is substituted or unsubstituted alkyl or phenyl; and  $R^D$  is H or substituted or unsubstituted alkyl or alkoxy.

In one more specific embodiment of the above formula,  $W$  is  $-NR^D$ ;  $R^A$  is H, or substituted or unsubstituted alkyl or alkoxy;  $R^B$  is H; and  $R^C$  is substituted or unsubstituted alkyl. In particular,  $R^A$  is  $-OC_2H_5$ ,  $R^B$  is H and  $R^C$  is  $-CH_2$ -phenyl. In another specific embodiment,  $W$  is  $-C(R^D)(R^E)$  with  $R^A$ ,  $R^B$ ,  $R^D$ , and  $R^E$  defined as above.

In the cyan dye-forming coupler, it is preferred that at least one  $(R)_p$  be present. Examples are cyano in the 4-position and cyano in the 3-position and Cl in the 4-position. One  $R^8$  is suitably of the formula

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10 wherein  $R^9$  and  $R^{10}$  are substituted or unsubstituted alkyl of up to 16 carbon atoms and R is a substituent with u being 0 to 3. Z is typically hydrogen or aryloxy.

The following formulas for suitable magenta, yellow and cyan couplers will serve to better illustrate the invention.

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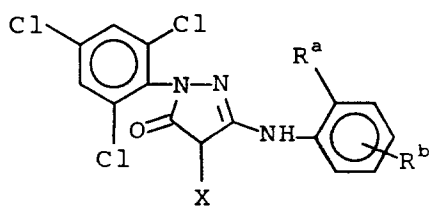
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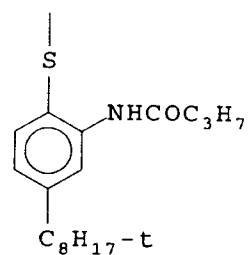
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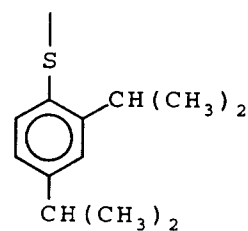
**Magenta Couplers**

	<u>R<sup>a</sup></u>	<u>R<sup>b</sup>/Position (N = 1)</u>	<u>X</u>
<b>M-1</b>	-Cl	-NHCOC <sub>13</sub> H <sub>27-n/5</sub>	
<b>M-2</b>	-Cl	-NHCOC <sub>13</sub> H <sub>27-n/5</sub>	
<b>M-3</b>	-Cl	NHCOOC <sub>16</sub> H <sub>33-n/5</sub>	

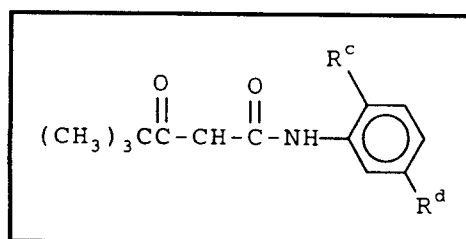
**M-4**      -Cl      -NHCOC<sub>14</sub>H<sub>24-n/5</sub>



**M-5**      -Cl      -SO<sub>2</sub>C<sub>12</sub>H<sub>25/4</sub>



### Yellow Couplers

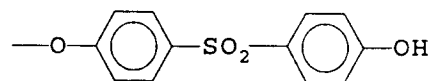


**R<sup>c</sup>**

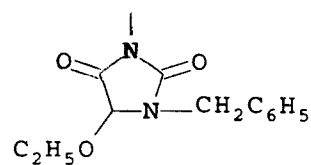
**R<sup>d</sup>**

**Y**

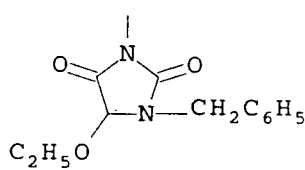
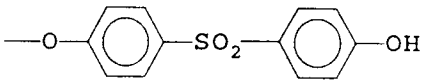
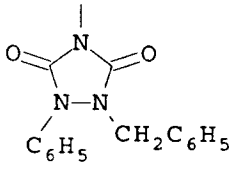
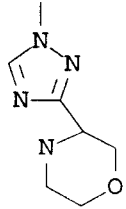
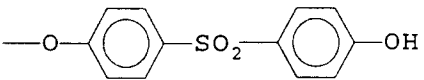
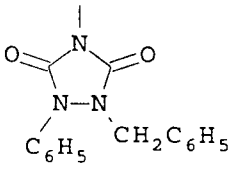
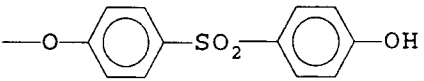
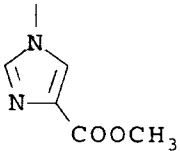
**Y-1**      -Cl      -NHSO<sub>2</sub>C<sub>16</sub>H<sub>23-n</sub>

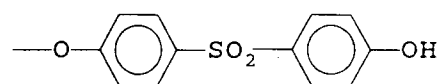
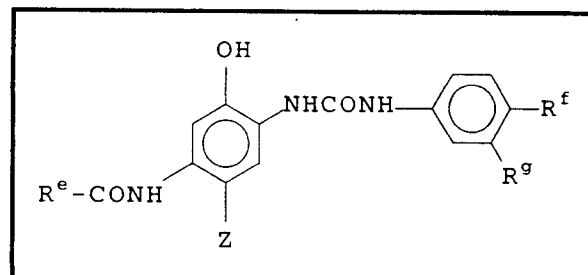


