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(54) Photographic element and process employing a combination of yellow couplers.

(57) A photographic element and process employ a light sensitive photographic silver halide layer sensitized to blue light and having associated therewith a combination of at least two yellow dye-forming couplers each containing an acylacetanilide parent, one of which comprises a phenolic coupling-off group containing a solubilizing substituent, and the other of which is a benzoylacetanilide comprising a heterocyclic coupling-off group.

EP 0 608 957 A1

Field of the Invention

This invention relates to the silver halide photographic art and more specifically to a photographic element and process which employ a particular combination of yellow dye-forming couplers.

Background of the Invention

The use of t-alkylacylacetanilide couplers (Type I), such as pivaloylacetanilides, with phenolic coupling-off groups in photographic elements is well established. However, in combination with a Development Inhibitor Releasing (DIR) coupler, these Type I couplers produce a photographic element with limited exposure latitude.

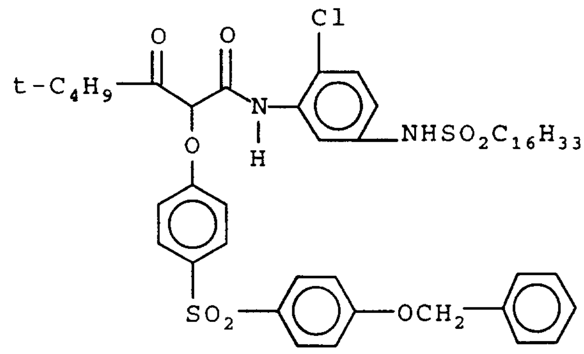
The term latitude is used to describe the ability of a photographic element to provide an acceptable image across a range of exposure levels. It is believed that these Type I couplers with phenolic coupling-off groups are not effectively balanced for competition with the DIR coupler to form dye. To overcome the limited exposure latitude, additional coupler laydown is required, but this added laydown of coupler dispersion with solvent, gel and coupler results in increased light scattering and optical degradation. This degradation is especially amplified when the scattering takes place in an uppermost color record where the effect of scattering is transferred throughout the element. Alternatively, the silver laydown can be increased to extend the latitude which also leads to increased light scatter and optical degradation in the underlying layers (once again, especially critical in an uppermost layer). In addition, yellow dye-forming elements can be comprised of two or more layers of differing exposure sensitivities. The exposure linearity of the combination of these two photographic layers is less than desired with the use of Type I couplers with phenolic coupling-off groups in combination with DIR couplers. Failure of the coupler to compete optimally with the DIR coupler results in the speed of the underlying layer being reduced which in turn results in a curve shape non-linearity. Correction of the resulting non-linearity requires larger emulsions which exhibit inferior granularity.

The use of arylacylacetanilide couplers (Type II), such as benzoylacetanilides, with heterocyclic coupling-off groups has also been used in photographic elements. Advantages realized with the use of such Type II couplers with heterocyclic coupling-off groups include better reactivity matching with DIR couplers (see U.S. 4,980,267). A superior reactivity match with DIR couplers also leads to lower coupler laydown. Additionally, improved curve linearity with smaller grain-size emulsions result when two or more layers of differing sensitivity are coated. If the underlying of two or more layers uses such a coupler it competes effectively with DIR couplers and results in optimal photographic speed.

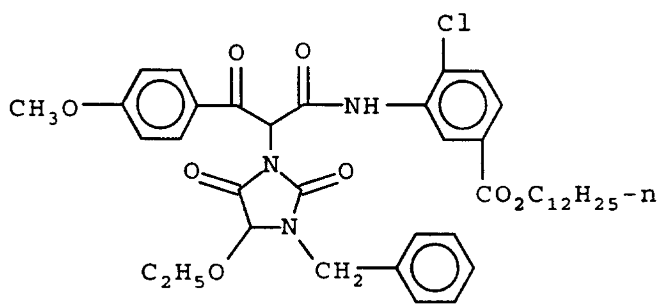
However, the use of these Type II couplers leads to problems with continued coupling which causes increases in blue minimum density levels in seasoned, high pH bleaches. In addition, the use of the Type II couplers in high pH color negative developers can lead to mismatched red, green and blue contrasts. While the red and green photographic elements respond with contrast changes to varying developer pH values, a Type II coupler is essentially insensitive to pH levels. This mismatch results in color degradation because the printer is unable to compensate for three individual records because the contrasts of the three individual records do not vary synchronously.

Combination of Type I couplers with either heterocyclic coupling-off groups or phenolic coupling-off groups without a solubilizing substituent together with Type II couplers with heterocyclic coupling-off groups are known in color negative films. For example, the following combination has been employed in a product:

CP-1



CP-2



CP-1 was present at 57 mol % and CP-2 at 43 mol % and the combination was employed in a single blue-sensitive layer. Coupler CP-1 does not contain a solubilizing group as in the invention. The combination of these two couplers did not provide balanced reactivity and therefore linearity, laydown, and color rendition were not optimum.

The lower reactivity of the Type I couplers with heterocyclic coupling-off groups results in a situation where reactivity matches with DIR couplers are not optimized, and, thus, laydowns are higher than necessary. In order to provide the needed exposure latitude, additional coupler laydown is required. Additional coupler dispersion with solvent, gel and coupler results in layer thickness increases and subsequent light scattering and optical degradation and the same problems present in the art for the use of a Type I coupler only are realized.

It is a problem to be solved to provide a photographic element and process which provides an improved linearity of response in the blue record across the range of exposures while maintaining the desired level of sharpness.

Summary of the Invention

A photographic element and process employ a light sensitive photographic silver halide layer sensitized to blue light and having associated therewith a combination of at least two yellow dye-forming couplers each containing an acylacetanilide parent, one of which comprises a phenolic coupling-off group containing a solubilizing substituent, and the other of which is a benzoylacetanilide comprising a heterocyclic coupling-off group.

By combining the use of a Type I coupler comprising a phenolic coupling-off group containing a solubilizing substituent together with a Type II coupler comprising a heterocyclic coupling-off group, significant benefits are realized in terms of linearity and sharpness while minimizing the limitations that these separate types would normally cause when used alone and such results are generally obtained at lower laydown levels then heretofore achievable.

Detailed Description of the Invention

The photographic element of the invention comprises at least two yellow image-dye forming couplers which suitably have the respective formulas:

I RC(=O)CHC(=O)NHPh
        |
        X

and

II PhC(=O)CHC(=O)NHPh
        |
        Y

wherein X has the formula -OPh(L)$_n$Sol, and wherein R is a substituted or unsubstituted aryl group or a fully substituted carbon atom, each Ph is a phenyl ring, independently substituted or not, Sol is a water solubilizing substituent, L is a divalent group linking the phenyl ring and Sol, n is 0 or 1, and Y is a heterocyclic ring, substituted or not.

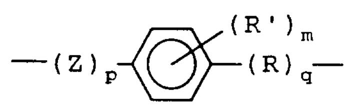
More suitable R groups are phenyl, t-butyl, t-pentyl, t-octyl, and adamantyl with phenyl and t-butyl most suitable.

The Ph is a phenyl group which may be optionally substituted. Any substituents may be suitable such as those illustrated in the example couplers.

L is a linking group which may or may not be present. Such a group does not necessarily play any major role in the photographic properties but may affect properties such as ballasting. Examples of suitable linking groups are:

-R^a-
--SO$_2$N(R^b)R^a-
-COOR^a-
-COO-
and

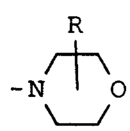
-SR^a-
-N(R^b)COR^a-
-COOCOR^a-



wherein Z represents -O-; -SO$_2$-; -S- ;or -NR^{b}SO$_2$-and each R, R', R^a and R^b independently represents an alkyl group, substituted or not, and R^b may be hydrogen. Further, n, p, and q may be 0 or 1, signifying the presence or absence of the linking group and the presence or absence of the specified linking group components. m may be from 0 to 4.

The Sol group is a water solubilizing substituent. Any strongly polar or readily ionizing group or one highly susceptible to hydrogen bonding can have this effect as is well-known. Suitable general examples are:

-OH, -NHSO$_2$R, -NHCOR, -NHCOCF$_3$, -NHCOOR, -NR$_2$, -NHCONR$_2$, -CONR$_2$, -CONHSO$_2$R, -SO$_3$H, -CO$_2$R, -(OR)$_n$, -OSO$_2$R, -P(O)0R$_2$, and

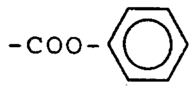
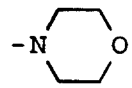


;

wherein each R is an independently selected substituent or hydrogen, and n is 0 to 3.

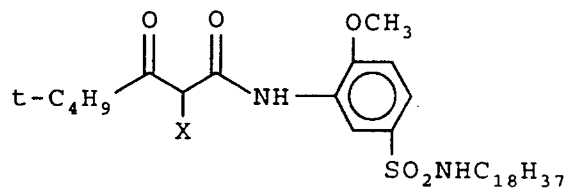
Examples of suitable specific solubilizing substituents are:

-COOH; -COOCH$_3$; -COOC$_2$H$_5$; -NHSO$_2$CH$_3$; -SO$_3$H; -OH; -SO$_2$NHCH$_3$; -SO$_2$NH$_2$;

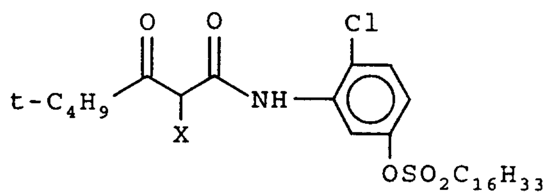
 ; and  .

