⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 250 201**
A2

⑫
EUROPEAN PATENT APPLICATION

㉑ Application number: **87305308.6**

㉒ Date of filing: **16.06.87**

㊿ Int. Cl.⁴: **G03C 7/34** , //C07C143/70

㉚ Priority: **18.06.86 US 875793**

㊸ Date of publication of application:
23.12.87 Bulletin 87/52

(84) Designated Contracting States:
DE FR GB NL

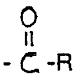
(71) Applicant: **EASTMAN KODAK COMPANY**
Patent Department 343 State Street
Rochester New York 14650(US)

(72) Inventor: **Lau, Philip T. S Eastman Kodak Company**
Patent Department 343 State Street
Rochester New York 14650(US)

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

(54) **Photographic silver halide element and process.**

(57) Photographic couplers comprise a naphtholic coupler moiety capable of forming a red or infrared absorbing dye upon oxidative coupling and comprising (i) an optional coupling-off group in the coupling position, (ii) a group, in the position ortho to the hydroxy group, which is represented by the formula:



$-\overset{\overset{O}{\|}}{C}-R$ wherein R is a substituent which enables the dye formed upon oxidative coupling to absorb in the red or infrared region of the spectrum without undesired dye instability, and (iii) a group Y in the 5-position of the naphtholic coupler moiety which is capable of promoting red or infrared dye formation, the group Y having sufficient bulk to provide a bathochromic shift in the absorption of the resulting red or infrared dye. These couplers are useful in photographic materials and processes enabling formation or red and infrared absorbing dyes.

EP 0 250 201 A2

PHOTOGRAPHIC SILVER HALIDE ELEMENT AND PROCESS

This invention relates to a new red and infrared dye-forming naphtholic couplers and to silver halide photographic elements and processes employing such couplers.

Photographic elements comprising red and infrared dye-forming naphtholic couplers are known. Such red and infrared dye-forming couplers are useful in, for example, integral dye sound track images in motion picture films. An example of such a photographic element is described in U.S. Patent 4,250,251 and U.S. Patent 4,178,183.

Although numerous red and infrared dye-forming couplers are known, a continuous search has gone on for novel naphtholic couplers which produce dyes which absorb in the red and infrared regions of the spectrum and which improve, or optimize for particular applications, particular properties of the coupler. For example, a search has gone on for novel naphtholic couplers which form red or infrared absorbing dyes which are bathochromically shifted and have broad absorption peaks. Satisfactory couplers sought preferably should provide reduction or elimination of silver needed for a sound track image while maintaining dye image stability, reactivity and compatibility with other components in the photographic element. The resulting dyes need to have the desired dye hue and need to be particularly stable to fading, such as fading induced by heat or ferrous ion solutions.

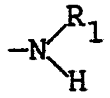
The present invention provides a novel class of red or infrared dye-forming naphtholic couplers having a group Y in the 5-position on the naphtholic coupler that is capable of promoting formation of red or infrared dye of increased stability. The group Y in the 5-position of the naphtholic coupler has sufficient bulk to provide a bathochromic shift in absorption of the resulting red or infrared dye formed upon oxidative coupling.

A photographic element according to the invention comprises a support bearing a photographic silver halide emulsion and a dye-forming coupler, wherein the dye-forming coupler is a naphtholic coupler capable of oxidative coupling to form a red or infrared absorbing dye and comprising,

(a) hydrogen or a coupling-off group in the coupling position;

(b) a group, in the position ortho to the hydroxy group, which is represented by the formula:

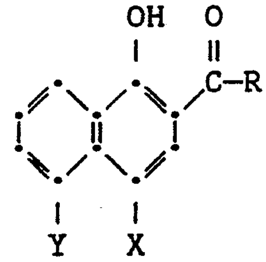
$-\overset{O}{\overset{\|}{C}}-R$, wherein R is a substituent which enables the dye formed upon oxidative coupling to absorb in the red or infrared region of the spectrum, preferably unsubstituted or substituted alkoxy, aryloxy, or



wherein R_1 is unsubstituted or substituted alkyl, heterocyclic, or unsubstituted or substituted aryl group, provided that when R_1 is aryl substituted by fluorosulfonyl, then further substituents are other than alkoxy or sulfone groups; and,

(c) a group Y in the 5-position on the naphtholic coupler which is capable of promoting red or infrared dye formation and wherein the group Y has sufficient bulk to provide a bathochromic shift in absorption of the resulting red or infrared dye. Combinations of a fluorosulfonyl substituent on an R_1 aryl group with either alkoxy or sulfone substituents leads to dye instability, especially in the fixing bath during processing.

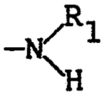
The red or infrared dye-forming naphtholic coupler moiety as described can be any red or infrared dye-forming naphtholic coupler moiety upon which the group Y is substituted in the 5-position to provide a bathochromic shift in absorption in the red or infrared dye formed from such a coupler moiety upon oxidative coupling. An example of such a naphtholic coupler moiety is represented by the formula:



wherein

X is hydrogen or a coupling-off group;

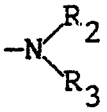
R is a substituent which enables the dye formed upon oxidative coupling to absorb in the red or infrared region of the spectrum, preferably unsubstituted or substituted alkoxy, aryloxy, or



wherein R_1 is unsubstituted or substituted alkyl, heterocyclic group, such as a 5 or 6 member heterocyclic group or unsubstituted or substituted aryl, as defined;

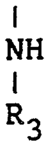
Y is a group having sufficient bulk to provide bathochromic shift in absorption of the red or infrared dye formed.

The group Y can be any group substituted in the 5-position of the naphtholic coupler moiety and which has sufficient bulk to provide a bathochromically shifted absorption in the red or infrared absorbing dye formed. Group Y is typically selected from the group consisting of



,

alkylthio, alkyl, aryl, alkoxy, aryloxy, arylthio, carbonamido, carbamoyl, sulfonamido, sulfamyl, ureido, sulfamido, heterocyclic, imido, ureido, and phosphonamido groups, each of which groups is unsubstituted or substituted by means of at least one group which increases steric bulk, and wherein R_2 and R_3 are individually hydrogen, unsubstituted or substituted alkyl or aryl, or together are the atoms necessary to complete a five or six member heterocyclic ring and wherein at least one of R_2 and R_3 is other than hydrogen. An example of a preferred group Y is represented by the formula:



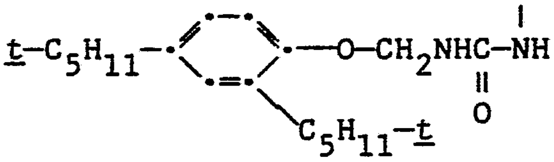
$$-NH-R_3$$

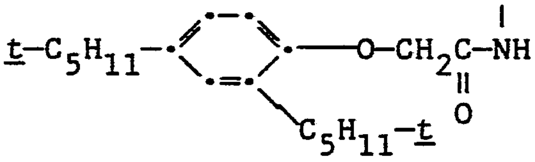
wherein R_3 is substituted or unsubstituted aryl, such as aryl containing 6 to 50 carbon atoms; substituted or unsubstituted alkyl, such as alkyl containing 4 to 24 carbon atoms; or

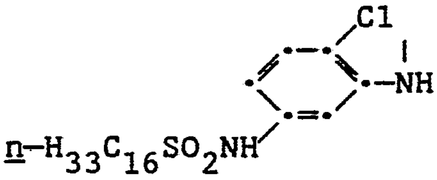
$-SO_2R_4$ or

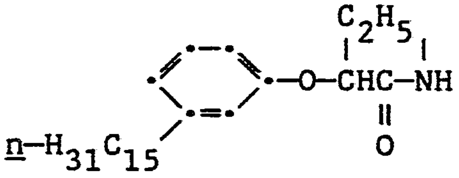
$\overset{O}{\overset{\|}{C}}$ $-R_4$ wherein R_4 is substituted or unsubstituted aryl, such as aryl containing 6 to 50 carbon atoms; substituted or unsubstituted alkyl, such as alkyl containing 1 to 30 carbon atoms; or heterocyclic.

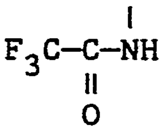
Examples of such Y groups are as follows:



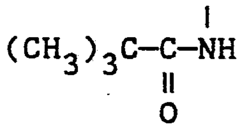




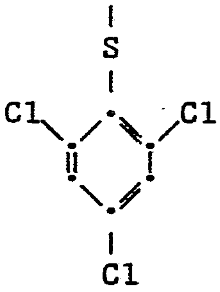


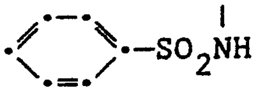


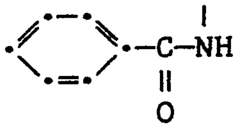
$F_3C-\underset{\underset{O}{\|}}{C}-\overset{|}{NH}$