**Y-2**      -Cl      -COOC<sub>12</sub>H<sub>25-n</sub>

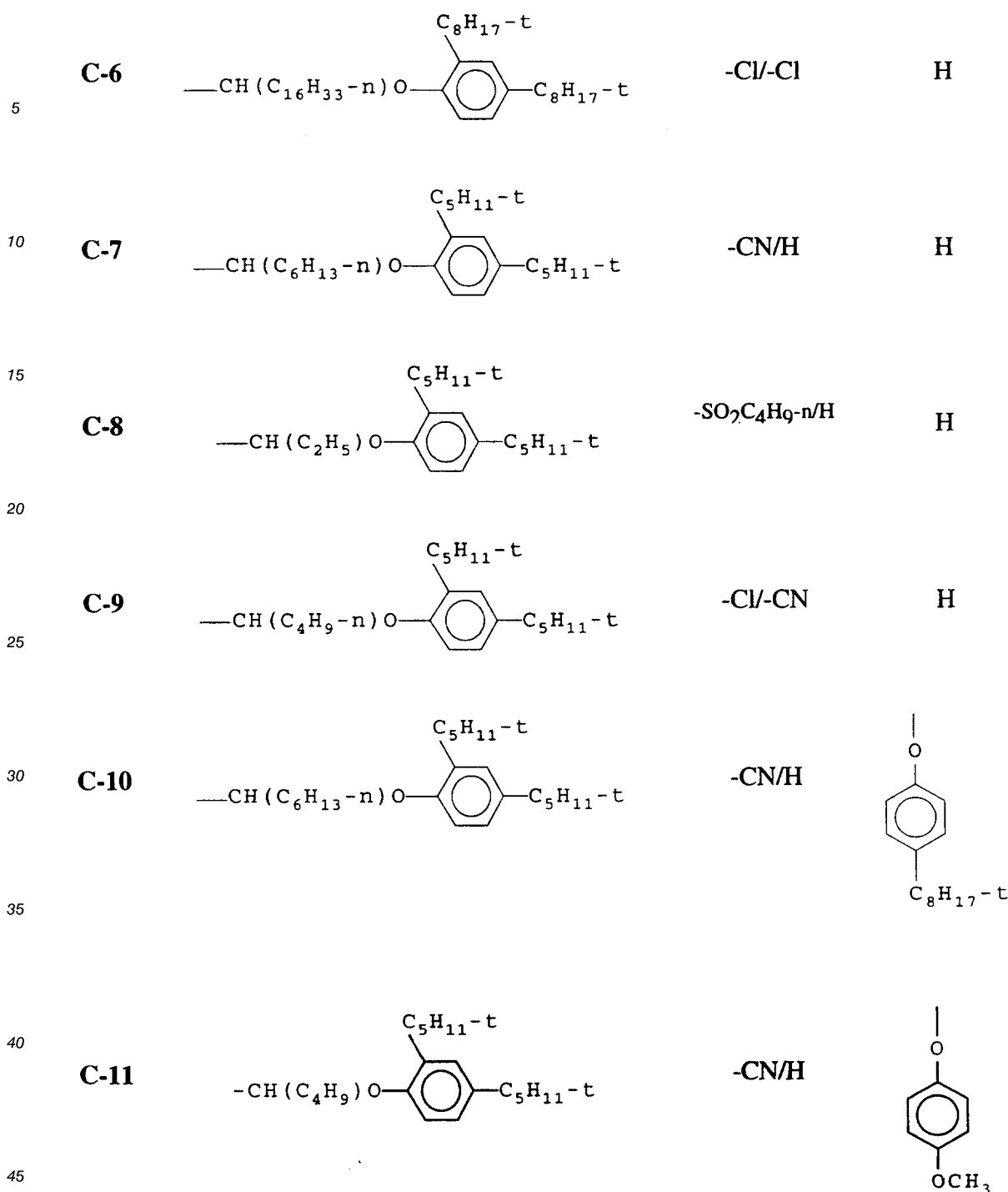




5	<b>Y-3</b>	-Cl	-NHSO <sub>2</sub> C <sub>16</sub> H <sub>23-n</sub>	
10	<b>Y-4</b>	-Cl	-COOC <sub>12</sub> H <sub>25-n</sub>	
15	<b>Y-5</b>	-Cl	-COOCH(CH <sub>3</sub> )COOC <sub>12</sub> H <sub>25-n</sub>	
20				
25	<b>Y-6</b>	-Cl	-NHSO <sub>2</sub> C <sub>16</sub> H <sub>33-n</sub>	
30	<b>Y-7</b>	-Cl	-NHSO <sub>2</sub> C <sub>16</sub> H <sub>33-n</sub>	
35	<b>Y-8</b>	-Cl	-COOCH(C <sub>4</sub> H <sub>9-n</sub> )COOC <sub>12</sub> H <sub>25-n</sub>	
40				
45	<b>Y-9</b>	-Cl	-COOCH(C <sub>4</sub> H <sub>9-n</sub> )COOC <sub>12</sub> H <sub>25-n</sub>	
50	<b>Y-10</b>	-OC <sub>16</sub> H <sub>33-n</sub>	--SO <sub>2</sub> NHCH <sub>3</sub>	
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Y-11  $-\text{OC}_{16}\text{H}_{33-n}$  $-\text{SO}_2\text{NHCH}_3$ **Cyan Couplers**

	<u><math>\text{R}^e</math></u>	<u><math>\text{R}^f/\text{R}^g</math></u>	<u><math>\text{Z}</math></u>
<b>C-1</b>		-CN/H	H
<b>C-2</b>		-Cl/-CN	H
<b>C-3</b>		-CN/H	H
<b>C-4</b>		-CN/H	H
<b>C-5</b>		-Cl/-CN	H



The materials of the invention can be used in any of the ways and in any of the combinations known in the art. Typically, the invention materials are incorporated in a silver halide emulsion and the emulsion coated as a layer on a support to form part of a photographic element. Alternatively, they can be incorporated at a location adjacent to the silver halide emulsion layer where, during development, they will be in reactive association with development products such as oxidized color developing agent. Thus, as used herein, the term "associated" signifies that the compound is in the silver halide emulsion layer or in an adjacent location where, during processing, it is capable of reacting with silver halide development products.

To control the migration of various components, it may be desirable to include a high molecular weight hydrophobe or "ballast" group in the component molecule. Representative ballast groups include substituted or unsubstituted alkyl or aryl groups containing 8 to 40 carbon atoms. Representative substituents on such groups include alkyl, aryl, alkoxy, aryloxy, alkylthio, hydroxy, halogen, alkoxy carbonyl, aryloxy carbonyl,

carboxy, acyl, acyloxy, amino, anilino, carbonamido, carbamoyl, alkylsulfonyl, arylsulfonyl, sulfonamido, and sulfamoyl groups wherein the substituents typically contain 1 to 40 carbon atoms. Such substituents can also be further substituted.

The photographic elements can be single color elements or multicolor elements. Multicolor elements contain image dye-forming units sensitive to each of the three primary regions of the spectrum. Each unit can comprise a single emulsion layer or 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. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer.

A typical multicolor photographic element comprises a support bearing a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta dye 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.

If desired, the photographic element can be used in conjunction with an applied magnetic layer as described in Research Disclosure, November 1992, Item 34390 published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire PO10 7DQ, ENGLAND.

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, available as described above, which will be identified hereafter by the term "Research Disclosure." The contents of the Research Disclosure, including the patents and publications referenced therein, are incorporated herein by reference, and the Sections hereafter referred to are Sections of the Research Disclosure.

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

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

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

It may be useful to use a combination of couplers any of which may contain known ballasts or coupling-off groups such as those described in U.S. Patent 4,301,235; U.S. Patent 4,853,319 and U.S. Patent 4,351,897. The coupler may also be used in association with "wrong" colored couplers (e.g. to adjust levels of interlayer correction) and, in color negative applications, with masking couplers such as those described in EP 213,490; Japanese Published Application 58-172,647; U.S. Patent 2,983,608; German Application DE 2,706,117C; U.K. Patent 1,530,272; Japanese Application A-113935; U.S. Patents 4,070,191 and 4,273,861; and German Application DE 2,643,965. The masking couplers may be shifted or blocked.

The invention materials may also be used in association with materials that accelerate or otherwise modify the processing steps e.g. of bleaching or fixing to improve the quality of the image. Bleach accelerator releasing couplers such as those described in EP 193,389; EP 301,477; U.S. 4,163,669; U.S. 4,865,956; and U.S. 4,923,784, may be useful. Also contemplated is use of the compositions in association

with nucleating agents, development accelerators or their precursors (UK Patent 2,097,140; U.K. Patent 2,131,188); electron transfer agents (U.S. 4,859,578; U.S. 4,912,025); antifogging and anti color-mixing agents such as derivatives of hydroquinones, aminophenols, amines, gallic acid; catechol; ascorbic acid; hydrazides; sulfonamidophenols; and non color-forming couplers.

For example, the invention materials may be substituted in whole or in part in the layers of a color negative photographic element comprising a support bearing the following layers from top to bottom:

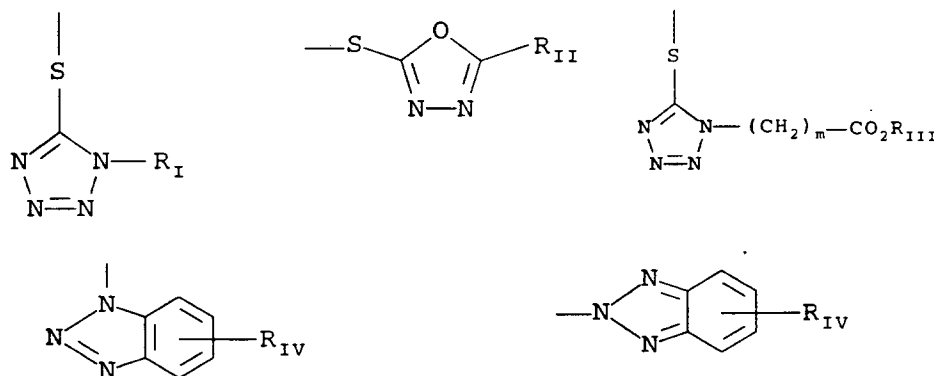
- (1) one or more overcoat layers containing ultraviolet absorber(s);
- (2) a two-coat yellow pack with a fast yellow layer containing "Coupler 1": Benzoic acid, 4-chloro-3-((2-(4-ethoxy-2,5-dioxo-3-(phenylmethyl)-1-imidazolidinyl)-3-(4-methoxyphenyl)-1,3-dioxopropyl)amino)-, dodecyl ester and a slow yellow layer containing the same compound together with "Coupler 2": Propanoic acid, 2-[[5-[[4-[2-[[[2,4-bis(1,1-dimethylpropyl)phenoxy]acetyl]amino]-5-[[2,2,3,3,4,4,4-heptafluoro-1-oxobutyl]amino]-4-hydroxyphenoxy]-2,3-dihydroxy-6-[(propylamino)carbonyl]phenyl]thio]-1,3,4-thiadiazol-2-yl]thio]-, methyl ester and "Coupler 3": 1-((dodecyloxy)carbonyl) ethyl(3-chloro-4-((3-(2-chloro-4-((1-tridecanoyl)ethoxy) carbonyl)anilino)-3-oxo-2-((4)(5)(6)-(phenoxy)carbonyl)-1H-benzotriazol-1-yl)propanoyl)amino))benzoate;
- (3) an interlayer containing fine metallic silver;
- (4) a triple-coat magenta pack with a fast magenta layer containing "Coupler 4": Benzamide, 3-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-N-(4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)-, "Coupler 5": Benzamide, 3-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-N-(4',5'-dihydro-5'-oxo-1'-(2,4,6-trichlorophenyl) (1,4'-bi-1H-pyrazol)-3'-yl)-, "Coupler 6": Carbamic acid, (6-((3-(dodecyloxy)propyl) amino)carbonyl)-5-hydroxy-1-naphthalenyl)-, 2-methylpropyl ester, "Coupler 7": Acetic acid, ((2-((3-((3-(dodecyloxy)propyl)amino) carbonyl)-4-hydroxy-8-((2-methylpropoxy)carbonyl) amino)-1-naphthalenyl)oxy)ethylthio)-, and "Coupler 8": Benzamide, 3-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-N-(4,5-dihydro-4-((4-methoxyphenyl) azo)-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)-; a mid-magenta layer and a slow magenta layer each containing "Coupler 9": a ternary copolymer containing by weight in the ratio 1:1:2 2-Propenoic acid butyl ester, styrene, and N-[1-(2,4,6-trichlorophenyl)-4,5-dihydro-5-oxo-1H-pyrazol-3-yl]-2-methyl-2-propenamide; and "Coupler 10": Tetradecanamide, N-(4-chloro-3-((4-((2,2-dimethyl-1-oxopropyl) amino)phenyl)azo)-4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)amino)phenyl)-, in addition to Couplers 3 and 8;
- (5) an interlayer;
- (6) a triple-coat cyan pack with a fast cyan layer containing Couplers 6 and 7; a mid-cyan containing Coupler 6 and "Coupler 11": 2,7-Naphthalenedisulfonic acid, 5-(acetylamino)-3-((4-(2-((3-((3-(2,4-bis(1,1-dimethylpropyl)phenoxy) propyl)amino)carbonyl)-4-hydroxy-1-naphthalenyl) oxy)ethoxy)phenyl)azo)-4-hydroxy-, disodium salt; and a slow cyan layer containing Couplers 2 and 6;
- (7) an undercoat layer containing Coupler 8; and
- (8) an antihalation layer.

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

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

Such compounds are also disclosed in "Developer-Inhibitor-Releasing (DIR) Couplers for Color Photography," C.R. Barr, J.R. Thirtle and P.W. Vittum in *Photographic Science and Engineering*, Vol. 13, p. 174 (1969), incorporated herein by reference. Generally, the developer inhibitor-releasing (DIR) couplers include a coupler moiety and an inhibitor coupling-off moiety (IN). The inhibitor-releasing couplers may be of the time-delayed type (DIAR couplers) which also include a timing moiety or chemical switch which produces a delayed release of inhibitor. Examples of typical inhibitor moieties are: oxazoles, thiazoles, diazoles,

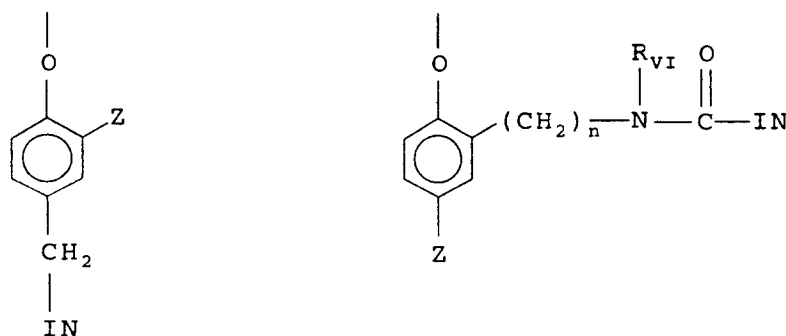
triazoles, oxadiazoles, thiadiazoles, oxathiazoles, thiatriazoles, benzotriazoles, tetrazoles, benzimidazoles, indazoles, isoindazoles, mercaptotetrazoles, selenotetrazoles, mercaptobenzothiazoles, selenobenzothiazoles, mercaptobenzoxazoles, selenobenzoxazoles, mercaptobenzimidazoles, selenobenzimidazoles, benzodiazoles, mercaptooxazoles, mercaptothiadiazoles, mercaptothiazoles, mercaptotriazoles, mercaptooxadiazoles, mercaptodiazoles, mercaptooxathiazoles, tellurotetrazoles or benzisodiazoles. In a preferred embodiment, the inhibitor moiety or group is selected from the following formulas:



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

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

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



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

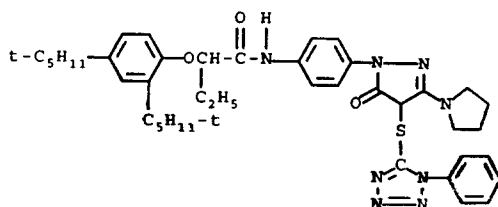
is bonded to the coupling-off position of the respective coupler moiety of the DIAR.

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

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D1

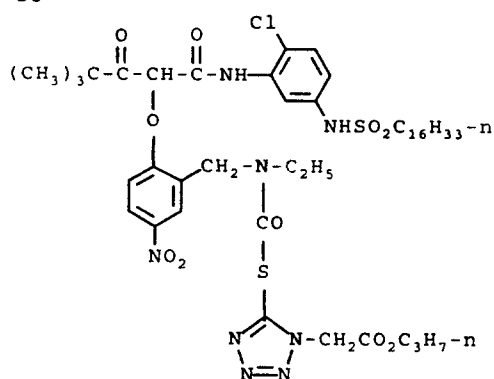
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D3

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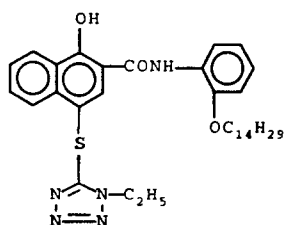


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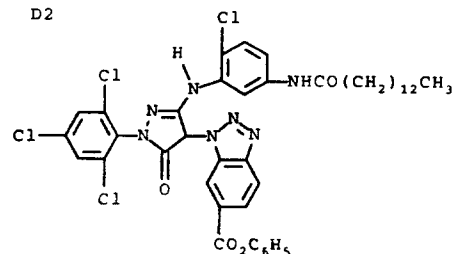
D5

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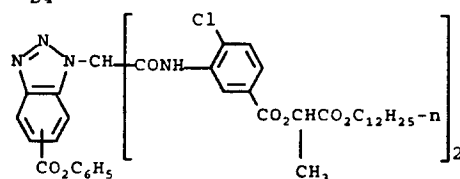


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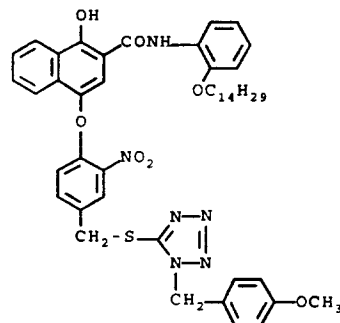
D2