Illustrative examples of Type I couplers are:

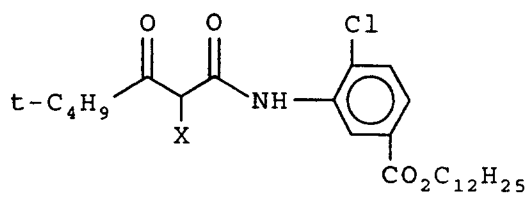
IA



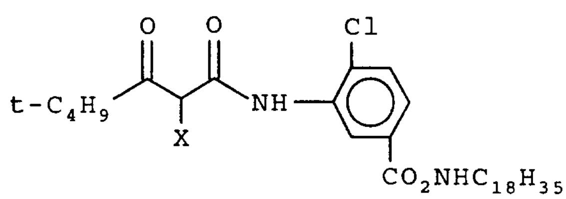
IB



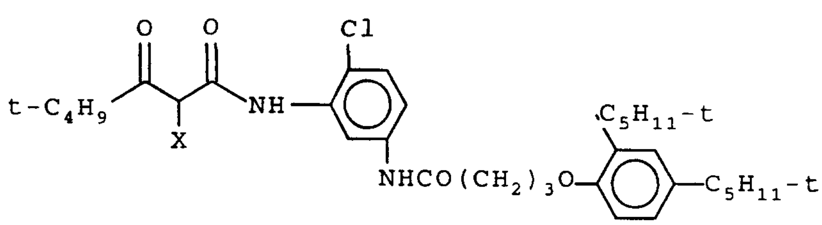
IC



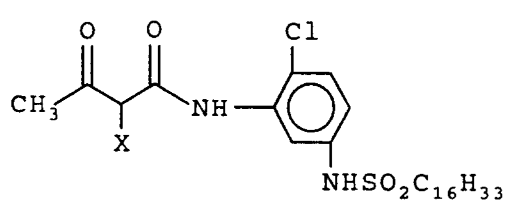
ID



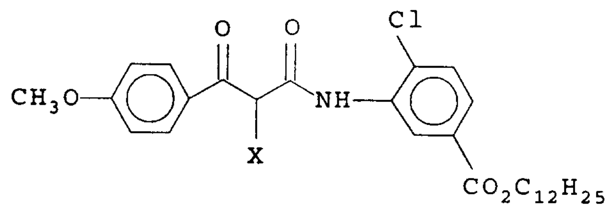
IE



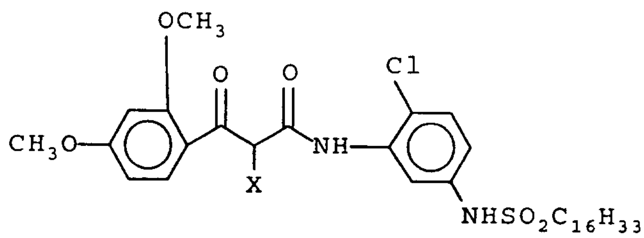
IF



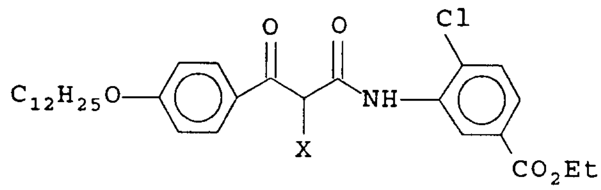
IG



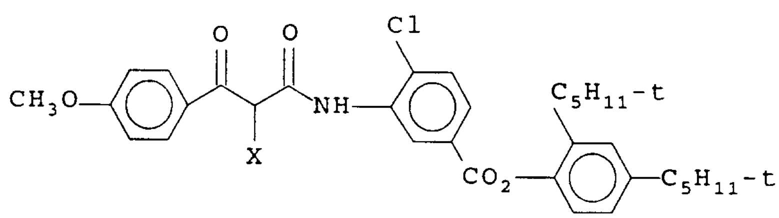
IH



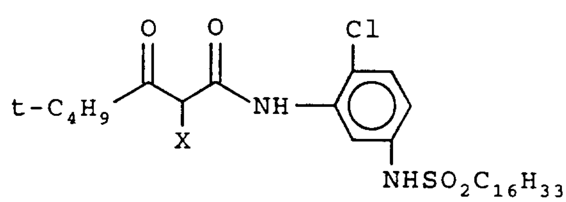
II



IJ



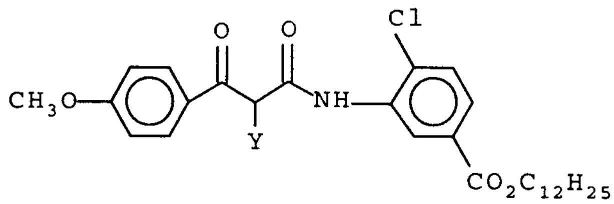
IK



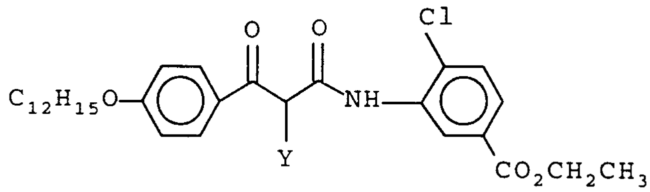
The generic definition of the Type I parent group is broad enough to include all of those parents of the Type II parents. On the other hand, the Type II parent is more narrowly defined. As detailed, the coupling-off groups for the two types are mutually distinct.

Illustrative examples of Type II couplers are as follows:

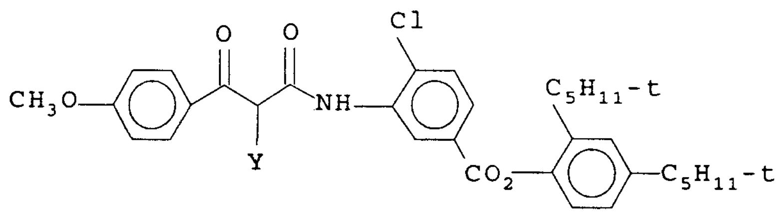
IIA



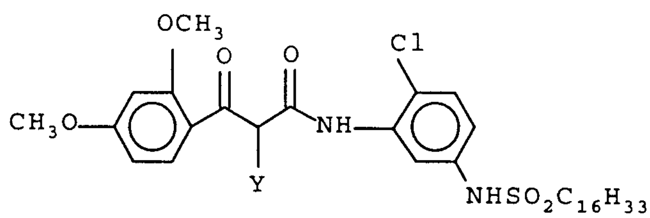
IIB



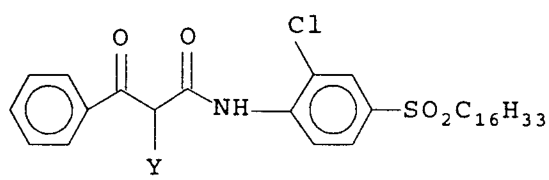
IIC



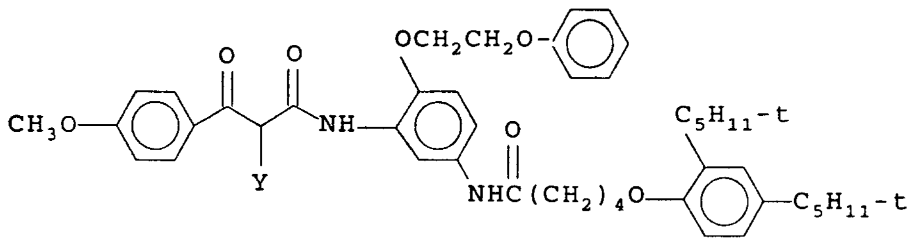
IID



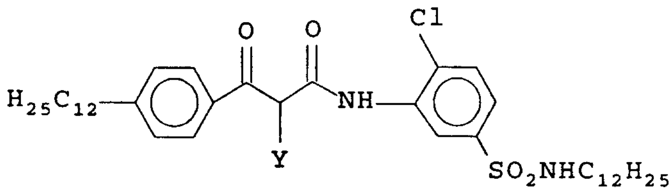
IIE



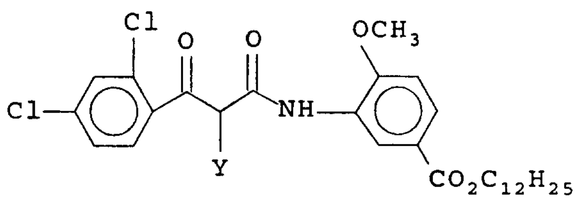
IIF



IIG

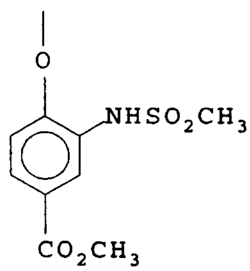


IIH

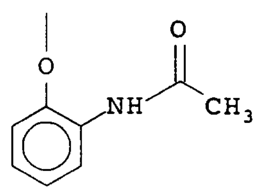


The phenolic coupling-off group in the Type I coupler may, if desired, contain one or more substituents on the phenoxy ring aside from the substituent containing the solubilizing group. These substituents may be any which are useful in the photographic arts as described hereafter. Illustrative examples of the phenolic coupling-off groups useful on the Type I couplers are as follows:

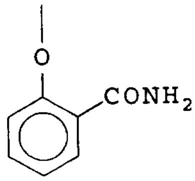
Ia



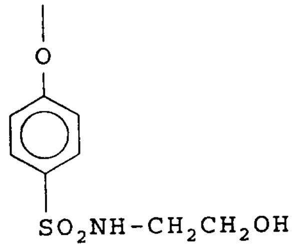
Ib



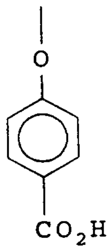
Ic



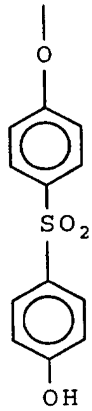
Id



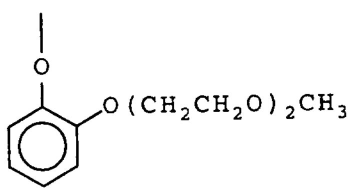
Ie



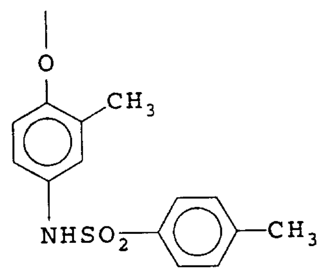
If



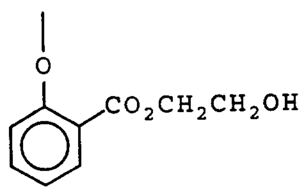
Ig



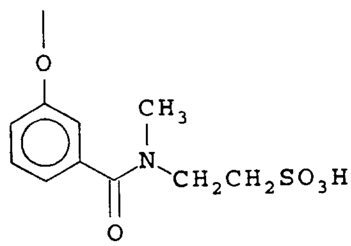
Ih



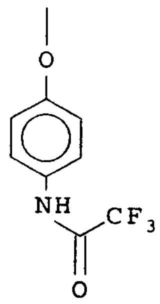
Ii



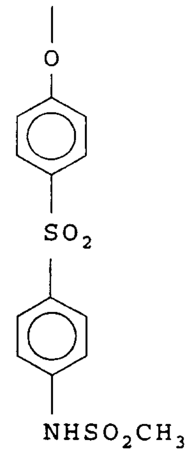
Ij



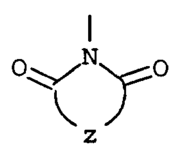
Ik



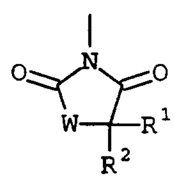
Il



The Y group in formula II represent a heterocyclic coupling-off group. Such a group is typically connected through a carbon or nitrogen atom in the heterocycle. Nitrogen is the preferred connecting link and in such case, Y 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. The compounds having this formula are typically hydantoin or succinimide compounds. In one specific embodiment, Y may be represented by the formula:

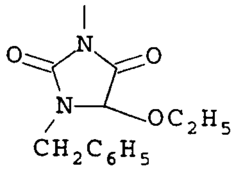


wherein W is -O-, -S-, -N(R^3)-, or -C(R^4)(R^5)-; R^1 is H, or substituted or unsubstituted alkyl, alkoxy, phenyl, or phenoxy; R^2 and R^5 are independently H or substituted or unsubstituted alkyl; R^3 is substituted or unsubstituted alkyl or phenyl; and R^4 is H or substituted or unsubstituted alkyl or alkoxy.

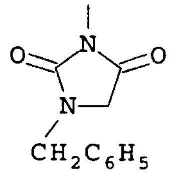
In one more specific embodiment of the above formula, W is -NR^3; R^1 is H, or substituted or unsubstituted alkyl or alkoxy; R^2 is H; and R^3 is substituted or unsubstituted alkyl. In particular, R^1 is -OC_2H_5, R^2 is H and R^3 is -CH_2-phenyl. In another specific embodiment, W is -C(R^4)(R^5) with R^1, R^2, R^4, and R^5 defined as above.

Illustrative examples of the Type II heterocyclic coupling-off groups are as follows:

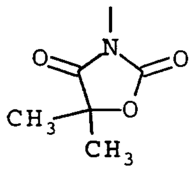
IIa



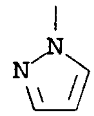
IIb



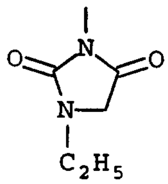
IIc



IId



IIe



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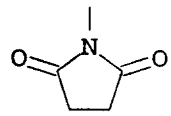
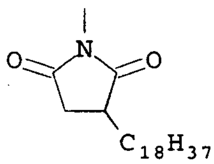
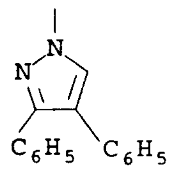


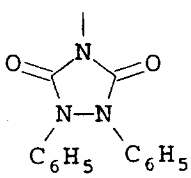
IIg



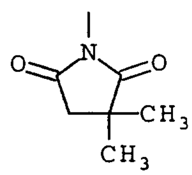
IIh



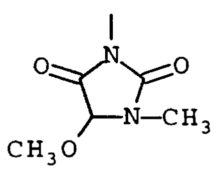
IIi



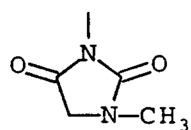
IIj



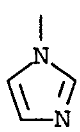
IIk



IIl



IIm



Suitable combinations of parent and coupling-off groups for Type I and Type II couplers are as shown in Tables I and II.

Table I

Type I Coupler Parent/Coupling-off Group Combinations					
No.	Combination	No.	Combination	No.	Combination
1	IK/f	2	IK/a	3	IK/d
4	IG/f	5	II/a	6	IC/d
7	IB/e	8	IC/i	9	ID/h
10	IE/g	11	IF/k	12	IG/b
13	II/c	14	IG/j	15	IH/l
16	IA/h	17	IA/d	18	IJ/b
19	IH/a	20	IJ/i	21	IB/j
22	ID/e	23	IF/i	24	IE/k

Table II

Type II Coupler Parent/Coupling-off Group Combinations					
No.	Combination	No.	Combination	No.	Combination
1	IIA/a	2	IIA/i	3	IIA/b
4	IIB/d	5	IIB/a	6	IIB/e
7	IIB/b	8	IIC/i	9	IIC/c
10	IIC/f	11	IIC/a	12	IID/g
13	IID/i	14	IID/b	15	IIA/c
16	IIE/a	17	IIE/h	18	IIE/i
19	IIF/b	20	IIF/c	21	IIG/a
22	IIG/d	23	IIH/e	24	IIH/b
25	IIC/j	26	IIA/k	27	IID/l

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-tetradecyl-pyrrolin-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,Ndipropylsulfamoylamino, 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, tetradecyloxycarbonyl, ethoxycarbonyl, benzyloxycarbonyl, 3-pentadecyloxycarbonyl, and dodecyloxycarbonyl; 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 cyclohexylcarbonyloxy; 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-benzothiazolyl; ; 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.

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 42 carbon atoms. Representative substituents on such groups include alkyl, aryl, alkoxy, aryloxy, alkylthio, hydroxy, halogen, alkoxycarbonyl, aryloxcarbonyl, carboxy, acyl, acyloxy, amino, anilino, carbonamido, carbamoyl, alkylsulfonyl, arysulfonyl, sulfonamido, and sulfamoyl groups wherein the substituents typically contain 1 to 42 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 P010 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 VII 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.

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 1988, pages 191-198.

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-(β-(methanesulfonamido) ethyl)aniline sesquisulfate hydrate,
4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline sulfate,
4-amino-3-β-(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.

Examples

The following examples will serve to better describe the invention. The formulas for the component materials are provided following the examples.

A color photographic recording material (Photographic Sample 101) for color negative development was prepared by applying the following layers in the given sequence to a transparent support of cellulose triacetate. The quantities of silver halide are given in g of silver per m^2. The quantities of other materials are given in g per m^2.

Layer 1 {Antihalation Layer} black colloidal silver sol containing 0.22 g of silver with 2.44 g gelatin.

Layer 2 {First (least) Red-Sensitive Layer} Red sensitized silver iodobromide emulsion [1.3 mol % iodide, average grain diameter 0.55 microns, average thickness 0.08 microns] at 0.43 g, red sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 1.0 microns, average thickness 0.09 microns] at 0.43 g, cyan dye-forming image coupler C-1 at 0.56 g, cyan dye-forming masking coupler CM-1 at 0.028 g, Bleach Accelerator Releasing (BAR) compound B-1 at 0.039 g with gelatin at 1.83 g.

Layer 3 {Second (more) Red-Sensitive Layer} Red sensitive silver iodobromide emulsion [4 mol % iodide, average grain diameter 1.3 microns, average grain thickness 0.12 microns] at 0.72 g, cyan dye-forming image coupler C-1 at 0.23 g, cyan dye-forming masking coupler CM-1 at 0.022 g, DIR compound D-1 at 0.011 g with gelatin at 1.66 g.

Layer 4 {Third (most) Red-Sensitive Layer} Red sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 2.6 microns, average grain thickness 0.13 microns] at 1.11 g, cyan dye-forming image coupler C-1 at 0.13 g, cyan dye-forming masking coupler CM-1 at 0.033 g, DIR compound D-1 at 0.022 g, DIR compound D-2 at 0.050 g with gelatin at 1.36 g.

Layer 5 {Interlayer} Yellow dye material YD-1 at 0.11 g and 1.33 g of gelatin.

Layer 6 {First (least) Green-Sensitive Layer} Green sensitized silver iodobromide emulsion [1.3 mol % iodide, average grain diameter 0.55 microns, average grain thickness 0.08 microns] at 0.59 g, green sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 1.0 microns, average grain thickness 0.09 microns] at 0.34 g, magenta dye-forming image coupler M-1 at 0.24 g, magenta dye-forming masking coupler MM-1 at 0.067 g with gelatin at 1.78 g.

Layer 7 {Second (more) Green-Sensitive Layer} Green sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 1.25 microns, average grain thickness 0.12 microns] at 1.00 g, magenta dye-forming image coupler M-1 at 0.089 g, magenta dye-forming masking coupler MM-1 at 0.067 g, DIR compound D-1 at 0.024 g, DIR compound D-3 at 0.006 g with gelatin at 1.48 g.

Layer 8 {Third (most) Green-Sensitive Layer} Green sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 2.16 microns, average grain thickness 0.12 microns] at 1.00 g, magenta dye-forming image coupler M-1 at 0.067 g, magenta dye-forming masking coupler MM-1 at 0.056 g, DIR compound D-3 at 0.006 g, DIR compound D-4 at 0.018 g with gelatin at 1.33 g.

Layer 9 {Interlayer} Yellow dye material YD-2 at 0.11 g with 1.33 g gelatin.

Layer 10 {First (less) Blue-Sensitive Layer} Blue sensitized silver iodobromide emulsion [1.3 mol % iodide, average grain diameter 0.55, average grain thickness 0.08 microns] at 0.22 g, blue sensitized silver iodobromide emulsion [6 mol % iodide, average grain diameter 1.0 microns, average grain thickness 0.26 microns] at 0.58 g, yellow dye-forming image coupler Y-1 at 0.29 g, yellow dye forming image coupler Y-2 at 0.72 g, DIR compound D-5 at 0.067 g, BAR compound B-1 at 0.003 g with gelatin at 2.6 g.