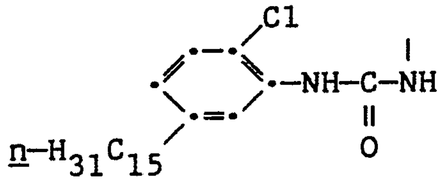


$(CH_3)_3C-\underset{\underset{O}{\|}}{C}-\overset{|}{NH}$



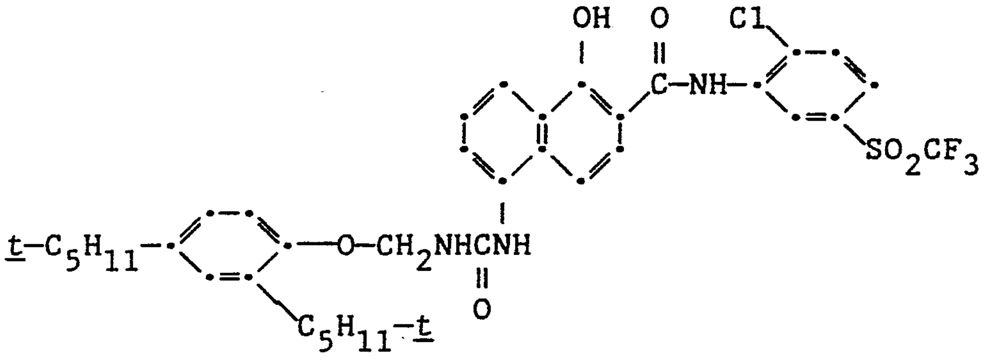


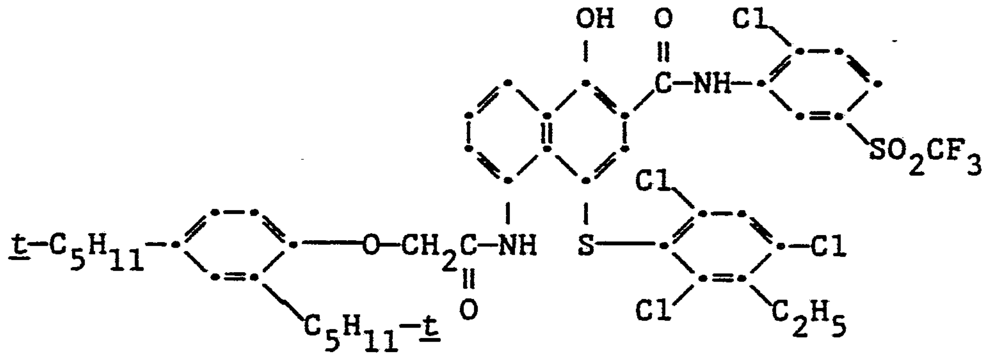


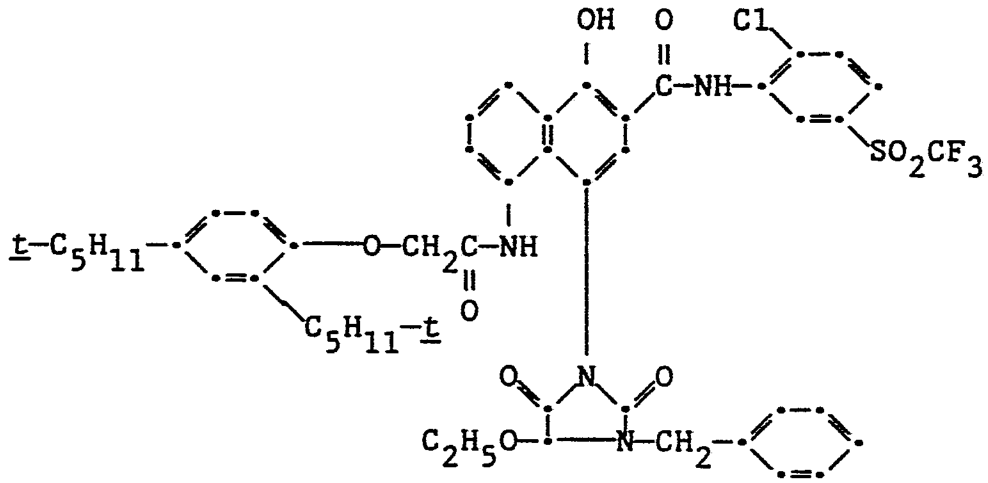


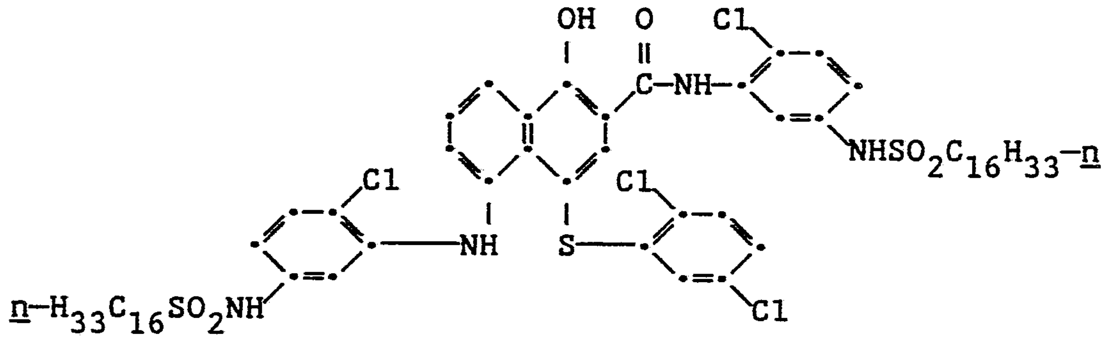
The naphtholic coupler moiety can contain substituents in other positions than the 2-and 5-positions. These substituents can be substituents known in the photographic art to be useful on red or infrared dye-forming naphtholic couplers. The coupling position of the naphtholic coupler, that is the 4-position, can be unsubstituted or substituted by a coupling-off group which can modify the equivalency of the coupler, its reactivity, its stability its dispersibility or which, upon release from the coupler, interacts with other components of the photographic element of components of the processing solutions.

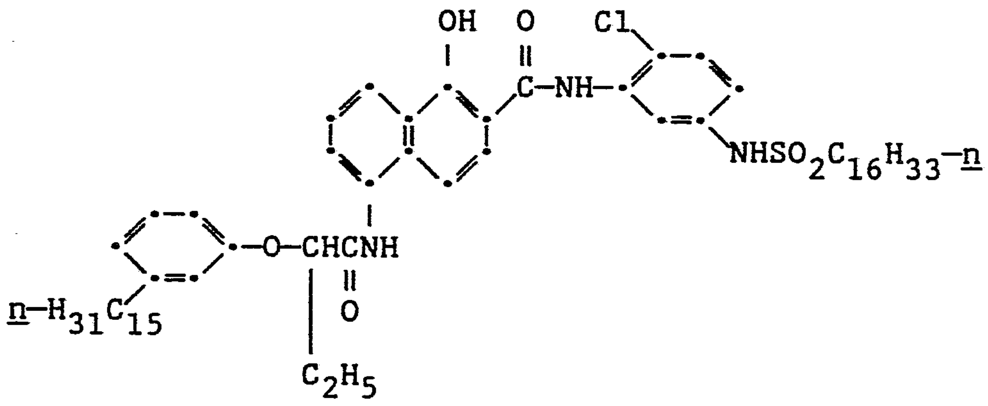
Examples of red or infrared dye-forming couplers are as follows:

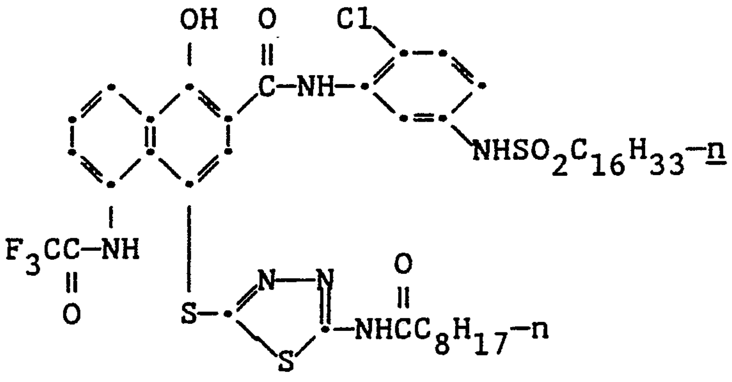


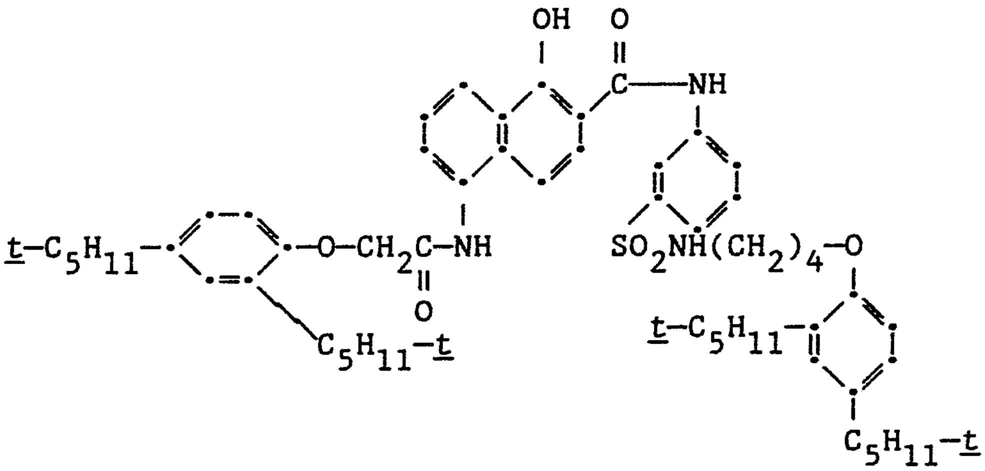


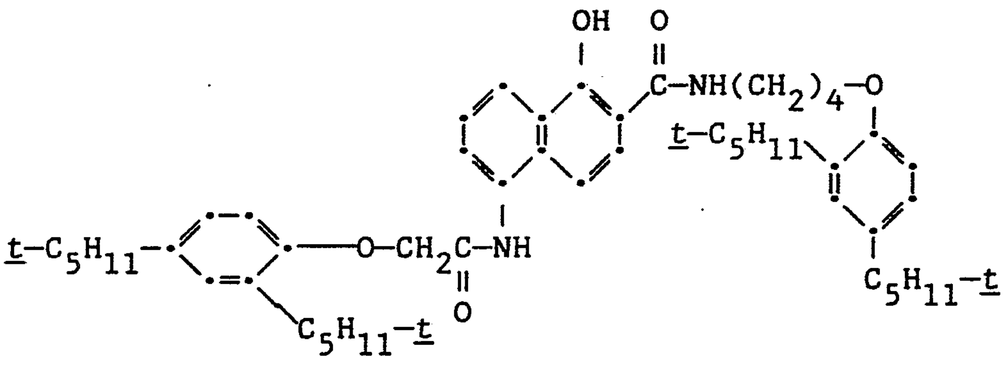


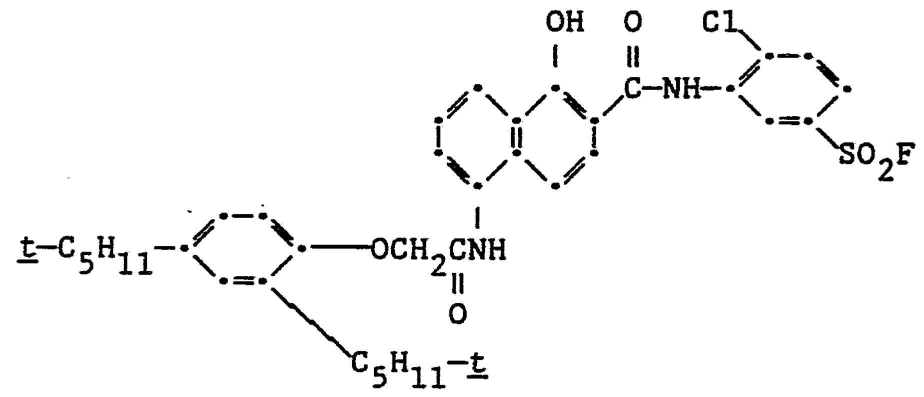


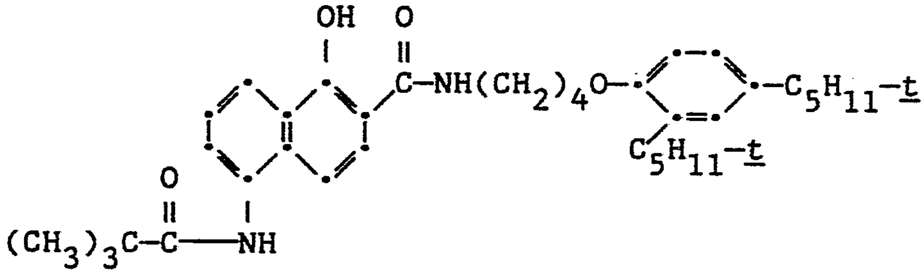


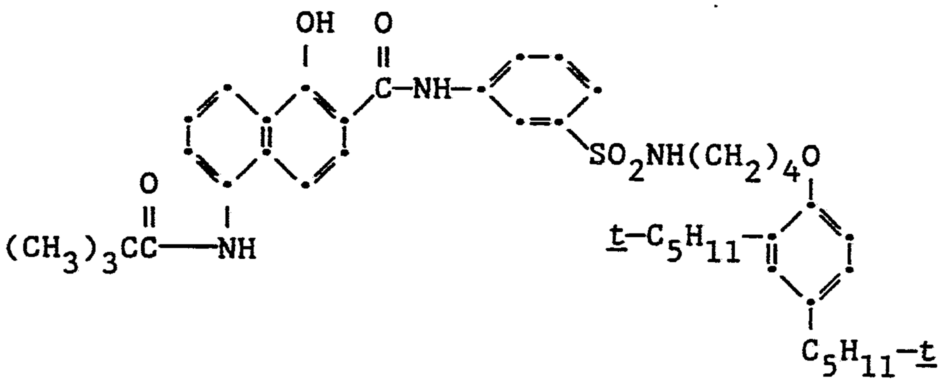


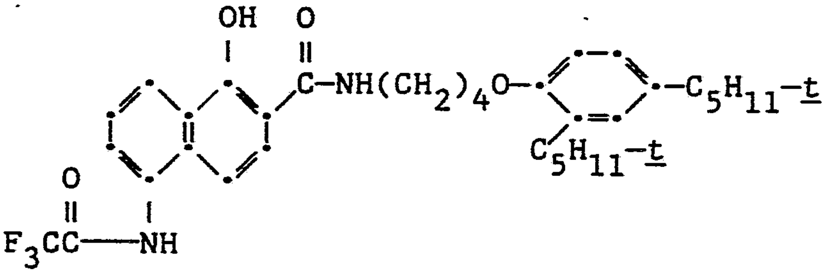


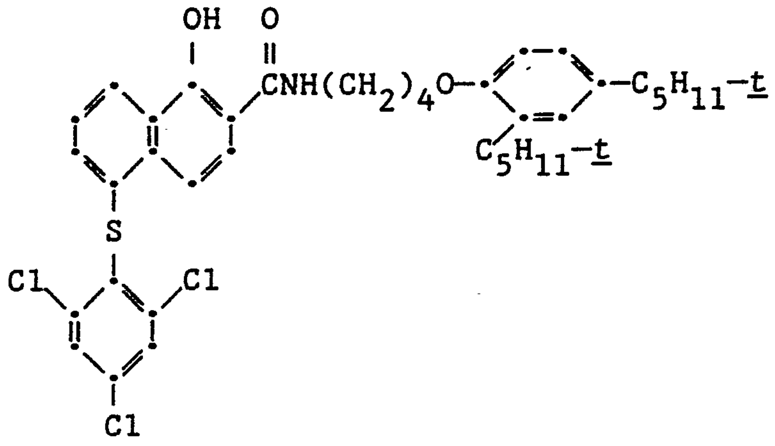


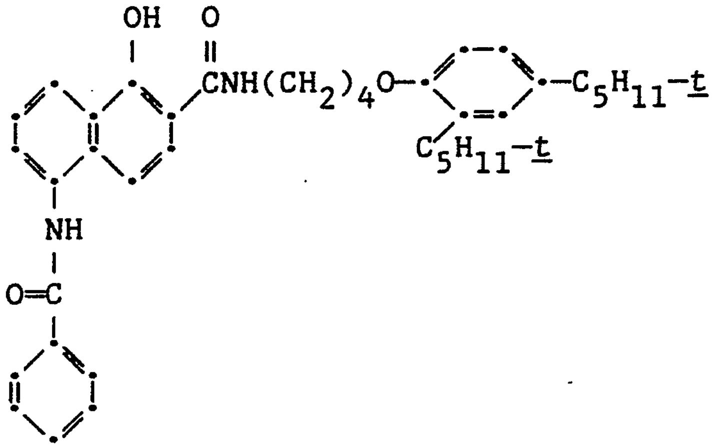


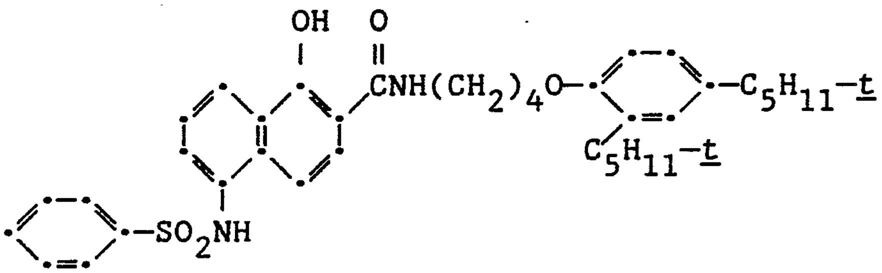


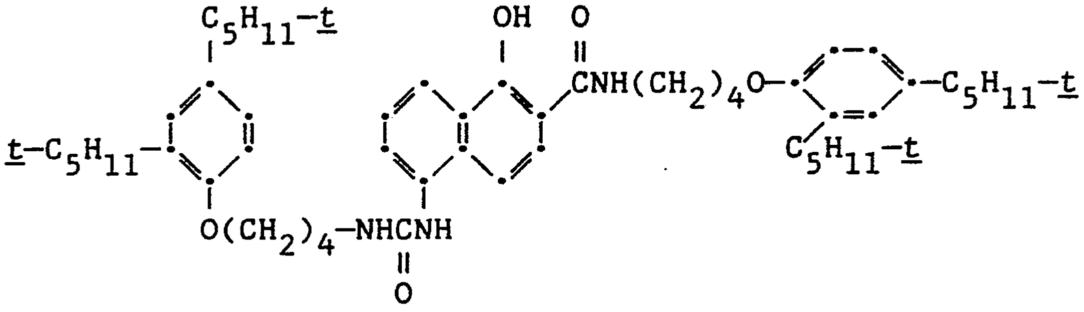


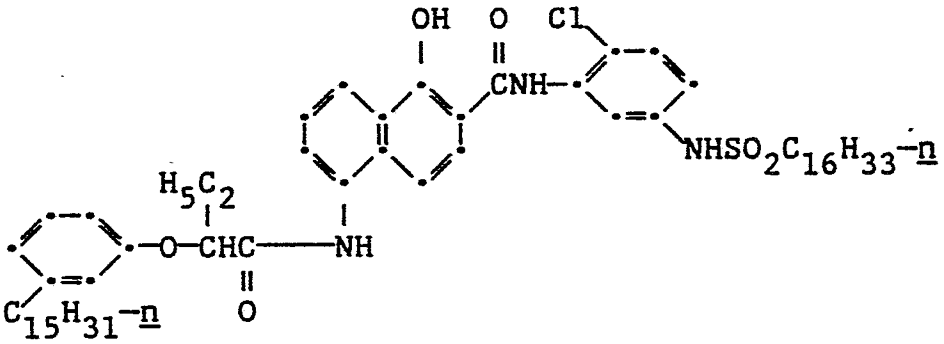


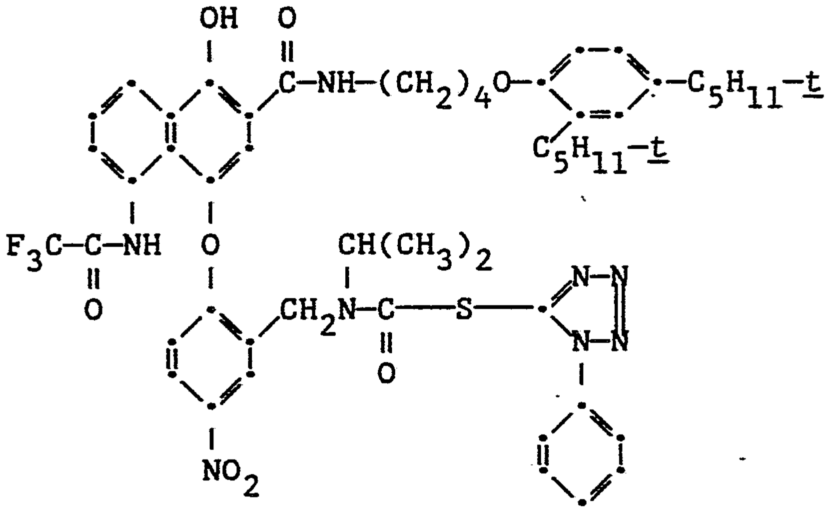

OH
O
CNH(CH2)4O
C5H11-t
C5H11-t
S
Cl
Cl
Cl

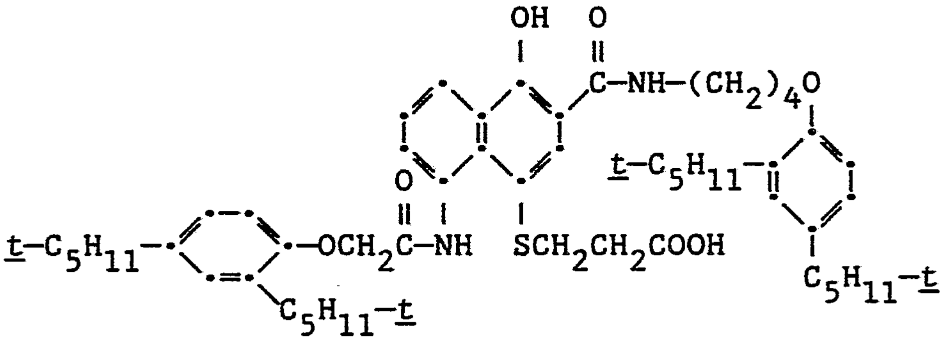

OH
O
CNH(CH2)4O
C5H11-t
C5H11-t
NH
O=C

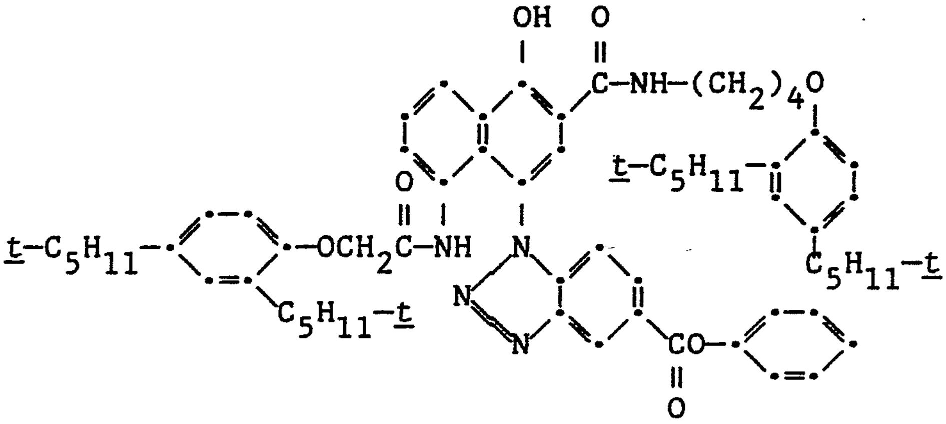

OH
O
CNH(CH2)4O
C5H11-t
C5H11-t
SO2NH

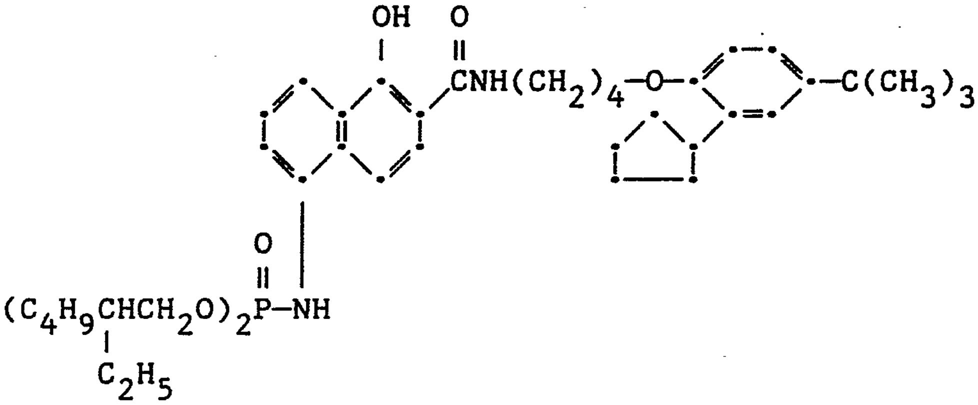

C5H11-t
t-C5H11
O(CH2)4-NHCNH
O
OH
O
CNH(CH2)4O