D4



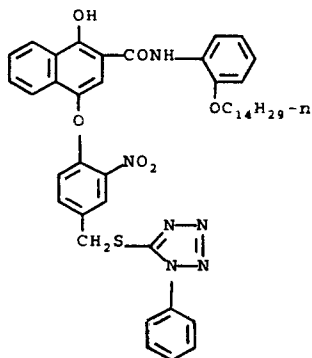
D6



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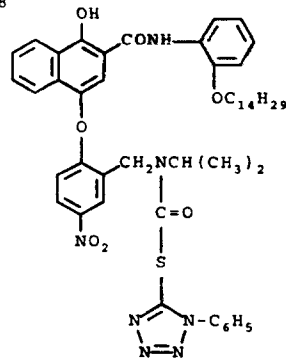
D7

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D8



Especially useful in this invention are tabular grain silver halide emulsions. Specifically contemplated tabular grain emulsions are those in which greater than 50 percent of the total projected area of the emulsion grains are accounted for by tabular grains having a thickness of less than 0.3 micron (0.5 micron

for blue sensitive emulsion) and an average tabularity (T) of greater than 25 (preferably greater than 100), where the term "tabularity" is employed in its art recognized usage as

$$T = ECD/t^2$$

where

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

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

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

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

Suitable tabular grain emulsions can be selected from among a variety of conventional teachings, such as those of the following: Research Disclosure, Item 22534, January 1983, published by Kenneth Mason Publications, Ltd., Emsworth, Hampshire PO10 7DD, England; U.S. Patent Nos. 4,439,520; 4,414,310; 4,433,048; 4,643,966; 4,647,528; 4,665,012; 4,672,027; 4,678,745; 4,693,964; 4,713,320; 4,722,886; 4,755,456; 4,775,617; 4,797,354; 4,801,522; 4,806,461; 4,835,095; 4,853,322; 4,914,014; 4,962,015; 4,985,350; 5,061,069 and 5,061,616.

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

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

With negative-working silver halide, the processing step described above provides a negative image. The described elements can be processed in the known C-41 color process as described in The British Journal of Photography Annual of 1982, pages 209 - 211 and 1988, pages 191-198. 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 followed by uniformly fogging the element to render unexposed silver halide developable. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

Preferred color developing agents are p-phenylenediamines such as:

4-amino-N,N-diethylaniline hydrochloride,

4-amino-3-methyl-N,N-diethylaniline hydrochloride,

4-amino-3-methyl-N-ethyl-N-(b-(methanesulfonamido) ethyl)aniline sesquisulfate hydrate,

4-amino-3-methyl-N-ethyl-N-(b-hydroxyethyl)aniline sulfate,

4-amino-3-b-(methanesulfonamido)ethyl-N,N-diethylaniline hydrochloride and

4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluene sulfonic acid.



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

It is understood throughout this specification and claims that any reference to a substituent by the identification of a group containing a substitutable hydrogen (e.g. alkyl, amine, aryl, alkoxy, heterocyclic, etc.), unless otherwise specifically stated, shall encompass not only the substituent's unsubstituted form, but also its form substituted with any photographically useful substituents. Usually the substituent will have less than 30 carbon atoms and typically less than 20 carbon atoms.

#### EXAMPLE 1

A cellulose triacetate film support was coated with the following layers, in sequence (coverages are in grams per meter squared) in order to prepare Photographic Sample 101:

Layer 1 (Antihalation layer): black colloidal silver sol containing 0.215 g of silver, cyan dye material CD-1 (0.032), magenta dye material MD-1 (0.022), yellow dye material YD-1 (0.129) and gelatin (2.44) were contained in this layer.

Layer 2 (Lowest Sensitivity Red-sensitive layer): This layer comprised a blend of a red-sensitized, tabular grain silver iodobromide emulsion (1.3% iodide, 0.50 microns diameter by 0.08 microns thick) (0.22) and a red-sensitized tabular grain silver iodobromide emulsion (4.1% iodide, 1.00 microns diameter by 0.09 microns thick) (0.32). A cyan dye-forming coupler C-1 (0.54) and a BAR coupler B-1 (0.09) were incorporated in this layer. Gelatin was also included (1.78).

Layer 3 (Medium Sensitivity Red-sensitive layer): This layer comprised a red-sensitized, tabular grain, silver iodobromide emulsion (4.1% iodide, 1.31 diameter by 0.12 microns thick) (0.54). This layer also comprised a cyan dye-forming coupler C-1 (0.23), a cyan dye-forming masking coupler CM-1 (0.022), DIR coupler D-1 (0.05), and a BAR coupler B-1 (0.003). Gelatin (1.66) was included.

Layer 4 (Highest Sensitivity Red-sensitive layer): This layer comprised a red-sensitized, tabular grain, silver iodobromide emulsion (4.1% iodide, 2.70 diameter by 0.13 microns thick) (1.08). This layer also comprised a cyan dye-forming coupler C-1 (0.17), a cyan dye-forming masking coupler CM-1 (0.050), DIR coupler D-1 (0.05), and a BAR coupler B-1 (0.002). Gelatin (1.36) was included.

Layer 5 (Interlayer): This layer comprised gelatin (1.33).

Layer 6 (Lowest Sensitivity Green-sensitive layer): This layer comprised a blend of a green-sensitized, tabular grain, silver iodobromide emulsion (1.3% iodide, 0.54 microns diameter by 0.08 microns thick) (0.59) and a green-sensitized, tabular grain, silver iodobromide emulsion (4.1% iodide, 1.03 microns diameter by 0.09 microns thick) (0.32). This layer also comprised a blend of magenta dye-forming couplers; M-Comp-1 (0.22) and M-Comp-2 (0.09). The layer also incorporated a BAR coupler B-2 (0.03) and gelatin (1.78).

Layer 7 (Medium Sensitivity Green-sensitive layer): This layer comprised a green-sensitized, tabular grain, silver iodobromide emulsion (4.1% iodide, 1.22 microns diameter by 0.11 microns thick) (0.97), a blend of magenta dye-forming couplers M-Comp-1 (0.09) and M-Comp-2 (0.03), and a magenta dye-forming masking coupler MM-1 (0.09). This layer also incorporated DIR coupler D-2 (0.02), BAR coupler B-1 (0.003), and gelatin (1.48).

Layer 8 (Highest Sensitivity Green-sensitive layer): This layer comprised a green-sensitized, tabular grain, silver iodobromide emulsion (4.1% iodide, 2.23 microns diameter by 0.13 microns thick) (0.97), a blend of magenta dye-forming couplers M-Comp-1 (0.09) and M-Comp-2 (0.03), and a magenta dye-forming masking coupler MM-1 (0.05). This layer also incorporated DIR coupler D-2 (0.01), DIR coupler D-3 (0.01), BAR coupler B-1 (0.003), and gelatin (1.33).

Layer 9 (Yellow filter layer): This layer comprised yellow dye material YD-2 (0.11) and gelatin (1.33).

Layer 10 (Lowest Sensitivity Blue-sensitive layer): This layer comprised a blend of a blue-sensitized, tabular grain, silver iodobromide emulsion (1.3% iodide, 0.54 microns diameter by 0.08 thick) (0.16), a blue-sensitized, tabular grain silver iodobromide emulsion (4.1% iodide, 1.02 micron diameter by 0.09 micron thick) (0.27), and a blue-sensitized, tabular grain, silver iodobromide emulsion (4.1% iodide, 1.38 microns diameter by 0.11 microns thick) (0.38). This layer incorporated a yellow dye-forming coupler Y-1 (0.91), DIR coupler D-4 (0.05), and BAR coupler B-1 (0.003), and gelatin (2.60).

Layer 11 (Highest Sensitivity Blue-sensitive layer): This layer comprised a blue-sensitized, conventional 3-D grain, silver iodobromide emulsion (9.0% iodide, 1.0 micron) (0.38) and a blue-sensitized, tabular grain, silver iodobromide emulsion (4.1% iodide, 3.53 microns diameter by 0.14 microns thick) (0.38). This layer also incorporated yellow dye-forming coupler Y-1 (0.27), DIR D-4 (0.04), BAR B-1 (0.005), and gelatin (1.97).

Layer 12 (UV filtration layer): This layer comprised dye UV-1 (0.11), UV-2 (0.11), and unsensitized silver bromide Lippmann emulsion (0.22). Gelatin was included (1.11).

Layer 13 (Protective layer): This layer comprised gelatin (0.92) and anti-matte polymethylmethacrylate beads (0.054).