Layer 11 {Second (more) Blue-Sensitive Layer} Blue sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 3.0 microns, average grain thickness 0.14 microns] at 0.23 g, blue sensitized silver iodobromide emulsion [9 mol % iodide, average grain diameter 1.0 microns] at 0.59 g, yellow dye-forming image coupler Y-1 at 0.092 g, yellow dye-forming image coupler Y-2 at 0.23 g, DIR compound D-5 at 0.051 g, BAR compound B-1 at 0.006 g with gelatin at 1.97 g.

Layer 12 {Protective Layer} 0.111 g of dye UV-1, 0.111 g of dye UV-2, unsensitized silver bromide Lippmann emulsion at 0.222 g, Cyan dye material CD-1 at 0.007 g with gelatin at 1.11 g.

Layer 13 {Protective Layer} Gelatin at 0.92 g.

This film was hardened at coating with 2% by weight to 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 10 and 11. In Layer 10 yellow dye-forming coupler Y-2 was omitted and yellow dye-forming coupler Y-1 was coated at 0.78 g. In Layer 11 yellow dye-forming coupler Y-2 was omitted and yellow dye-forming coupler Y-1 was coated at 0.22 g.

Photographic Sample 103 was prepared by applying the following layers in the given sequence to a transparent support of cellulose triacetate. The quantities of silver halide are given in g of silver per m^2. The quantities of other materials are given in g per m^2.

Layer 1 {Antihalation Layer} black colloidal silver sol containing 0.22 g of silver, Cyan dye material CD-2 at 0.033 g, Magenta dye material MD-1 at 0.022 g, Yellow dye material YD-3 at 0.133 g with 2.44 g gelatin.

Layer 2 {First (least) Red-Sensitive Layer} Red sensitized silver iodobromide emulsion [1.3 mol % iodide, average grain diameter 0.55 microns, average thickness 0.08 microns] at 0.28 g, red sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 1.0 microns, average thickness 0.09 microns] at 0.33 g, cyan dye-forming image coupler C-1 at 0.56 g, BAR compound B-1 at 0.089 g with gelatin at 1.83 g.

Layer 3 {Second (more) Red-Sensitive Layer} Red sensitive silver iodobromide emulsion [4 mol % iodide, average grain diameter 1.3 microns, average grain thickness 0.12 microns] at 0.56 g, cyan dye-forming image coupler C-1 at 0.23 g, cyan dye-forming masking coupler CM-1 at 0.022 g, DIR compound D-2 at 0.050 g, BAR compound B-1 at 0.003 g with gelatin at 1.66 g.

Layer 4 {Third (most) Red-Sensitive Layer} Red sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 2.6 microns, average grain thickness 0.13 microns] at 1.22 g, cyan dye-forming image coupler C-1 at 0.17 g, cyan dye-forming masking coupler CM-1 at 0.050 g, DIR compound D-6 at 0.003 g, DIR compound D-2 at 0.050 g, BAR compound B-1 at 0.002 g with gelatin at 1.36 g.

Layer 5 {Interlayer} 1.33 g of gelatin.

Layer 6 {First (least) Green-Sensitive Layer} Green sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 1.0 microns, average grain thickness 0.09 microns] at 0.78 g, magenta dye-forming image coupler M-2 at 0.067 g, magenta dye-forming image coupler M-3 at 0.22 g, BAR compound B-2 at 0.033 g with gelatin at 1.78 g.

Layer 7 {Second (more) Green-Sensitive Layer} Green sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 1.25 microns, average grain thickness 0.12 microns] at 1.00 g, magenta dye-forming image coupler M-2 at 0.028 g, magenta dye-forming image coupler M-3 at 0.089 g, BAR compound B-1 at 0.003 g, magenta dye-forming masking coupler MM-1 at 0.089 g, DIR compound D-4 at 0.022 g with gelatin at 1.48 g.

Layer 8 {Third (most) Green-Sensitive Layer} Green sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 2.16 microns, average grain thickness 0.12 microns] at 1.00 g, magenta dye-forming image coupler M-2 at 0.030 g, magenta dye-forming image coupler M-3 at 0.096 g, BAR compound B-1 at 0.003 g, magenta dye-forming masking coupler MM-1 at 0.044 g, DIR compound D-3 at 0.008 g, DIR compound D-4 at 0.008 g with gelatin at 1.33 g.

Layer 9 {Interlayer} Yellow dye material YD-2 at 0.11 g with 1.33 g gelatin.

Layer 10 {First (less) Blue-Sensitive Layer} Blue sensitized silver iodobromide emulsion [1.3 mol % iodide, average grain diameter 0.55, average grain thickness 0.08 microns] at 0.11 g, blue sensitized silver iodobromide emulsion [4.1 mol % iodide, average grain diameter 0.85, average grain thickness 0.09 microns] at 0.26 g, blue sensitized silver iodobromide emulsion [4.1 mol % iodide, average grain diameter 1.32, average grain thickness 0.14 microns] at 0.26 g, yellow dye-forming image coupler Y-1 at 0.22 g, yellow dye forming image coupler Y-2 at 0.69 g, DIR compound D-5 at 0.049 g, BAR compound B-1 at 0.003 g with gelatin at 2.6 g.

Layer 11 {Second (more) Blue-Sensitive Layer} Blue sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 3.0 microns, average grain thickness 0.14 microns] at 0.39 g, blue sensitized silver iodobromide emulsion [9 mol % iodide, average grain diameter 1.0 microns] at 0.39 g, yellow dye-forming image coupler Y-1 at 0.065 g, yellow dye-forming image coupler Y-2 at 0.20 g, DIR compound D-5 at 0.044 g, BAR compound B-1 at 0.006 g with gelatin at 1.97 g.

Layer 12 {Protective Layer} 0.111 g of dye UV-1, 0.111 g of dye UV-2, unsensitized silver bromide Lippmann emulsion at 0.222 g, Cyan dye material CD-2 at 0.006 g, Magenta dye material MD-2 at 0.001 g with gelatin at 1.11 g.

Layer 13 {Protective Layer} Gelatin at 0.92 g.

This film was hardened at coating with 2% by weight to 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 104 was prepared like Photographic Sample 103 except for changes in Layers 10 and 11. In Layer 10 yellow dye-forming coupler Y-1 was omitted and yellow dye-forming coupler Y-2 was coated at 0.94 g. In Layer 11 yellow dye-forming coupler Y-1 was omitted and yellow dye-forming coupler Y-2 was coated at 0.28 g.

Photographic Sample 105 was prepared like Photographic Sample 103 except for changes in Layers 10 and 11. In Layer 10 yellow dye-forming coupler Y-2 was omitted and yellow dye-forming coupler Y-3 was added at 0.89 g. In Layer 11 yellow dye-forming coupler Y-2 was omitted and yellow dye-forming coupler Y-3 was coated at 0.26 g.

Photographic Sample 106 was prepared like Photographic Sample 103 except for Layers 10 and 11. In Layer 10, the blue sensitized silver iodobromide emulsion [4.1 mol % iodide, average grain diameter 0.85, average grain thickness 0.09 microns] was coated at 0.28 g and yellow dye-forming coupler Y-2 was coated at 0.72 g. In Layer 11, the yellow dye-forming coupler Y-2 was coated at 0.21 g.

Photographic Sample 107 was prepared like Photographic Sample 106 except for changes in Layers 10 and 11. In Layer 10 yellow dye-forming coupler Y-1 was omitted and yellow dye-forming coupler Y-2 was coated at 0.94 g. In Layer 11 yellow dye-forming coupler Y-1 was omitted and yellow dye-forming coupler Y-2 was coated at 0.28 g.

Photographic Sample 108 was prepared by applying the following layers in the given sequence to a transparent support of cellulose triacetate. The quantities of silver halide are given in g of silver per m^2. The quantities of other materials are given in g per m^2.

Layer 1 {Antihalation Layer} black colloidal silver sol containing 0.156 g of silver, Cyan dye material CD-2 at 0.033 g, Magenta dye material MD-1 at 0.021 g, Yellow dye material YD-3 at 0.104 g with 2.44 g gelatin.

Layer 2 {First (least) Red-Sensitive Layer} Red sensitized silver iodobromide emulsion [1.3 mol % iodide, average grain diameter 0.55 microns, average thickness 0.08 microns] at 0.47 g, red sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 1.0 microns, average thickness 0.09 microns] at 0.46 g, cyan dye-forming image coupler C-1 at 0.56 g, cyan dye-forming masking coupler CM-1 at 0.033 g, BAR compound B-1 at 0.039 g with gelatin at 1.83 g.

Layer 3 {Second (more) Red-Sensitive Layer} Red sensitive silver iodobromide emulsion [4 mol % iodide, average grain diameter 1.3 microns, average grain thickness 0.12 microns] at 0.72 g, cyan dye-forming image coupler C-1 at 0.26 g, cyan dye-forming maskÿ g coupler CM-1 at 0.022 g, DIR compound D-1 at 0.011 g with gelatin at 1.66 g.

Layer 4 {Third (most) Red-Sensitive Layer} Red sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 2.6 microns, average grain thickness 0.13 microns] at 1.11 g, cyan dye-forming image coupler C-1 at 0.13 g, cyan dye-forming masking coupler CM-1 at 0.033 g, DIR compound D-1 at 0.024 g, DIR compound D-2 at 0.050 g with gelatin at 1.36 g.

Layer 5 {Interlayer} Yellow dye material YD-1 at 0.11 g and 1.33 g of gelatin.

Layer 6 {First (least) Green-Sensitive Layer} Green sensitized silver iodobromide emulsion [1.3 mol % iodide, average grain diameter 0.55 microns, average grain thickness 0.08 microns] at 0.62 g, green sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 1.0 microns, average grain thickness 0.09 microns] at 0.32 g, magenta dye-forming image coupler M-1 at 0.24 g, magenta dye-forming masking coupler MM-1 at 0.067 g with gelatin at 1.78 g.