C5H11-t
C5H11-t

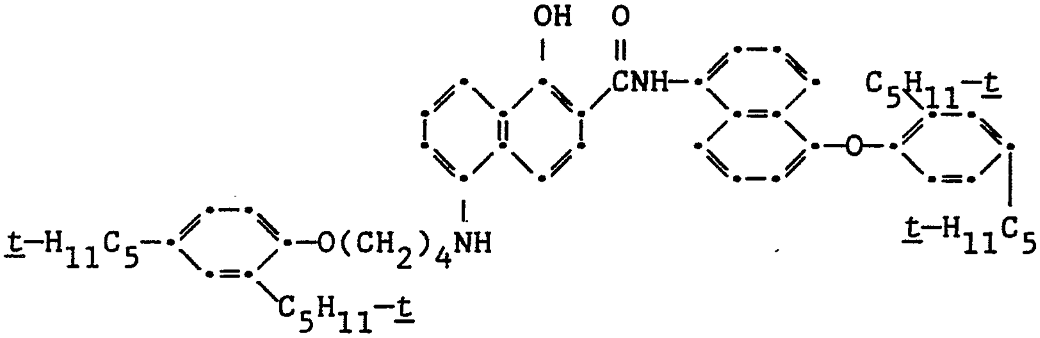


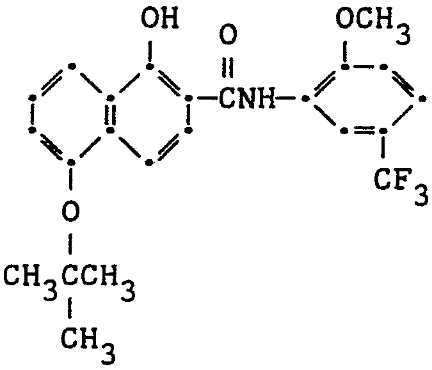


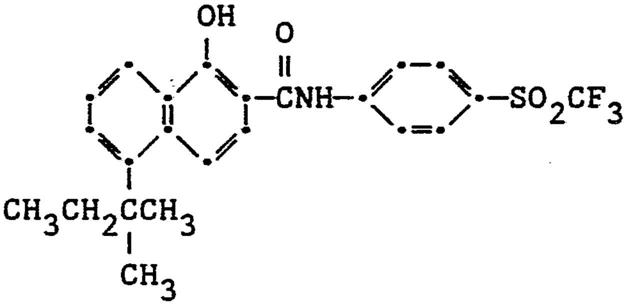


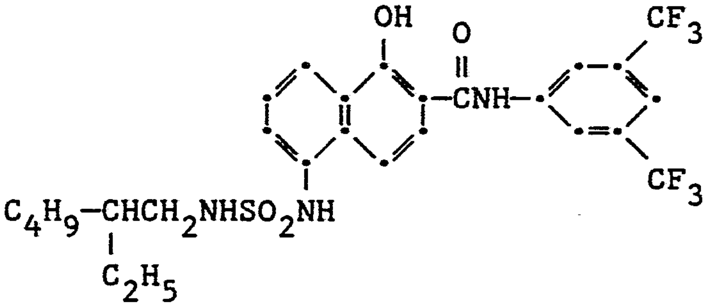


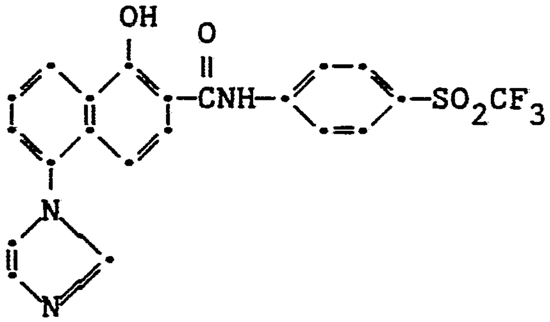


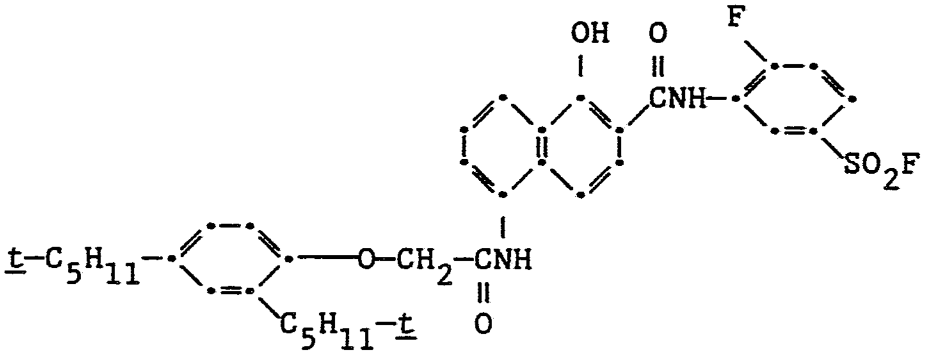


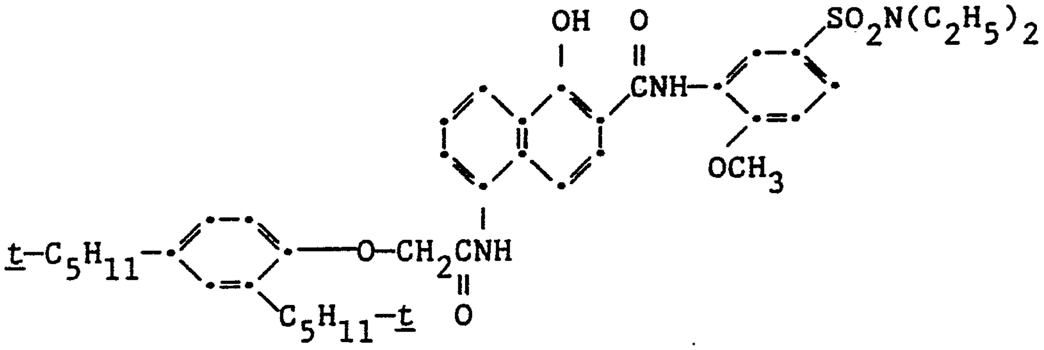


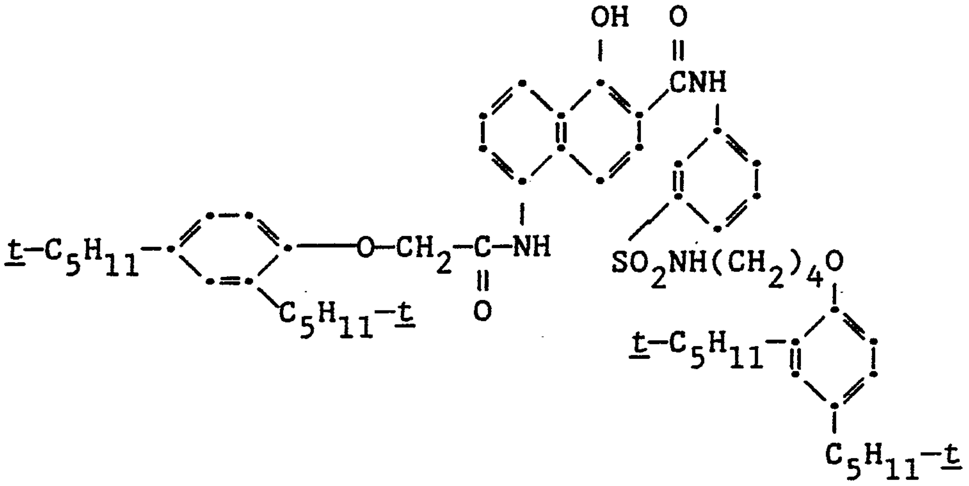

OH
O
CNH
SO2CF3
CH3CH2CCH3
CH3

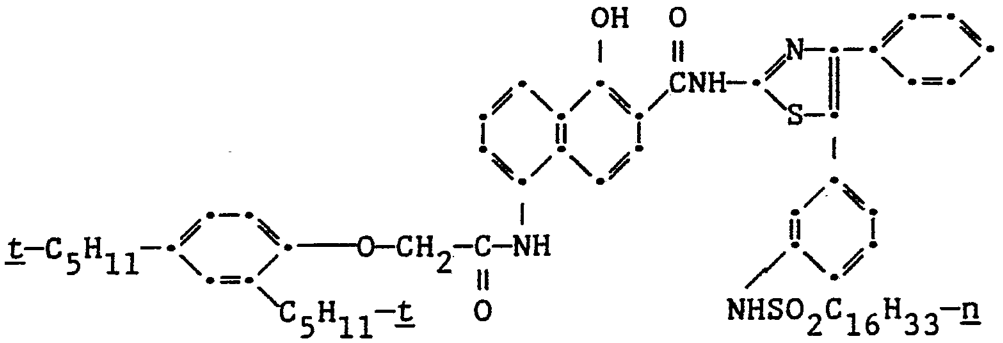

OH
O
CNH
CF3
CF3
C4H9—CHCH2NHSO2NH
C2H5


OH
O
CNH
SO2CF3
N
N

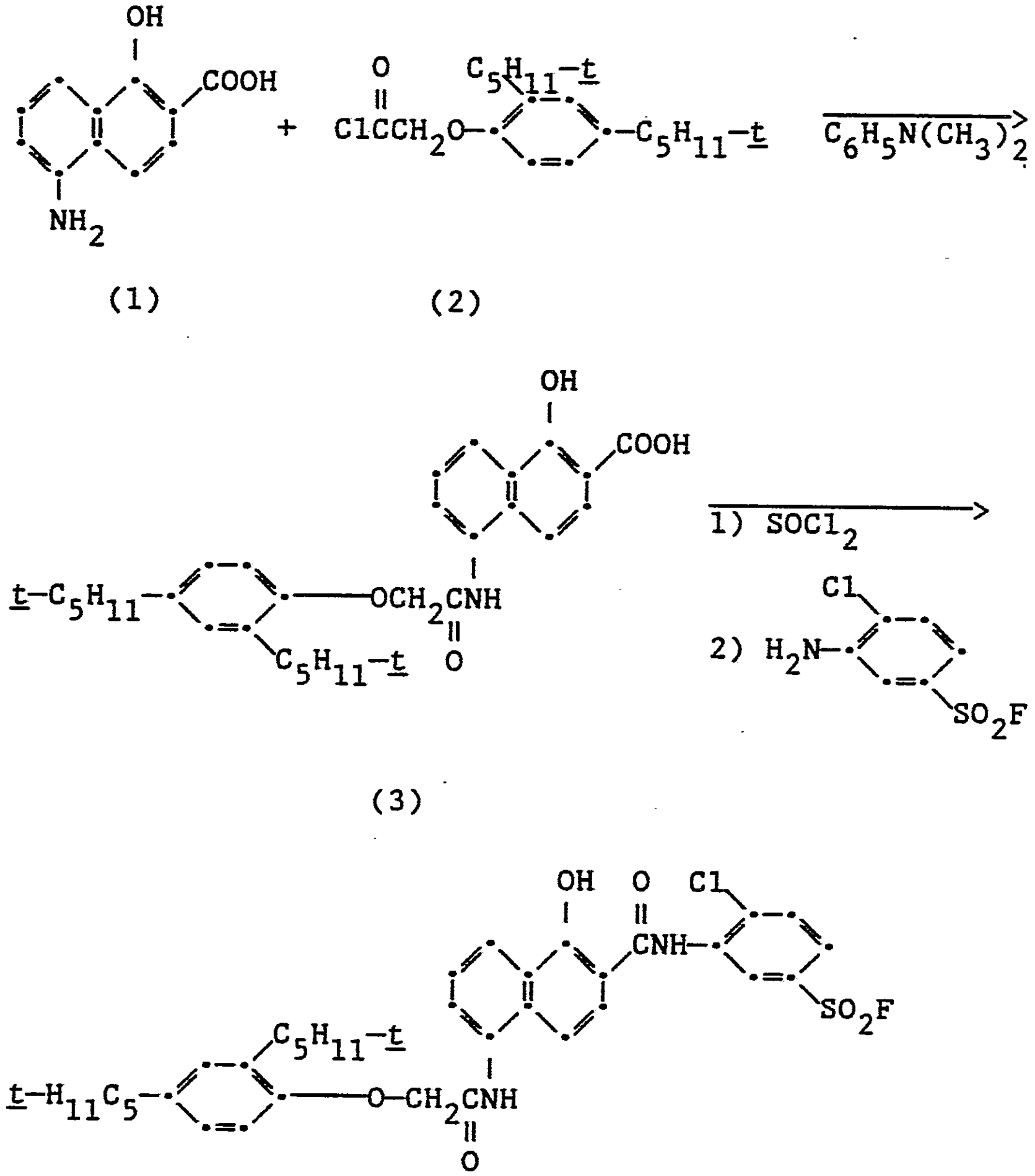

OH
O
F
CNH
SO2F
t—C5H11
O—CH2—CNH
O
C5H11—t







The red or infrared dye-forming naphtholic couplers according to the invention can be synthesized by methods known in the organic synthesis art. The process of synthesis typically involves first attachment of the bulky substituent to an amino group in the 5-position of a 2-carboxy-1-naphthol and then conversion of the 2-carboxy group to its corresponding amide or ester. An illustrative method of preparation is as follows: Synthesis Example A-



(1) (2) (3)

To a stirred solution of 20.3 gm (0.1 mol) 2-carboxy-5-amino-1-naphthol (1) in 700 ml tetrahydrofuran containing 36.4 gm (0.3 mol) dimethylaniline and 30 ml water was added dropwise 31.1 gm (0.1 mol) 2,4-di-tert-pentyl-phenoxyacetyl chloride (2). After 3 hours at room temperature the reaction mixture was poured into ice-water containing 15 ml concentrated hydrochloric acid. The resulting solid precipitate was collected, washed, and recrystallized from alcohol and then from aqueous dimethylformamide to yield a gray solid, m.p.>200°C. Elemental analysis, nmr, and infrared spectra were used to identify the desired intermediate 2-carboxy-1-naphthol compound (3).