This film was hardened at coating with 1.75% by weight of total gelatin of hardener H-1. Surfactants, coating aids, oxidized developer scavengers, soluble absorber dyes and stabilizers were added to the various layers of this sample as is commonly practiced in the art.

Photographic Sample 102 was prepared like Photographic Sample 101 except for changes in Layers 6, 7, and 8. Magenta dye-forming couplers M-Comp-1 and M-Comp-2 were omitted in all three layers and replaced with magenta dye-forming coupler M-1. Layer 6: M-1 (0.22) Layer 7: M-1 (0.12) Layer 8: M-1 (0.12)

Photographic Sample 103 was prepared like Photographic Sample 102 except for changes in Layers 6, 7, & 8. In all three layers, the level of M-1 was reduced and magenta dye-forming coupler M-Comp-1 was added. Layer 6: M-1 (0.11), M-Comp-1 (0.27) Layer 7: M-1 (0.05), M-Comp-1 (0.09) Layer 8: M-1 (0.05), M-Comp-1 (0.09). The blended couplers provided about 75 mol % of the comparison pyrazolotriazole coupler to 25 mol % of the magenta coupler of the invention.

The resulting film examples were exposed through a graduated step wedge to a light source at 5500 deg K. The exposed elements were processed in a standard C-41 process (as described in the British Journal of Photography Annual, 1988, pages 196-198) for the typical response to the C-41 process and also processed through 8 variations of the C-41 developer to determine sensitivity of the elements to these variations.

The 8 variations are arrived at by independently varying three separate developer parameters from standard conditions in order to determine the effect of the variation on a selected photographic property. The standard condition for the developer was:

A. color developer concentration	4.5 g/l
B. developer pH	10.05
C. bromide concentration	1.3 g/l

The above parameters were then varied as follows:

Test	A	B	C
1*	4.5	10.05	1.3
2	3.5	9.95	0.8
3	5.5	9.95	0.8
4	3.5	10.15	0.8
5	5.5	10.15	0.8
6	3.5	9.95	1.8
7	5.5	9.95	1.8
8	3.5	10.15	1.8
9	5.5	10.15	1.8

\* This is the target or normal value of each of the parameters.

Thus the extremes for each variable were tested with all possible combinations of the extremes for the other two variables. With the nine developer responses, the dependent variables (red, green, blue color densities, color gamma, speed, etc.) were regressed through the nine developer concentrations (CD-4, Br-, pH) which resulted in estimates of sensitivity per color record (sensitivity is expressed as a delta per 2 sigma of the average trade concentration for a given component). For the photographic elements 101 and 102, the results are tabulated below for two photographic parameters: normal gamma (defined as the contrast, by record, throughout the normal (typical) exposure region of the element) and over color (density) balance (defined as density, by record, in the overexposure region (2 stops above normal) of the element). Both parameters are critical for a photofinisher to correctly achieve a balanced print.

**TABLE I****NORMAL GAMMA SENSITIVITY**

	Br-			pH			CD-4		
	R	G	B	R	G	B	R	G	B
#101 (comparison)	-0.06	-0.05	-0.07	0.04	0.14	0.06	0.09	0.08	0.08
Divergence	----- .02 -----			----- 0.10 -----			----- .01 -----		
#102 (invention)	-0.06	-0.08	-0.07	0.04	0.08	0.06	0.09	0.09	0.08
Divergence	----- .02 -----			----- .04 -----			----- .01 -----		

**TABLE II****OVER COLOR BALANCE SENSITIVITY**

	Br-			pH			CD-4		
	R	G	B	R	G	B	R	G	B
#101 (comparison)	-0.14	-0.12	-0.16	0.06	0.18	0.11	0.15	0.14	0.15
Divergence	----- .04 -----			----- .12 -----			----- .01 -----		
#102 (invention)	-0.14	-0.15	-0.16	0.06	0.11	0.11	0.15	0.15	0.15
Divergence	----- .02 -----			----- .05 -----			----- .00 -----		

As described above, it is desirable for the sensitivity estimates to approach zero for all developer components and to be as closely matched Red-to-Green-to-Blue as possible. The data indicate the invention provides an improvement in this regard for sensitivity to both Br- and pH variations while maintaining a well-balanced response to CD-4.

**EXAMPLE 2**

The three photographic elements (#101, #102, #103) were then tested for their sensitometric response in a cross-section of photofinishing trade sites (50 sites evaluated). Exposed film (exposed as in example 1) was taken to the 50 sites and processed in their currently running C-41 process. A ternary plot was generated for the above red, green, and blue sensitometric responses (normal gamma balance and over color balance were plotted.) Statistical information concerning the effect of developer variations in actual field conditions was generated. A 95% confidence interval ellipse was estimated for each of the data sets on the ternary plots. The area of each ellipse was measured and the results are recorded in Table III. The larger the area, the larger the variability for the particular parameter.

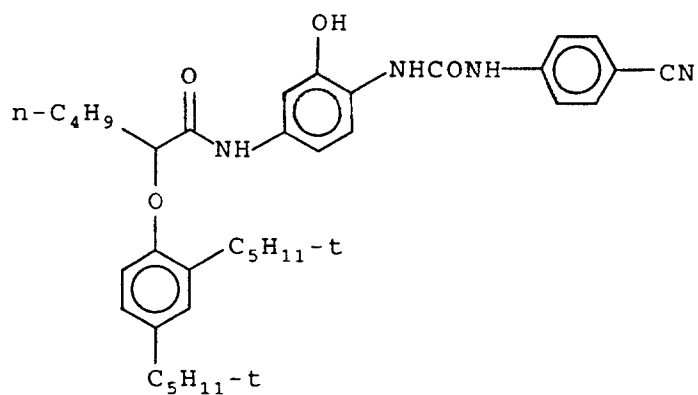
TABLE III

PHOTOFINISHING TRADE RESPONSE		
	Normal Gamma Balance	Over Color Balance
#101 (comparison)	2701	7913
#102 (invention)	674	2543
#103 (comparison)	2701	8783

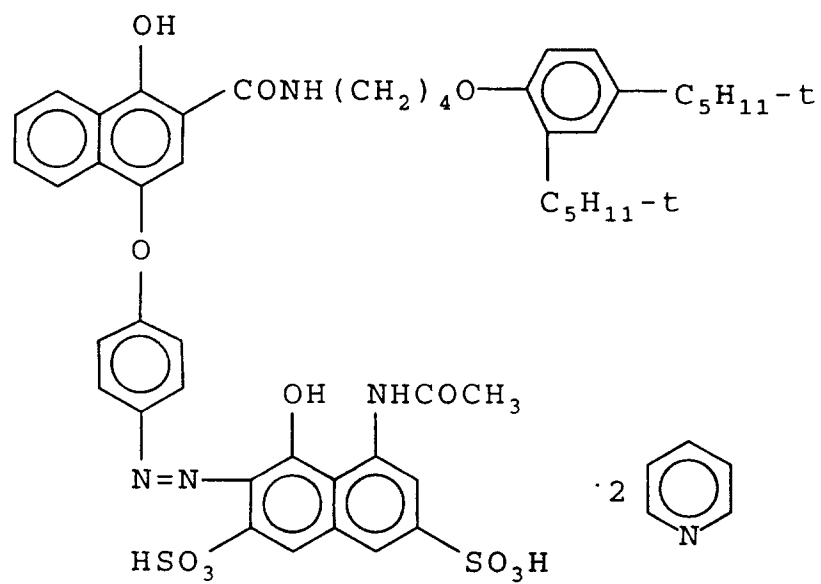
The data indicate a large improvement is realized with the invention (75% reduction in ellipse area for gamma balance and at least a 68% reduction ellipse area for color balance; ideally, the area of the ellipse would be zero). This example also demonstrates that when the comparison pyrazolotriazole coupler is used in combination with the coupler of the invention in a mol ratio of 3 : 1, respectively, the desired response is not obtained. The improvement is not realized when a pyrazolotriazole coupler is included in an amount exceeding the molar concentration of the invention coupler. Preferably, the element is substantially free of the pyrazotriazole coupler.