Layer 7 {Second (more) Green-Sensitive Layer} Green sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 1.25 microns, average grain thickness 0.12 microns] at 1.00 g, magenta dye-forming image coupler M-1 at 0.091 g, magenta dye-forming masking coupler MM-1 at 0.067 g, DIR compound D-1 at 0.024 g with gelatin at 1.48 g.

Layer 8 {Third (most) Green-Sensitive Layer} Green sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 2.16 microns, average grain thickness 0.12 microns] at 1.00 g, magenta dye-forming image coupler M-1 at 0.072 g, magenta dye-forming masking coupler MM-1 at 0.056 g, DIR compound D-3 at 0.008 g, DIR compound D-4 at 0.011 g with gelatin at 1.33 g.

Layer 9 {Interlayer} Yellow dye material YD-2 at 0.11 g with 1.33 g gelatin.

Layer 10 {First (less) Blue-Sensitive Layer} Blue sensitized silver iodobromide emulsion [1.3 mol % iodide, average grain diameter 0.55, average grain thickness 0.08 microns] at 0.24 g, blue sensitized silver iodobromide emulsion [6 mol % iodide, average grain diameter 1.0 microns, average grain thickness 0.26 microns] at 0.61 g, yellow dye-forming image coupler Y-1 at 0.29 g, yellow dye forming image coupler Y-2 at 0.72 g, cyan dye-forming coupler C-1 at 0.016 g, DIR compound D-5 at 0.067 g, BAR compound B-1 at 0.003 g with gelatin at 2.6 g.

Layer 11 {Second (more) Blue-Sensitive Layer} Blue sensitized silver iodobromide emulsion [4 mol % iodide, average grain diameter 3.0 microns, average grain thickness 0.14 microns] at 0.23 g, blue sensitized silver iodobromide emulsion [9 mol % iodide, average grain diameter 1.0 microns] at 0.59 g, yellow dye-forming image coupler Y-1 at 0.090 g, yellow dye-forming image coupler Y-2 at 0.23 g, cyan dye-forming coupler at 0.022 g, DIR compound D-5 at 0.051 g, BAR compound B-1 at 0.006 g with gelatin at 1.97 g.

Layer 12 {Protective Layer} 0.111 g of dye UV-1, 0.111 g of dye UV-2, unsensitized silver bromide Lippmann emulsion at 0.222 g with gelatin at 1.11 g.

Layer 13 {Protective Layer} Gelatin at 0.92 g.

This film was hardened at coating with 2% by weight to 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 109 was prepared like Photographic Sample 108 except for changes in Layers 10 and 11. In Layer 10 yellow dye-forming coupler Y-2 was omitted and yellow dye-forming coupler Y-3 was added at 0.87 g. In Layer 11 yellow dye-forming coupler Y-2 was omitted and yellow dye-forming coupler Y-3 was coated at 0.27 g.

TABLES 1 and 2 show the photographic responses associated with Photographic Samples 101 and 103 relative to three examples of prior art (Photographic Samples 102, 104 and 105). Each formulation is processed through two developers. These developers have been pH adjusted to provide pH values which are high (10.15) or low (9.95) of standard developer aim pH, 10.04. A percentage contrast change is used to reflect the effect on contrast of pH variations from 9.95 to 10.15.

TABLE 1

Image CouplerLevels (g/sq m) by Layer		% Contrast Change (pH =10.15/ pH = 9.95)			Photographic Sample Number
Most Sensitive Y-1/Y-2	Least Sensitive Y-1/Y-2	Red	Green	Blue	
0.215/0	0.753/0	10.7	5.8	-1.4	102(C)
0.089/0.226	0.280/0.700	9.3	11.7	14.1	101(Inv)

In the first formulation, all Type II parents with Type II heterocyclic coupling-off groups, the blue layer contrast is invariant. This insensitivity leads to a mismatch with the red and green contrasts, which both increase with increasing developer pH. In the second formulation, a combination of a Type I parent and Type I phenolic coupling-off group and a Type II parent and coupling-off group, the blue layer contrast covaries with the other two records. One of the advantages of this covariation is better print quality as the printer algorithms are able to adjust for the covarying contrasts of all 3 records. In the first formulation, the contrast mismatch prevents proper printing.

TABLE 2

Image CouplerLevels (g/sq m) by Layer		% Contrast Change (pH = 10.15/ pH = 9.95)			Photographic Sample Number
Most Sensitive Y-1/Y-2 or Y-3	Least Sensitive Y-1/Y-2 or Y-3	Red	Green	Blue	
0/0.268 0/Y-2	0/0.913 0/Y-2	10.4	24.7	9.5	104(C)
0.063/0.253 Y-1/Y-3	0.215/0.859 Y-1/Y-3	6.5	22.9	11.7	105(C)
0.063/0.196 Y-1/Y-2	0.215/0.666 Y-1/Y-2	11.1	29.9	14.7	103(Inv)

The three formulations shown in TABLE 2 covary in all 3 color records allowing for better printing relative to a photographic element containing a single Type II yellow image coupler (TABLE 1). This advantage in two of the examples is realized despite the presence of some Type II coupler (Y-1). The use of Type I coupler (Y-3) with a heterocyclic (Type II) coupling off group, however, requires a greater laydown with its accompanying layer thickness increase and light scattering characteristics. The additional laydown is also more expensive and creates added environmental and disposal problems.

Tables 3-5 show blue minimum densities associated with similar formulations, Photographic Samples 101, 106 and 108. Each formulation is shown with two bleaches. These bleaches have been pH adjusted to provide pH values of 4.75, (standard PDTA bleach pH) or 5.25, (standard PDTA/EDTA bleach pH), and bleaches which are 0.75 pH units higher. The unexposed color negative film is then processed through these bleaches, and the resulting blue density is measured.

TABLE 3

Image Coupler Levels (g/sq m) by Layer		Blue Minimum Density		Photographic Sample Number
Most Sensitive Y-1/Y-2	Least Sensitive Y-1/Y-2	Fresh PDTA Bleach @ pH = 4.75	Fresh PDTA Bleach @ pH = 5.50	
0.215/0	0.753/0	0.970	1.043	102(C)
0.089/0.226	0.280/0.700	0.957	0.997	101(Inv)

In the first formulation, all Type II coupler, the blue layer minimum density increases with pH growth. In the second formulation, Type I coupler with phenolic coupling-off group and Type II coupler with heterocyclic coupling-off group, the blue layer minimum density growth is reduced.

TABLE 4

Image Coupler Levels (g/sq m) by Layer		Blue Minimum Density		Photographic Sample Number
Most Sensitive Y-1/Y-2	Least Sensitive Y-1/Y-2	Fresh PDTA/EDTA Bleach @ pH = 5.25	Fresh PDTA/EDTA Bleach @ pH = 6.00	
0/0.268	0/0.913	0.853	0.892	106(C)
0.063/0.205	0.215/0.698	0.874	0.964	107(Inv)

TABLE 5

Image Coupler Levels (g/sq m) by Layer		Blue Minimum Density		Photographic Sample Number
Most Sensitive Y-1/Y-2 or Y-3	Least Sensitive Y-1/Y-2 or Y-3	Fresh PDTA/EDTA Bleach @ pH = 5.25	Fresh PDTA/EDTA Bleach @ pH = 6.00	
0.087/0.285 Y-1/Y-3	0.279/0.913 Y-1/Y-3	1.043	1.085	108(C)
0.087/0.218 Y-1/Y-2	0.279/0.698 Y-1/Y-2	1.059	1.136	109(Inv)

The continued coupling of a combination of Type I coupler with a Type I phenolic coupling off group and Type II coupler with a Type II heterocyclic coupling-off group is intermediate between the Y-1 (Table 3) and Y-2 (Table 4) individually. Relative to a combination of a Type I parent with a Type II coupling-off group and a Type II parent with a Type II coupling-off group, this combination gives a slightly higher blue minimum density growth with elevation in bleach pH. However, much lower laydowns are realized with the coupler combination of the invention (TABLE 5).

TABLES 6 and 7 show latitude measurements for Photographic Samples 101 and 103 relative to prior art positions (Photographic Samples 102, 104 and 105). Latitude was calculated as the log E exposure range over which the contrast remains above 0.60. A white light exposure through a step-wise gradient tablet followed by standard color negative processing was used.

TABLE 6

Image Coupler Levels (g/sq m) by Layer		Blue Layer Latitude	Photographic Sample Number
Most Sensitive Y-1/Y-2 or Y-3	Least Sensitive Y-1/Y-2 or Y-3		
0/0.268 /Y-2	0/0.913 /Y-2	2.46	104(C)
0.063/0.253 Y-1/Y-3	0.215/0.859 Y-1/Y-3	2.62	105(C)
0.063/0.196 Y-1/Y-2	0.215/0.666 Y-1/Y-2	2.54	103(Inv)

Comparing samples 103 and 104, the table shows the advantage in exposure latitude for a combination of Type I and Type II couplers versus a Type I coupler alone. The use of another comparison coupler combination in the form of a Type I coupler with Type II coupling off group (Y-3) in conjunction with a Type II coupler (Y-1), as in Sample 105, results in improved latitude but requires a much greater laydown with its accompanying layer thickness increase and corresponding unfavorable light scattering characteristics as compared to Sample 103.

TABLE 7

Image Coupler Levels (g/sq m) by Layer		Blue Layer Latitude	Photographic Sample Number
Most Sensitive Y-1/Y-2	Least Sensitive Y-1/Y-2		
0.215/0	0.753/0	1.87	102(C)
0.089/0.226	0.280/0.700	2.06	101(Inv)

The two formulations show the advantage in exposure latitude for a combination of Type I and Type II couplers relative to Type II alone.