Then, 30 ml of thionyl chloride was added dropwise to a stirred solution of 9.6 gm (0.02 mol) (3) in 30 ml tetrahydrofuran. After 3 hours at room temperature, the volatile components were removed at reduced pressure and room temperature. A solution of the resultant acid chloride in 50 ml tetrahydrofuran was added dropwise to a stirred solution of 3-amino-4-chlorobenzenesulfonyl fluoride in 30 ml tetrahydrofuran. After 3 hours at room temperature, the reaction mixture was poured into ice-water containing 15 ml of concentrated hydrochloric acid and the product was collected, washed, and dried. Ethyl acetate recrystallization yielded the desired white solid product, m.p. 245-246°C, with the correct elemental analysis for the desired naphtholic coupler.

The couplers of this invention can be used in the ways and for the purposes that couplers are used in the photographic art.

Typically, the couplers are incorporated in silver halide emulsions and the emulsions coated on a support to form a photographic element. Alternatively, the couplers can be incorporated in photographic elements adjacent to the silver halide emulsion where, during development, the coupler will be in reactive association with development products such as oxidized color developing agent. Thus, as used herein, the term "associated therewith" signifies that the coupler is in the silver halide emulsion layer or in an adjacent location where, during processing, it will come into reactive association with silver halide development products.

The photographic elements can be single color elements or multicolor elements. Multicolor elements contain dye image-forming units sensitive to each of the three primary regions of the spectrum. Each unit can be comprised of a single emulsion layer or of multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art. 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, e.g., as by the use of microvessels as described in Whitmore U.S. Patent 4,362,806, issued December 7, 1982.

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, at least one of the layers of the element comprising a coupler of this invention. The element can contain additional layers, such as filter layers, interlayers, overcoat layers, subbing layers, and the like.

The silver halide emulsions employed in the elements of this invention can be either negative-working or positive-working.

The red and infrared dye-forming naphtholic couplers are particularly useful in combination with coupler solvents.

The red or infrared dye-forming naphtholic coupler is useful in a photographic element in any location that enables the formation of red or infrared dye from the coupler upon oxidative coupling during processing. The coupler can, for example, be in at least one silver halide photographic emulsion layer, an overcoat layer, an interlayer, or in various combinations of layers of a photographic element.

An illustrative element is a photographic element comprising a support bearing at least one silver halid photographic emulsion layer comprising a coupler according to the invention and a coupler solvent as described. The photographic element can be used, for example, for forming a sound track or for forming a silver image and a sound track. In a preferred photographic element a coupler as described enables formation of an integral dye sound track. If a sound track comprising both dye and silver is desired, the coupler can be of the bleach inhibitor release (BIR) type; that is, it can release a bleach inhibitor. The bleach inhibitor moiety is conventionally attached to the coupling position either directly or through a timing group.

Coupler solvents contemplated for use in combination with the above couplers include, for example lower alkyl esters of phthalic acid, lower alkyl substituted triphenyl phosphates and lower alkyl N-substituted aliphatic amides having at least 10 carbon atoms.

The following are exemplary of preferred coupler solvents:

dimethyl phthalate
diethyl phthalate
di-n-butyl phthalate
di-i-amyl phthalate
di-n -amyl phthalate
tri-o-cresyl phosphate
tri-m-cresyl phosphate
tri-p-cresyl phosphate
o-cresyl diphenyl phosphate
N,N-diethyl lauramide
N,N-di-n-butyl lauramide
N,N-diethyl capramide.

Coupler to coupler solvent weight ratios of from 5:1 to 1:2 are generally preferred. For the lower alkyl esters of phthalic acids employed as coupler solvents it is preferred that the coupler to solvent weight ratio be in the range of from 1:1 to 1:2. For the triphenyl phosphate coupler solvents it is preferred that the weight ratio of coupler to coupler solvent be in the range of from 4:1 to 1:1. For the N-substituted aliphatic amides it is preferred that the weight ratio of coupler to coupler solvent be in the range of from 4:1 to 2:1.

Coupler solvents of the type described above and techniques for dissolving couplers therein are known to those skilled in the art. Techniques are also well known for dispersing coupler-containing coupler solvents in hydrophilic colloid-containing coating compositions useful in forming photographic elements. The coupler-containing coupler solvent is typically dispersed in the hydrophilic colloid-containing coating composition in the form of particles of relatively small size, typically from about 0.3 to about 3.0 microns in mean diameter, usually by colloid milling.

The term "integral sound track" indicates that a sound track and a photographic image are formed in separate portions of the same element and that following exposure the separate areas are concurrently and identically processed (i.e. requiring no process steps other than those required for processing the photographic image portion) to form sound track and photographic records, respectively.

In a form capable of recording multicolor images the photographic element contains in addition to the support and the single layer unit described above at least two additional layer units. The single layer unit described above can contain a red-sensitized silver halide emulsion and be employed to form a cyan dye image as well as an infrared absorbing dye image. The same dye can form both the cyan and the infrared absorbing dye image, but is preferred in that instance that the single layer unit described above be modified to include in addition a conventional cyan dye-forming coupler. The cyan dye-forming coupler is preferably dispersed in separate coupler solvent particles from those containing the infrared absorbing dye-forming coupler or coated without employing a coupler solvent. A second layer unit is present containing a blue-sensitive silver halide emulsion and a yellow dye-forming coupler, and a third layer unit is present containing a green-sensitized silver halide emulsion and a magenta dye-forming coupler. The construction of the second and third layer units and their relationship to the first layer unit is conventional.

In another form, which is specifically preferred, the photographic element is provided with four separate layer units. Three layer units are conventional cyan, magenta and yellow dye-forming layer units of the type found in conventional silver halide photographic elements intended to form multicolor dye images. The fourth layer unit can be identical to the single layer unit described above. In a preferred form the silve halide emulsion in the fourth layer unit is sensitized to a portion of the spectrum to which the remaining layers are relatively insensitive. For example, the fourth layer unit emulsion can be spectrally sensitized to the infrared portion of the spectrum or to portions of the visible spectrum which lie at the fringes of the spectral regions the remaining layer units are intended to record.

Still other variant forms of the photographic elements can be employed. For example, the emulsion of the sound track layer unit can be employed with only its native spectral sensitivity. In this instance the response of the sound track layer unit is confined to exposure to ultraviolet and the adjacent blue portion of the spectrum, the blue response varying to some extent with the silver halide chosen. In still another variant form the speed rather than the spectral response of the sound track recording layer unit can be different from that of another, image-forming layer unit. The sound track recording layer can be either faster or slower than an image-forming layer unit of similar spectral response. A combination of both differing spectral response and speed can also be employed to allow selective exposure of the sound track and image-forming layer units.

While any photographically useful amount of particles of the infrared absorbing dye-forming coupler and coupler solvent can be present in the layer units described above, for sound track applications employing typical photocells it is preferred that these particles be present in a concentration sufficient to provide a maximum dye density of at least 1.0 over the spectral region of from 750 to 850 nm, preferably at least 2. Such dye densities can be obtained readily with the preferred coupler-coupler solvent combinations within the concentration ranges conventionally employed for coupler solvent particles containing cyan, magenta and yellow dye-forming couplers. Generally, coupler concentrations ranging from about 0.40 to 1.30 g/m^2 are contemplated, preferably from about 0.65 to 1.05 g/m^2, optimally from about 0.75 to 0.95 g/m^2.

The photographic silver halide emulsion layers, adjacent hydrophilic colloid-containing layers and other layers, including overcoat, subbing and interlayer coatings of conventional character, can contain various colloids alone or in combination as vehicles. Suitable hydrophilic vehicle materials include both naturally-occurring substances such as proteins, for example gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like.

The photographic elements can be prepared and can contain addenda known to be useful in the photographic art, particularly those addenda known to be useful in photographic elements for forming red or infrared absorbing dyes, such as described in U.S. Patent 4,250,251 and Research Disclosure, December, 1978, Item No 17643 published by Kenneth Mason Publications, Ltd., The Old Harbourmaster's, 8 North Street, Emsworth, Hampshire PO107DD, England.

The silver halide emulsion and remaining layers of the photographic elements can be coated on any conventional photographic support. For projection film application including an integral sound track the support is transparent. For such applications conventional photographic film supports can be employed such as cellulose nitrate film, cellulose acetate film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and similar resinous film supports.