## Compound formulas for Examples

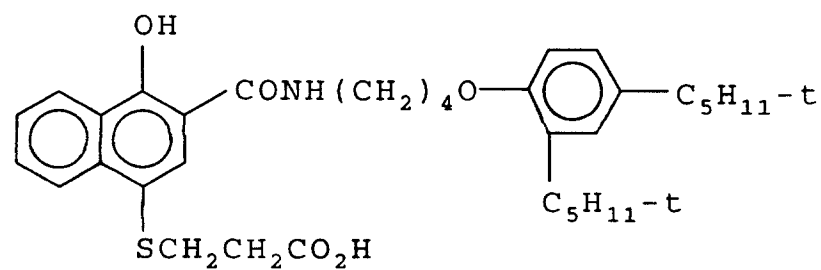
C-1:



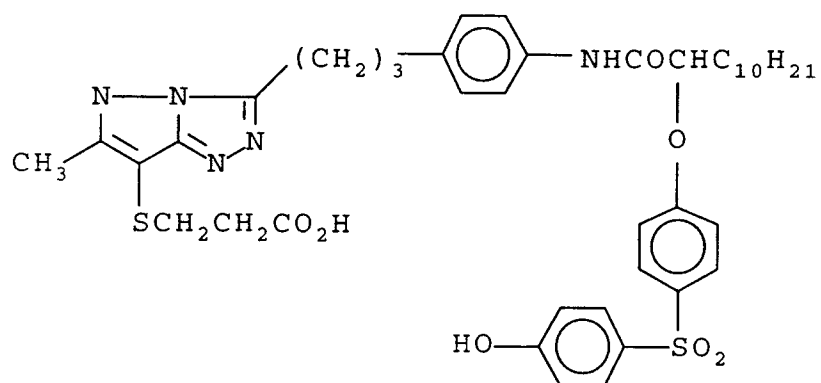
CM-1



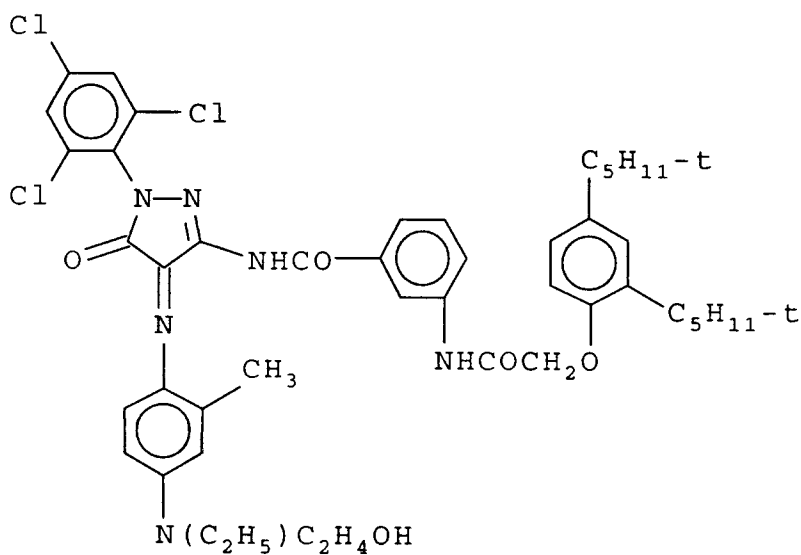
B-1



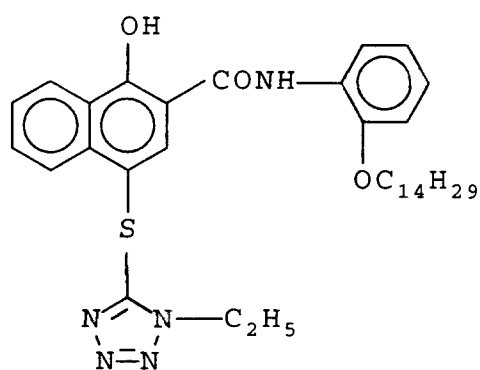
B-2



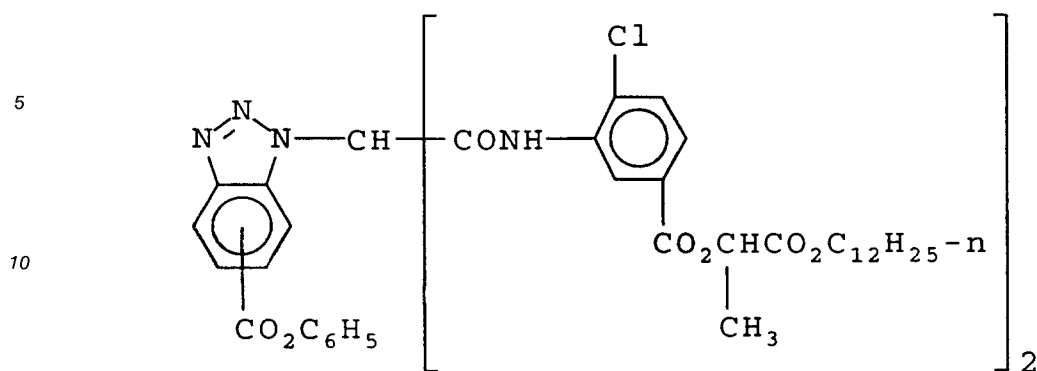
MD-1



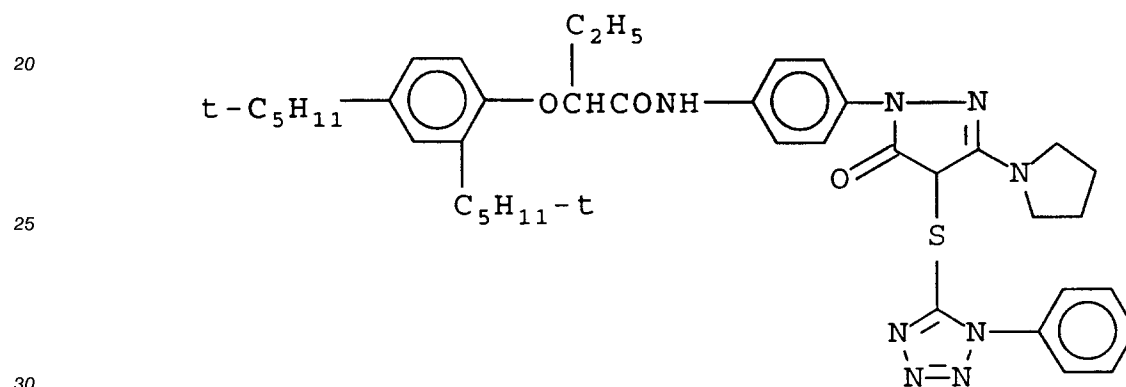
D-1



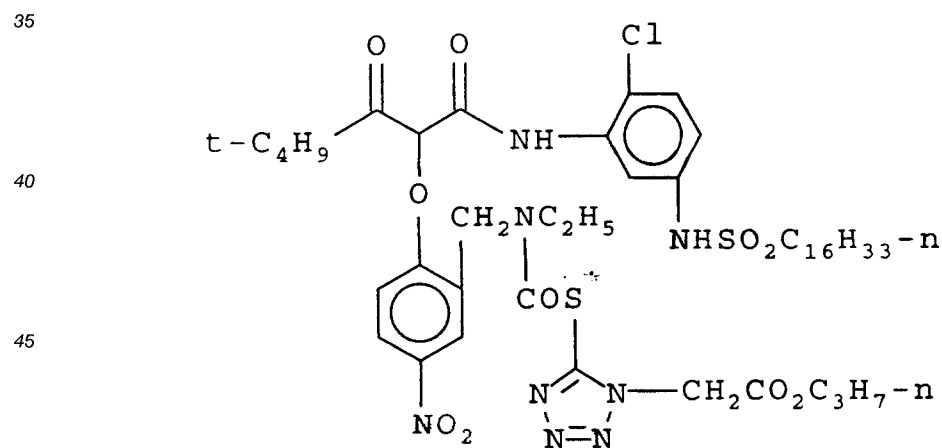
D-2:



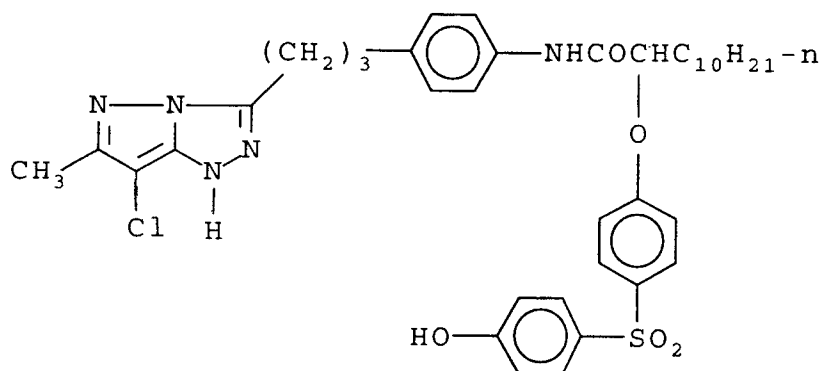
D-3:



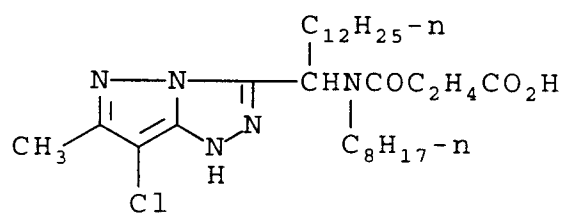
D-4



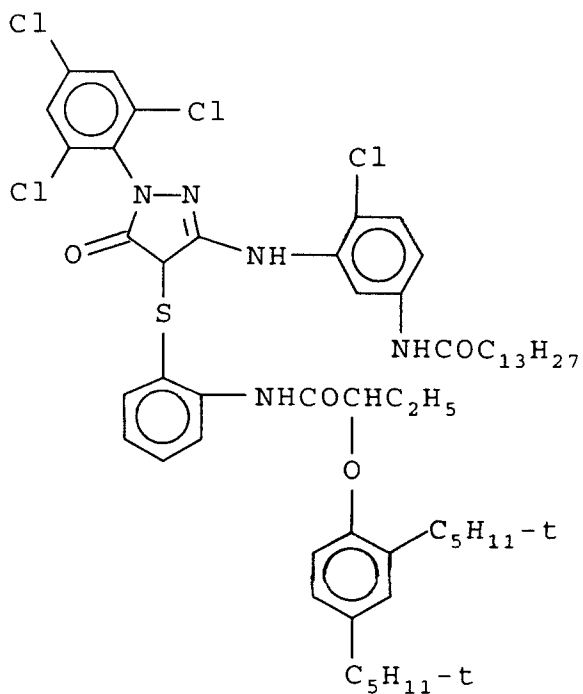
M-Comp-1:



M-Comp-2:



M-1:





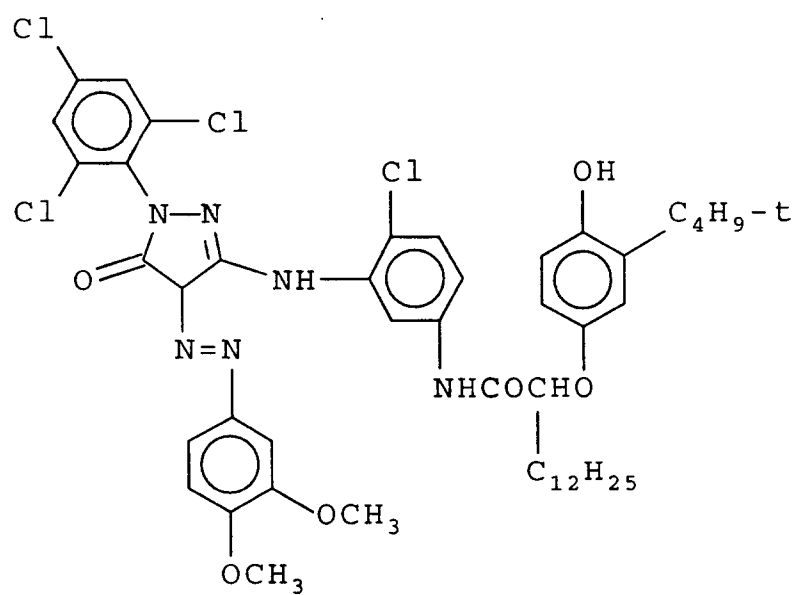
MM-1

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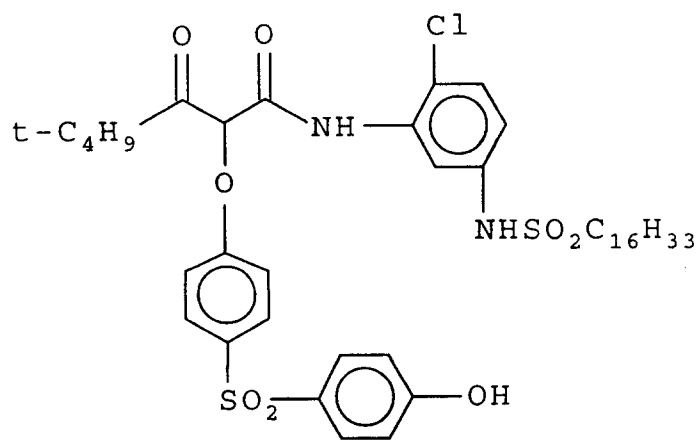
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Y-1:

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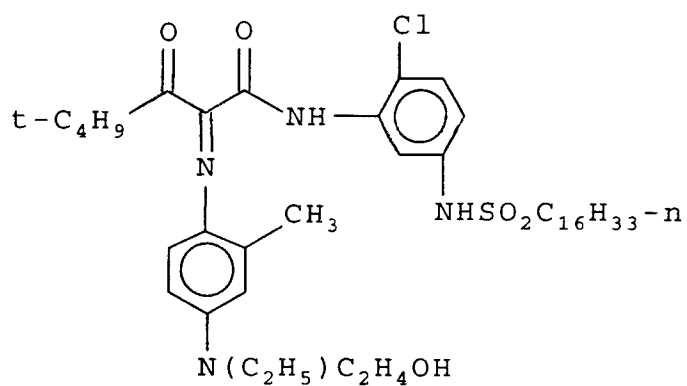


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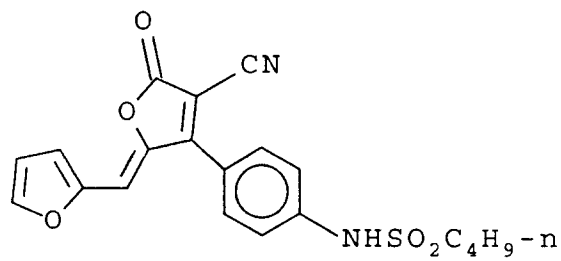
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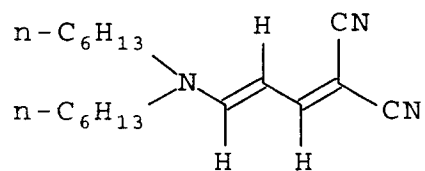
YD-1:



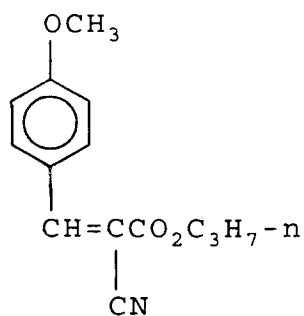
YD-2:



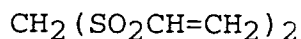
UV-1:



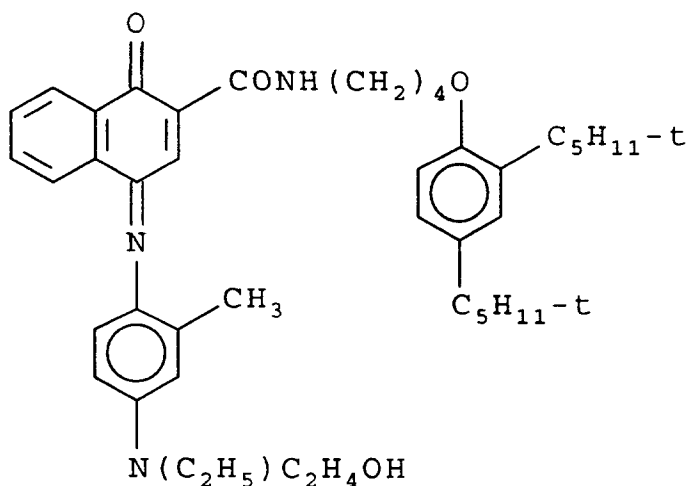
UV-2:



H-1:

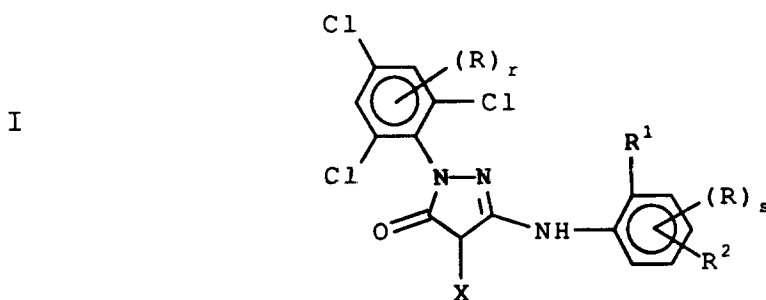


CD-1:



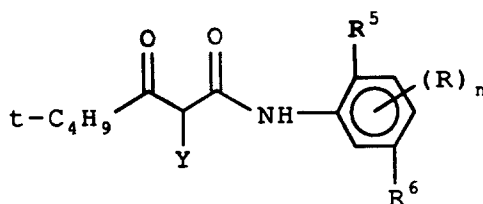
## Claims

1. A photographic element comprising at least one light sensitive silver halide layer sensitized to one or more of green, blue, and red light, and having associated therewith a 3-anilino-1-phenyl-5-pyrazolone magenta dye-forming coupler, a two-equivalent trialkylacetylacetanilide yellow dye-forming coupler, and a 2-ureido-5-carbonamidophenol cyan dye-forming coupler.
2. The element of Claim 1 wherein the element contains at least one green sensitive layer containing the magenta coupler, at least one blue sensitive layer containing the yellow coupler, and at least one red sensitive layer containing the cyan coupler.
3. The element of Claim 2 wherein said magenta coupler is represented by formula I, said yellow coupler is represented by formula II, and said cyan coupler is represented by formula III:

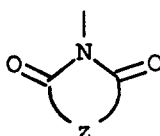


wherein  $R^1$  and  $R^2$  are independently hydrogen, halogen, trifluoromethyl, cyano, nitro, or substituted or unsubstituted alkyl, alkoxy, aryloxy, alkylthio, carbonamido, carbamoyl, sulfonamido, sulfamoyl, alkylsulfonyl, arylsulfonyl, alkoxycarbonyl, acyloxy, and acyl groups; each R is independently a substituent with r being 0 to 2 and s being 0 to 3 and X is a substituted or unsubstituted arylthio or alkylthio group;

II

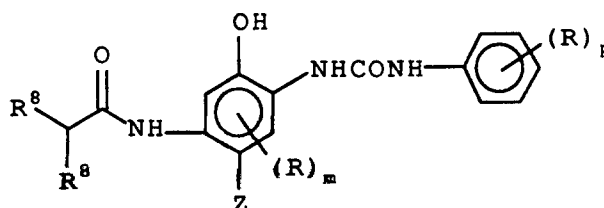


wherein  $R^5$  and  $R^6$  are independently hydrogen, halogen, cyano, nitro, trifluoromethyl, or substituted or unsubstituted alkyl, alkoxy, aryloxy, alkylthio, carbonamido, carbamoyl, sulfonamido, sulfamoyl, alkylsulfonyl, arylsulfonyl, alkoxycarbonyl, acyloxy, and acyl groups; each R is independently a substituent with n being 0 to 3; and Y is an aryloxy group or a substituted or unsubstituted imidazole, pyrazole, or heterocyclic group represented by the formula:



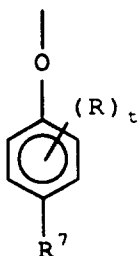
wherein z represents the atoms necessary to complete a heterocyclic ring;

III



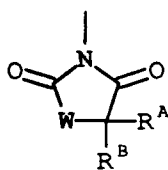
wherein each  $R^8$  is independently a substituted or unsubstituted alkyl, alkoxy, aryloxy, alkylthio, carbonamido, aryl, carbamoyl, sulfonamido, sulfamoyl, alkylsulfonyl, arylsulfonyl, acyloxy, acyl, or alkoxycarbonyl group; each R is independently a substituent with m being 0 to 2 and p being 0 to 5; and Z is hydrogen or a coupling-off group.

4. The element of Claim 3 wherein Y is represented by the formula:



wherein  $R^7$  is selected from the group consisting of hydrogen, halogen, cyano, nitro, trifluoromethyl and substituted or unsubstituted alkyl, alkoxy, alkylthio, carbonamido, carbamoyl, sulfonamido, sulfamoyl, alkylsulfonyl, arylsulfonyl, alkoxycarbonyl, acyloxy, and acyl groups and each R is independently a substituent with t being 0 to 4;

or by the formula:



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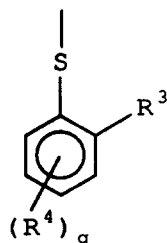
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wherein W is -O-, -S-, -N(R<sup>C</sup>)-, or -C(R<sup>D</sup>)(R<sup>E</sup>)-; R<sup>A</sup> is H, or substituted or unsubstituted alkyl, alkoxy, phenyl, or phenoxy; R<sup>B</sup> and R<sup>E</sup> are independently H or substituted or unsubstituted alkyl; R<sup>C</sup> is substituted or unsubstituted alkyl or phenyl; and R<sup>D</sup> is H or substituted or unsubstituted alkyl or alkoxy.

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5. The element of Claim 4 wherein Y is a heterocycle having the second formula shown in Claim 5 and in which W is -NR<sup>C</sup>; R<sup>A</sup> is H, or substituted or unsubstituted alkyl or alkoxy; R<sup>B</sup> is H; and R<sup>C</sup> is substituted or unsubstituted alkyl.
6. The element of any of claims 3-5 wherein X is other than hydrogen
7. The element of any of claims 3-6 wherein X is represented by the formula:

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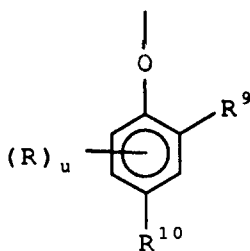
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wherein R<sup>3</sup> and R<sup>4</sup> are individually hydrogen, halogen, carboxyl, or substituted or unsubstituted alkyl, alkoxy, aryloxy, carbonamido, ureido, carbamate, sulfonamido, carbamoyl, sulfamoyl, acyloxy, alkoxycarbonyl, aryloxycarbonyl, and amino groups; q is 0 to 3; and R<sup>4</sup> may be para and/or meta to the sulfur atom.

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8. The element of any of claims 3-7 wherein each individual R<sup>8</sup> is represented by the formula:



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wherein, R<sup>9</sup> and R<sup>10</sup> are alkyl; each R is independently a substituent with u being 0 to 3; and wherein Z is hydrogen or alkoxy.

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9. A process for forming an image from an exposed element as claim in any of claims 1-8 comprising contacting said element with a color developing agent.

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European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 94 20 0186

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
P,X	EP-A-0 539 024 (KONICA CORPORATION) 28 April 1993 * example 1 *	1,2,9	G03C7/32
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P,X	EP-A-0 539 023 (KONICA CORPORATION) 28 April 1993 * example 1 *	1,2,9	
	---		
A	EP-A-0 329 016 (AGFA-GEVAERT AG) 23 August 1989 * page 3, line 1 - page 3, line 14 * * examples 1,2 *	1,9	
	-----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			G03C
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 9 May 1994	Examiner Markowski, V
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document			