TABLE 8 shows linearity measurements for Photographic Sample 101 relative to prior art Sample 102. Non-linearity is measured as the speed separation between the contrasts of the two blue layers of differing sensitivities. The juncture where the less sensitive layer becomes the dominant layer in contrast is determined for each photographic coating. The speed separation between the contrasts of the two blue layers is determined at this point and indicates non-linearity when non-zero values result. Non-linearities cause difficulty for printer algorithms as well as adversely affecting the color reproduction.

TABLE 8

Image Coupler Levels (g/sq m) by Layer		Blue Layer Non-Linearity	Photographic Sample Number
Most Sensitive Y-1/Y-2	Least Sensitive Y-1/Y-2		
0.215/0.000	0.753/0.000	0.03	102(C)
0.089/0.226	0.280/0.700	0.00	101(Inv)

The two formulations show the advantage in linearity for a combination of Type I and II couplers relative to Type II alone.

TABLE 9 shows the photographic responses associated with Photographic Sample 103 of the invention relative to two examples of the prior art (Photographic Samples 104 and 105). Each formulation is given a white light exposure, and the modulated transfer function (MTF) at 2.5 cycles/mm is measured. The measure correlates with light scatter or sharpness. Red element response is employed as the element which is farthest removed from the light source, and, therefore, the layer most affected by light scatter by overlying elements.

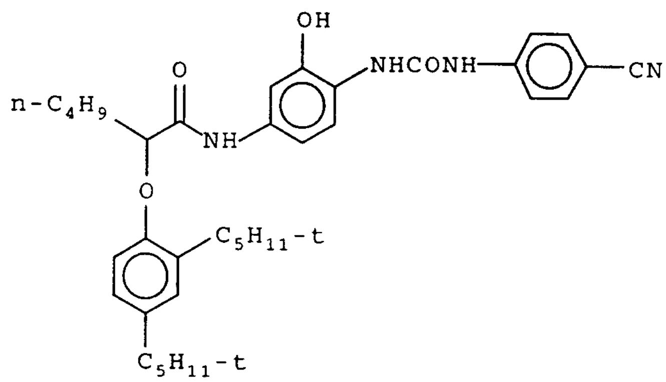
TABLE 9

Image Coupler Levels (g/sq m) by Layer		Blue Layer Non-Linearity	Sharpness (MTF) Red	Photographic Sample Number
Most Sensitive 1/Y-2 or Y-3	Least Sensitive Y-1/Y-2 or Y-3			
0/0.268 0/Y-2	0/0.913 0/Y-2	0.03	105	104(C)
0.063/0.253 Y-1/Y-3	0.215/0.859 Y-1/Y-3	0.00	101	105(C)
0.063/0.196 Y-1/Y-2	0.215/0.666 Y-1/Y-2	0.00	105	103(Inv)

Two of the three formulations shown in TABLE 9 have approximately the same coated coupler laydown and show similar effects on the underlying red sharpness measure. The third formulation, a Type I coupler with a Type II coupling-off group in combination with a Type II coupler, however, requires a greater laydown with its accompanying layer thickness increase and light scattering characteristics. This is evidenced in the lower sharpness values for Photographic Sample 105 relative to the other two samples. Thus, the combination of the invention provides the advantage of improved sharpness without undue increase in coating weight and the disadvantages that such an increase entails.

The formulas for the compounds employed in the Examples are as follows:

C-1: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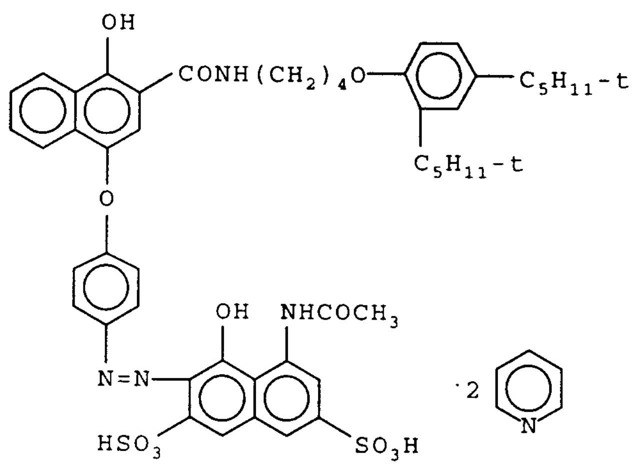
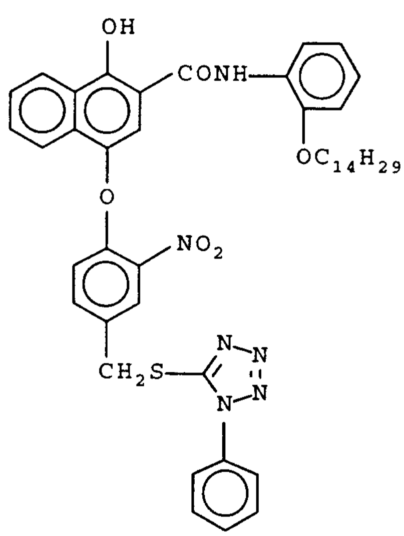
CN
O
n-C4H9
NH
O
C5H11-t
C5H11-t

CM-1


OH
CONH(CH2)4O
C5H11-t
C5H11-t
O
OH
NHCOCH3
N=N
HSO3
SO3H
·2
N

D-1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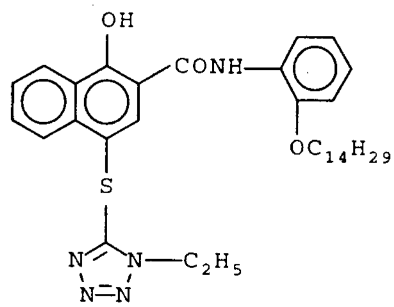
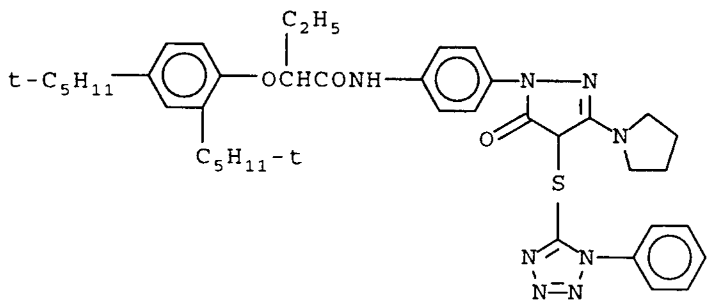
OC14H29
O
NO2
CH2S
N
N
N
N

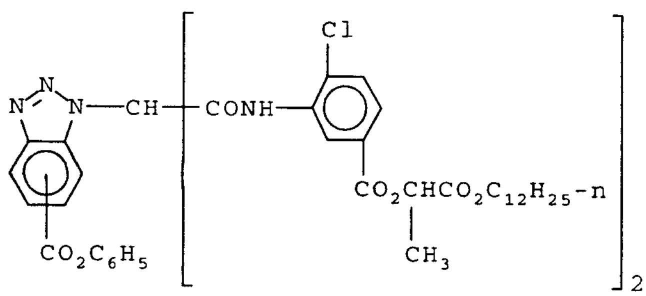
D-2


OH
CONH
OC14H29
S
N
N—C2H5
N=N

D-3:


C2H5
t-C5H11
OCHCONH
N
N
O
N
C5H11-t
S
N
N
N=N

D-4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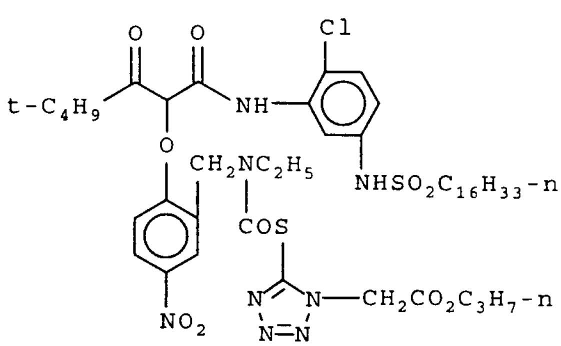
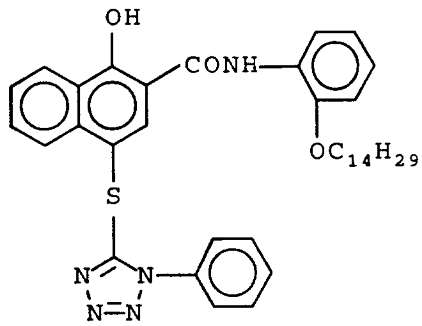
N
N
CH
CONH
CO2CHCO2C12H25-n
CH3
CO2C6H5
2

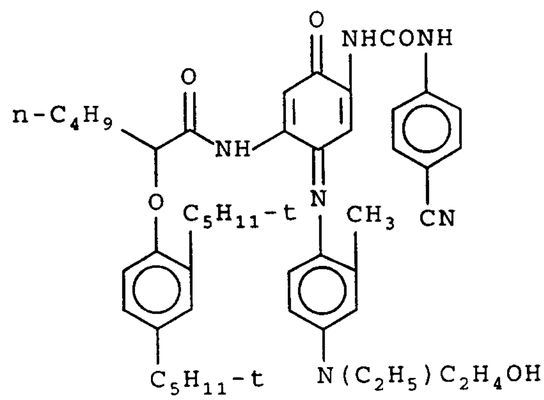
D-5:


O
O
Cl
t-C4H9
NH
O
CH2NC2H5
NHSO2C16H33-n
COS
N
N—CH2CO2C3H7-n
NO2
N=N

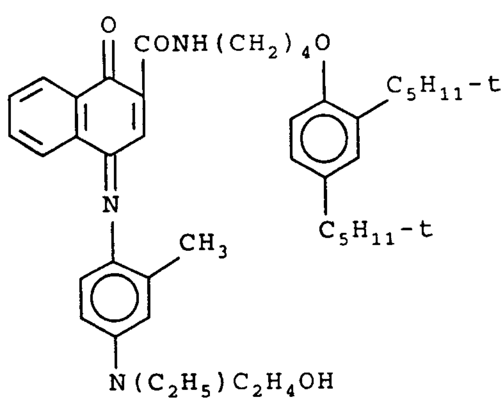
D-6:


OH
CONH
OC14H29
S
N
N
N=N

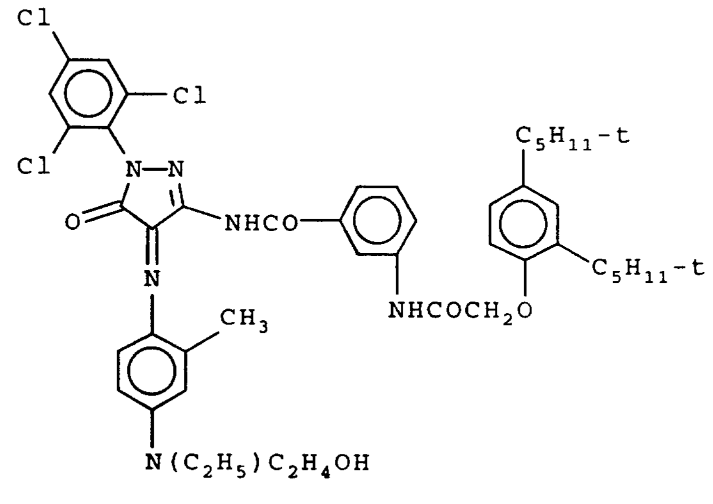
CD-1:


O
NHCONH
O
n-C4H9
NH
N
O
C5H11-t
CH3
CN
C5H11-t
N(C2H5)C2H4OH

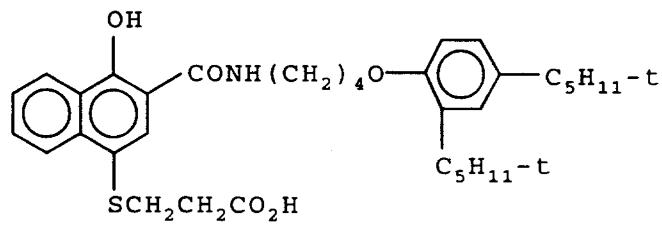
CD-2:


O
CONH(CH2)4O
C5H11-t
N
CH3
C5H11-t
N(C2H5)C2H4OH

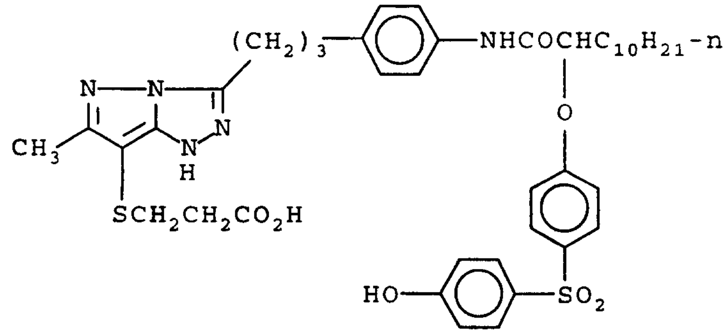
MD-1:


Cl
Cl
Cl
N—N
O
NHCO
N
CH3
N(C2H5)C2H4OH
C5H11-t
C5H11-t
NHCOCH2O

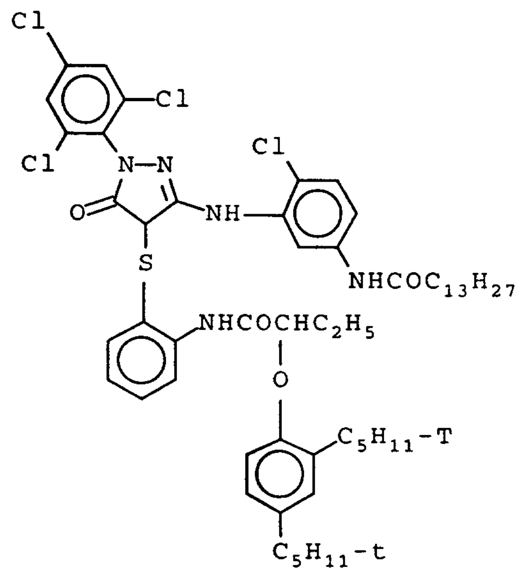
B-1:


OH
CONH(CH2)4O
C5H11-t
C5H11-t
SCH2CH2CO2H

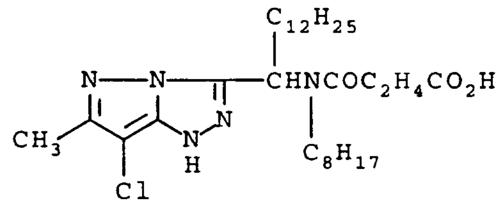
B-2:


(CH2)3
NHCOCHC10H21-n
N
N
N
N
CH3
H
SCH2CH2CO2H
O
HO
SO2

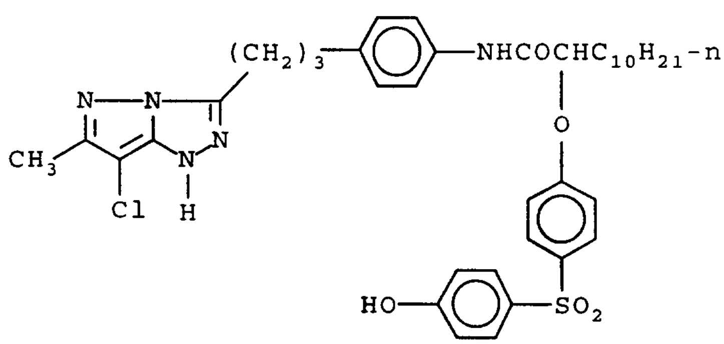
M-1:


Cl
Cl
Cl
Cl
N—N
O
NH
S
NHCOC13H27
NHCOCHC2H5
O
C5H11-T
C5H11-t

M-2:


C12H25
N—N
CHNCOC2H4CO2H
N
N
CH3
H
C8H17
Cl

M-3:


(CH2)3
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N—N
N
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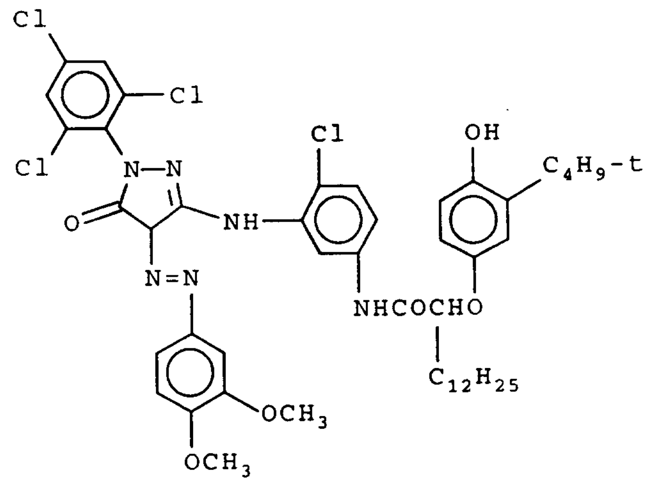
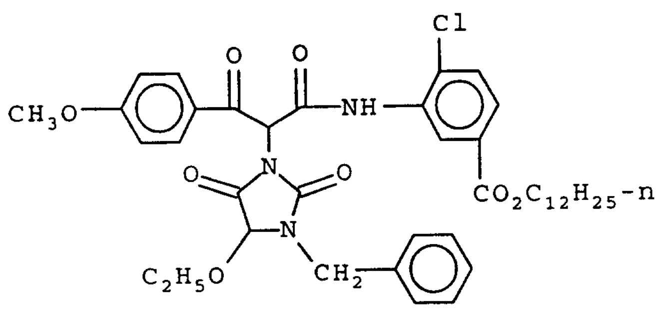
N
Cl
H
HO
SO2

MM-1:


Cl
Cl
Cl
N
N
O
NH
Cl
OH
C4H9-t
N=N
NHCOCHO
C12H25
OCH3
OCH3

Y-1: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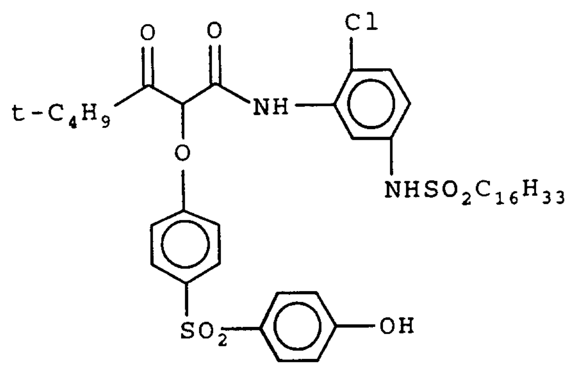
CH3O
NH
N
O
O
CO2C12H25-n
N
C2H5O
CH2

Y-2: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Cl
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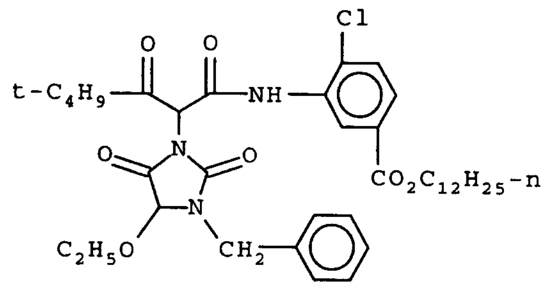
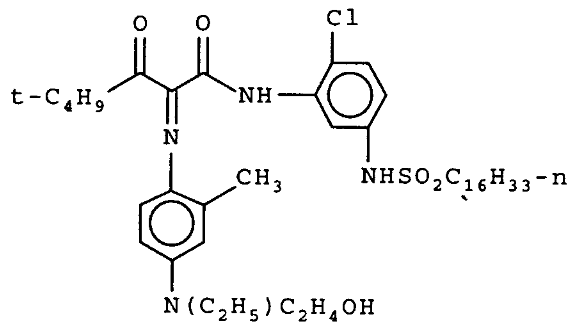
NH
O
NHSO2C16H33
SO2
OH