In one preferred mode of exposure the photographic element is panchromatically exposed and an edge portion of the film is exposed to infrared radiation to form the sound track. When this mode of exposure is undertaken, the silver halide grains in the sound track recording layer unit are spectrally sensitized with infrared absorbing spectral sensitizing dyes.

The photographic elements can be processed to form dye images which correspond to or are reversals of the silver halide rendered selectively developable by imagewise exposure by conventional techniques. Multicolor reversal dye images can be formed in photographic elements having differentially spectrally sensitized silver halide layers by black-and-white development followed by a single color development step, as illustrated by the Kodak Ektachrome E4 and E6 and Agfa processes described in British Journal of Photography Annual, 1977, pp. 194-197, and British Journal of Photography , pp. 668-669. The photographic elements can be adapted for direct color reversal processing (i.e., production of reversal color images without prior black-and-white development) (Kodak, Ektachrome, Kodacolor and Flexicolor are trademarks of Eastman Kodak Company, U.S.A.).

Multicolor dye images which correspond to the silver halide rendered selectively developable by imagewise exposure, typically negative dye images, can be produced by processing, as illustrated by the Kodak Kodacolor C-22, the Kodak Flexicolor C-41 and the Agfa color processes described in British Journal of Photography Annual, 1977, pp. 201-205. The photographic elements can also be processed by the Kodak Ektaprint-3 and -300 processes as described in Kodak Color Dataguide, 5th Ed., 1975, pp. 18-19, and the Agfa color process as described in British Journal of Photography Annual, 1977, pp. 205-206.

In a specific preferred application the photographic elements are employed to form a motion picture film for projection containing an integral sound track useful in a projector having an S-1 photocell. The photographic element is comprised of a transparent film support on which are coated, in the order recited, a red-sensitized cyan dye-forming coupler containing first layer unit, a green-sensitized magenta dye-forming coupler containing a second layer unit, a blue-sensitive yellow dye-forming coupler containing third layer unit and an infrared-sensitized fourth layer unit containing coupler solvent particles according to this invention, as has been described above. The picture recording portion of the element is flashed to infrared and is then exposed to the blue, green and red portions of the spectrum through a master image film. The master image film has a transparent support and has been processed so that it carries a positive multicolor dye image. The edge of the photographic element on which the integral sound track is to be formed is panchromatically exposed through a positive sound track master by a light source to which at least the fourth layer unit is sensitive. In a preferred form this is a white light source which exposes the red-sensitized, green-sensitized and blue-sensitive layer units. The fourth layer unit by reason of its native sensitivity to blue light is also exposed by the white light source. The white light source can also emit infrared to expose the fourth layer unit. The photographic element after exposure of both the picture and sound track areas is reversal processed. In reversal processing of negative-working silver halide emulsions, positive dye images are formed in unexposed areas. Since the picture area was uniformly flashed to infrared, no density attributable to the fourth layer unit is present in the picture area. In the sound track area the major portion of the infrared density is attributable to the fourth layer unit, but the other layer units can also add to the total infrared density.

In processing to form dye images in the manner described above any conventional color developing agent can be employed which will permit the formation of a dye. Depending upon the specific color developing agent selected, the maximum dye densities, the wavelength of the peak densities and the increased breadth of bathochromic absorption will vary. The color developing agent 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethylaniline sulfate hydrate has been observed to produce infrared absorbing dye images having a maximum density in excess of 1.0, often in excess of 2.0, not only at 800 nm, but over the entire spectral region of from about 725 to about 850 nm.

The following examples further illustrate the invention.

Examples 1-6

Photographic elements were prepared by coating a cellulose acetate butyrate film support with a photosensitive layer containing a silver bromoiodide emulsion at 0.91 gm Ag/m^2, gelatin at 3.78 g/m^2, and one of the couplers identified below dispersed in one-half its weight of dibutyl phthalate and coated at 1.62 x 10^{-3} moles/m^2. The photosensitive layer was overcoated with a layer containing gelatin at 1.08 g/m^2 and bis-vinylsulfonylmethyl ether at 1.75 weight percent based on total gelatin.

Samples of each element were exposed through a graduated-density test object and processed at 40°C employing the following color developer Solution A:

Color Developer Solution A

4-Amino-3-methyl-N-ethyl-N-β-hydroxyethylaniline sulfate 3.55 g
Potassium sulfite 2.0 g
Potassium carbonate (anhydrous) 30.0 g
Potassium bromide 1.25 g
Potassium iodide 6.0 mg
Water to: 1.0 L
pH adjusted to: 10.0

Development was followed by the conventional steps of bleaching, fixing, washing, and drying. Spectral absorption curves for the resulting well-defined step images were plotted for each element to determine the dye absorption maximum (λ-max) listed in Table I. Processed strips of each element containing a dye image were subjected either to a six week wet oven (60°C/70% RH) keeping test or to a five minute ferrous ion solution test.

Ferrous Ion Solution (made under nitrogen purging)

Degassed distilled water 750 ml
Ethylenediaminetetraacetic acid 32.12 g
Ammonium hydroxide (conc. soln.) 15 ml
Ferrous sulfate 7 H_2O 27.8 g
Ammonium hydroxide and water to: 1.0 L
(Nitric acid to adjust pH downward) pH 5.0

The results are given in following Table I.

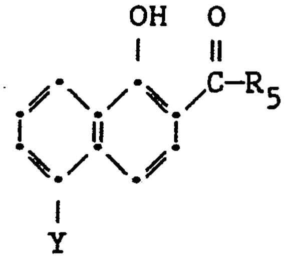
The results presented in Table I indicate that the bulky C-5 substituents provide the couplers of this invention with the capacity to form dyes of much longer wavelength absorption than those from the comparison couplers. In addition, it can be seen that with any given ballast group in the 2-position, increasing the bulk of the 5-substituent generally increases the dye stability to attack by ferrous ion. Dyes produced according to the invention are also resistant to fading under conditions of high humidity at elevated temperatures.

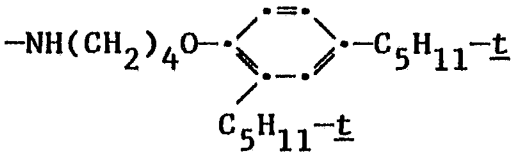
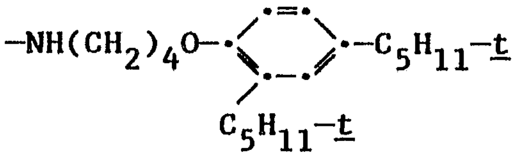
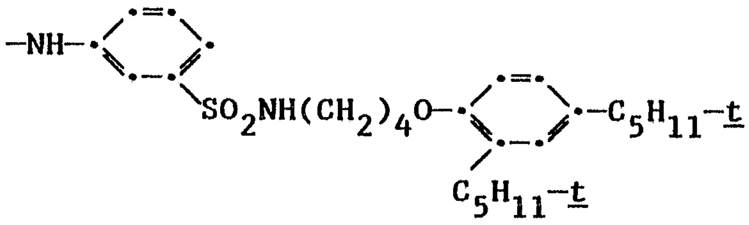
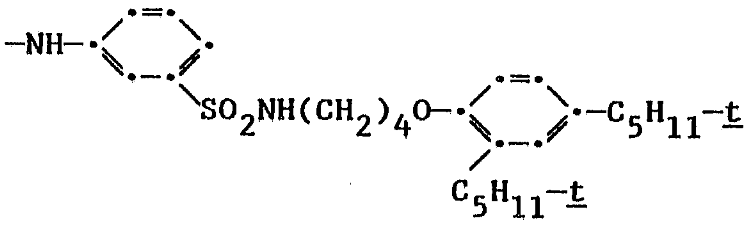
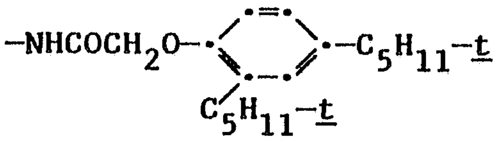
TABLE I

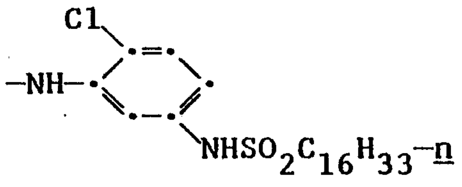
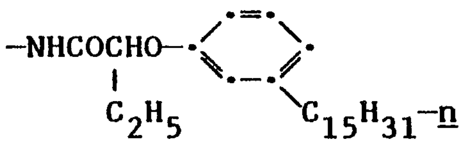
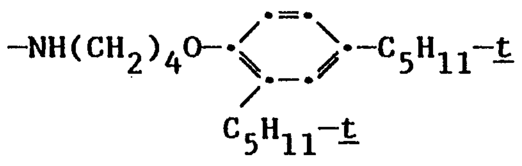
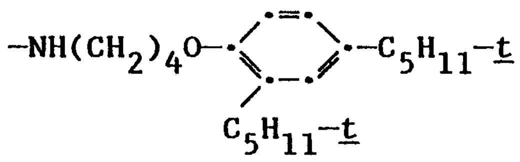
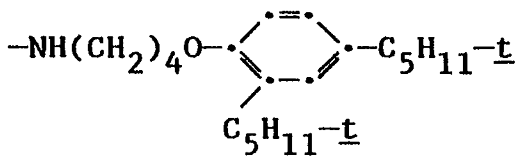
Example	Coupler	λ-max	% Density Loss or Gain 6 Wk. W.O.*	 FeII Solution
Comparison A	C-1	700	-10±2	-68±10
Comparison B	C-2	707	-5	-88
Comparison C	C-3	709	-4	-18
1	1	727	-4	-88
2	2	729	+1	-3
3	3	757	-4	-47
4	4	742	0	-28
5	5	752	-15	-10

*W.O. herein means wet oven (60°C/70% RH).