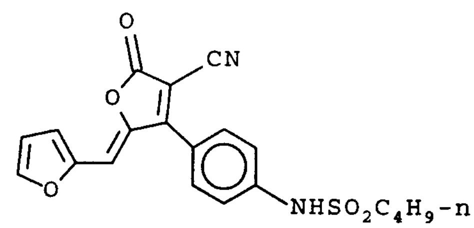
Y-3:



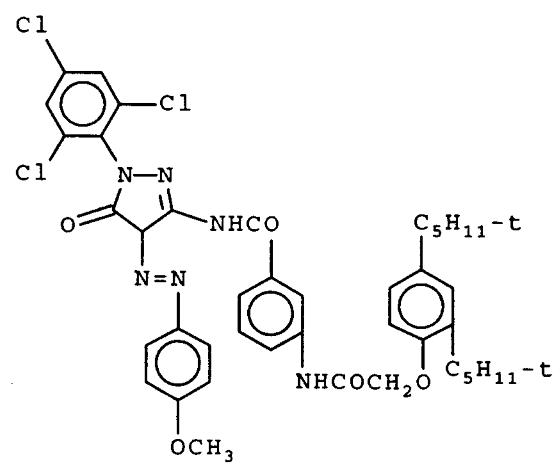
YD-1:



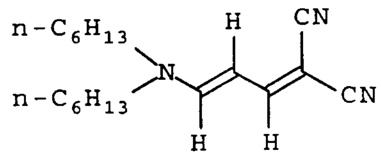
YD-2:



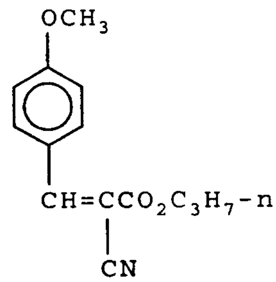
YD-3:



UV-1:



UV-2:



H-1:

$CH_2(SO_2CH{=}CH_2)_2$

Claims

1. A photographic element comprising a light sensitive photographic silver halide layer sensitized to blue light and having associated therewith a combination of at least two yellow dye-forming couplers each containing an acylacetanilide parent, one of which comprises a phenolic coupling-off group containing a solubilizing substituent, and the other of which is a benzoylacetanilide which comprises a heterocyclic coupling-off group.

2. The element of Claim 1 wherein the couplers have the following formulas, respectively:

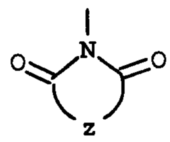
```
I        RC(=O)CHC(=O)NHPh
                  |
                  X

II      PhC(=O)CHC(=O)NHPh
                  |
                  Y
```

wherein X has the formula -OPh(L)$_n$Sol, and wherein R is a substituted or unsubstituted aryl group or a fully substituted carbon atom, each Ph is a phenyl ring, independently substituted or not, Sol is a water solubilizing substituent, L is a divalent group linking the phenyl ring and Sol, n is 0 or 1, and Y is a heterocyclic ring, substituted or not.

3. The element of Claim 2 wherein the heterocyclic ring Y is bonded to the rest of the coupler through a nitrogen atom in the heterocyclic ring and wherein R is a fully substituted carbon atom.

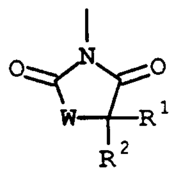
4. The element of any of claims 1-3 wherein at least two blue sensitive layers contain the two yellow dye-forming couplers.

5. The element of any of claims 2-4 wherein Y is a substituted or unsubstituted imidazole, pyrazole group, or heterocyclic group represented by the formula:



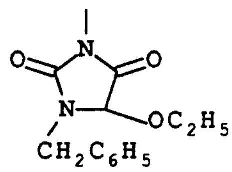
wherein z represents the atoms necessary to complete a heterocyclic ring.

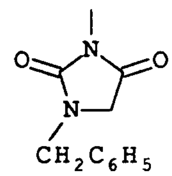
6. The element of Claim 5 wherein Y is represented by the formula:

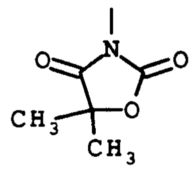


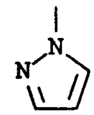
wherein W is -O-, -S-, -N(R^3)-, or -C(R^4)(R^5)-; R^1 is H, or substituted or unsubstituted alkyl, alkoxy, phenyl, or phenoxy; R^2 and R^5 are independently H or substituted or unsubstituted alkyl; R^3 is substituted or unsubstituted alkyl or phenyl; and R^4 is H or substituted or unsubstituted alkyl or alkoxy.

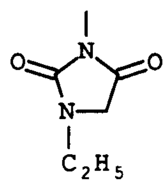
7. The element of any of claims 2-5 wherein Y has one of the formulae:

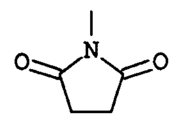
IIa 

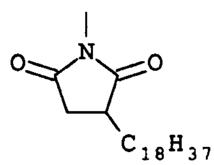
IIb 

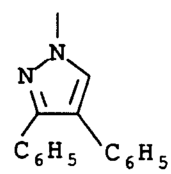
IIc 

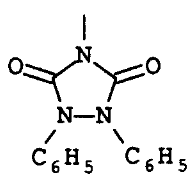
IId 

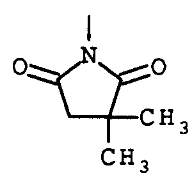
IIe 

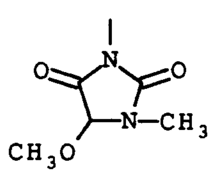
IIf 

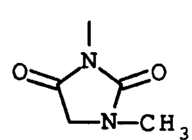
IIg 

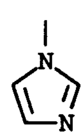
IIh 

IIi 

IIj 

IIk 

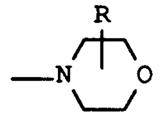
IIl 

IIm 

8. The element of any of claims 5-7 wherein Y is asubstituted or unsubstituted hydantoin, succinimide, imidazole or pyrazole group.

9. The element of any of claims 2-8 wherein Sol is:

-OH, $-NHSO_2R$, -NHCOR, $-NHCOCF_3$, -NHCOOR, $-NR_2$, $-NHCONR_2$, $-CONR_2$, $-CONHSO_2R$, $-SO_3H$, $-CO_2R$, $-(OR)_n$, $-OSO_2R$, $-P(O)0R_2$, and

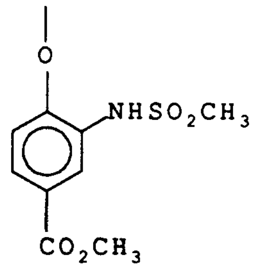


;

wherein each R is an independently selected substituent or hydrogen and n is 0 to 3.

10. The element of any of claims 2-9 wherein X is:

Ia



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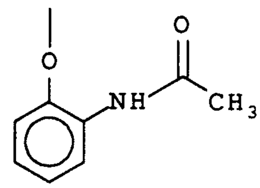

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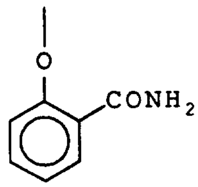

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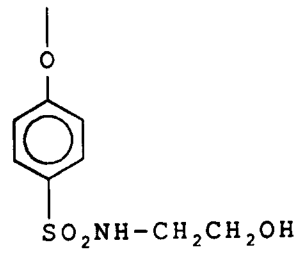

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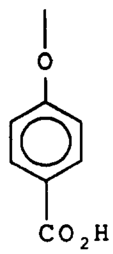

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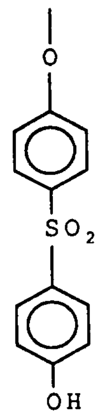
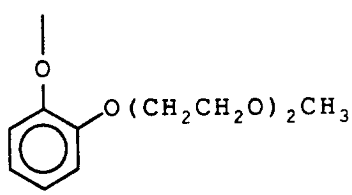


Ig



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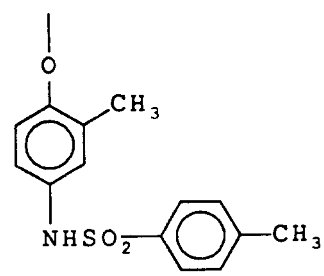

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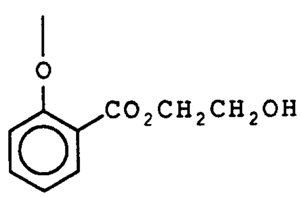

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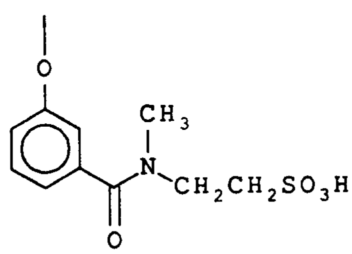

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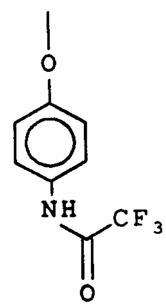
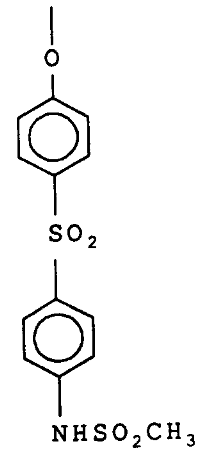


and

Il



European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 20 0187

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)
X Y	EP-A-0 214 832 (KONISHIROKU) * page 49, line 1 - line 37 * * page 57, line 37 - line 40 * * page 69, line 29 - line 43 *	1-3,5-10 4	G03C7/36
Y	EP-A-0 488 310 (KONICA) * page 82, line 39 - page 83, line 9 * * page 85, line 12 - line 33 *	4	

TECHNICAL FIELDS SEARCHED (Int.Cl.5)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	9 March 1994	Magrizos, S

CATEGORY OF CITED DOCUMENTS

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