Structures of the couplers in Table I are as follows:



Coupler	R_5	Y
1		$-NHCOCF_3$
2		$-NHCOC(CH_3)_3$
3		$-NHCOC(CH_3)_3$
4		

Coupler	R_5	Y
5		
C-1		—H
C-2		$-NHSO_2CH_3$
C-3		$-NHCOCH_3$

Example 6

This comparative example illustrates that desirable properties of photographic couplers comprising a napholic moiety capable of forming a red or infrared absorbing dye depend not only upon the effects of the 5-position substituent Y, but also upon substituents at the 2-position.

A photographic coating of very fine grain silver bromide emulsion (807 mg Ag/m^2) and 3229 mg Ag/m^2 of gelatin on a film support was overcoated with 1080 mg/m^2 of gelatin and 86 mg/m^2 of bis (vinylsulfonyl) ether hardener. Strips of this element were imagewise exposed to light through a step tablet and then developed ten minutes at 24°C in developers prepared by adding a 2.5 ml solution containing 1.25 mmole of each of the couplers of Table IIA in dimethylformamide to 250 mL of the following developer solution (Developer Solution A):

Developer Solution A: CD-2 color developer (as described in column 23 of U.S. Patent 4,340,664 3.2 g
Sodium Sulfite 0.65 g
Potassium Bromide 1.0 g
Potassium Phosphate 13.25 g
Water to 1 L, pH 12

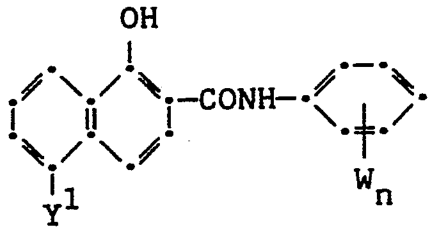
Development was followed by a 5 minute water wash, and 30 seconds in a fixer solution (Fixer Solution A) before final water washing and drying.

The fixer sensitivity (dye density loss) was observed and indicated in following Table II and compared with the fixer sensitivity for the dye from coupler 5 of the invention in Part B of Table II. Coupler 5 was incorporated in an emulsion layer as in Example 1 and, after imagewise exposure, processed in a developer solution (Developer Solution A) containing CD-2 color developer.

Fixer Solution A had the following composition:

Ammonium Thiosulfate 120 g
Potassium Metabisulfite 20 g
Potassium Iodide 2 g
Water to 1 L

Table II

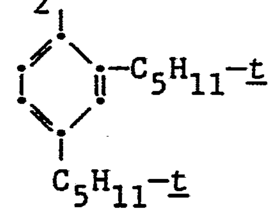


A. Comparison Couplers

Y^1	W_n	λmax	Fixer Sens.*
–H	$2-SO_2F$	702	5
–H	$3-SO_2F$	726	4
–H	$4-SO_2CF_3$	721	0
–H	$4-CF_3$	712	0
–H	$2-SO_2CH_3$, $5-SO_2F$	683	5
–H	2–Cl, $5-SO_2CH_3$	705	0
–H	$3-SO_2F$, $4-OCH_3$	694	5
–H	$3-CF_3$, $4-OCH_3$	681	0
–H	$2-OCH_3$, $5-SO_2F$	788	4

Y^1	W_n	λmax	Fixer Sens.*
$-OCH_3$	2-OCH_3, 5-SO_2F	724	2
-H	2-OCH_3, 5-SO_2NH_2	688	1
-H	2-OCH_3, 5-$SO_2N(C_2H_5)_2$	705	0
-H	2-OCH_3, 5-SO_2CF_2H	711	0
-H	2-OC_2H_5, 5-SO_2F	762	3
-H	2-F, 4-SO_2F	740	0

B. Invention Coupler

Y^1	W_n	λmax	Fixer Sens.*
$-NHCOCH_2O$ 	2-Cl, 5-SO_2F	754	0

*Fixer sensitivity ranking of dye density loss from 0 (none) to 5 (severe).

Data in Table II indicates that the presence of a fluorosulfonyl substituent on the anilino ring can lead to undesired dye sensitivity in the fixer. The presence of additional alkoxy or sulfone substituents appears to enhance this sensitivity while the presence of halogen substituents stabilizes the dye. Best stability to the fixer while maintaining the desired long wavelength absorption was achieved by a dye formed from a coupler of this invention which contains a bulky Y group.

Examples 7-18 Coupler Solvent Effects on Dye Hue and Stability

Photographic elements were prepared and processed as in Example 1 except that both dibutyl phthalate (DBP) and diethyl lauramide (DEL) coupler solvents were employed as noted in Table III and color developer Solutions B and C were used which contained 2.45 g per liter of 4-amino-3-methyl-N,N-diethylaniline hydrochloride or 5.0 gm per liter of 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)-ethylaniline sulfate, respectively, in place of the Solution A developing agent.

The λ-max and density at λ800 nm were determined for the dyes formed in each element and processed strips were subjected to a 77°C low humidity keeping test for one week. The resulting percent change in density is noted for each in Table III.

TABLE III

Example	Coupler	Solvent	C:S wt Ratio	Developer B			Developer C		
				λ-max	D-800	%ΔD	λ-max	D-800	%ΔD
7	3	DBP	1:2.0	760	1.11	-11.7	745	0.88	+4.6
8	3	DBP	1:0.5	765	1.13	-89.4	750	0.92	-9.8
9	3	DEL	1:2.0	757	1.06	-29.2	745	0.83	+10.8
10	3	DEL	1:0.5	763	1.18	-84.7	750	0.94	+1.1
11	4	DBP	1:2.0	742	1.30	+1.5	732	1.13	+3.5
12	4	DBP	1:0.5	750	1.18	+20.3	735	1.22	+4.1
13	4	DEL	1:2.0	742	1.40	-41.4	727	1.02	+5.9
14	4	DEL	1:0.5	748	1.40	-11.4	733	1.27	-2.4
15	5	DBP	1:2.0	754	1.44	-20.8	740	1.33	-0.8
16	5 (Poor ctg)	DBP	1:0.5	755	0.45	-15.6	730	0.32	0
17	5	DEL	1:2.0	755	1.41	-87.9	750	1.40	-80.7
18	5	DEL	1:0.5	760	1.25	-57.6	752	1.34	-5.2

The choice of coupler solvent and coupler solvent level can affect the dye hue obtained with any given developer. A bathochromic shift is attained by lowering the coupler solvent level from 1:2 to 1:0.5, which often results in increased 800 nm absorption useful for optical sound track images.

Couplers dispersed in the lower level of diethyl lauramide gave dyes with Developer C which were among the best for resistance to fading by dry heat.

Unlike the infrared dyes of the prior art which have double peaks in their absorption spectra indicative of microcrystallization, the infrared dyes of this invention have broad bathochromically shifted absorptions independent of the level of residual unused coupler present with the dye.

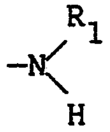
Claims

1. A photographic element comprising a support bearing a photographic silver halide emulsion and a red or infrared dye-forming coupler,
characterised in that
said dye-forming coupler is a naphtholic coupler capable of oxidative coupling to form a red or infrared absorbing dye and comprising

(a) hydrogen or a coupling-off group in the coupling position;

(b) a group, in the position ortho to the hydroxy group, which is represented by the formula:

$-\overset{\overset{O}{\|}}{C}-R$ wherein R is unsubstituted or substituted alkoxy, aryloxy or

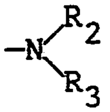


$$-N\begin{matrix}R_1\\H\end{matrix}$$

wherein R_1 is unsubstituted or substituted alkyl, heterocyclic, or aryl group, provided that when R_1 is a fluorosulfonylaryl group, further substituents are other than alkoxy or sulfone; and

(c) a group Y in the 5-position on said naphtholic coupler having sufficient bulk to provide a bathochromic shift in absorption of the resulting red or infrared dye.

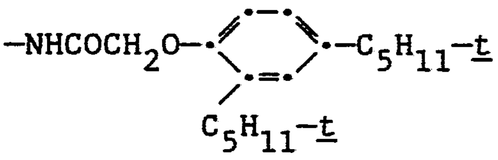
2. A photographic element as in claim 1 wherein said group Y is selected from the group consisting of



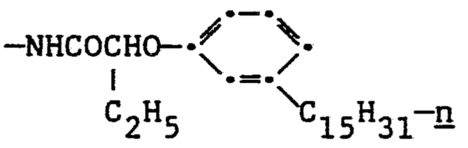
$$-N\begin{matrix}R_2\\R_3\end{matrix}$$,

alkylthio, aryl, aryloxy, arylthio, carbonamido, carbamoyl, sulfonamido, sulfamyl, sulfamido, heterocyclic, imido, ureido, and phosphonamido groups, each of which groups is unsubstituted or substituted by means of at least one group which increases steric bulk and wherein R_2 and R_3 are individually hydrogen, unsubstituted or substituted alkyl or aryl, or together are the atoms necessary to complete a five or six member heterocyclic ring and wherein at least one of R_2 and R_3 is other than hydrogen.

3. A photographic element as in claim 1 wherein said group Y is
$-NHCOCF_3$, $-NHCOC(CH_3)_3$,

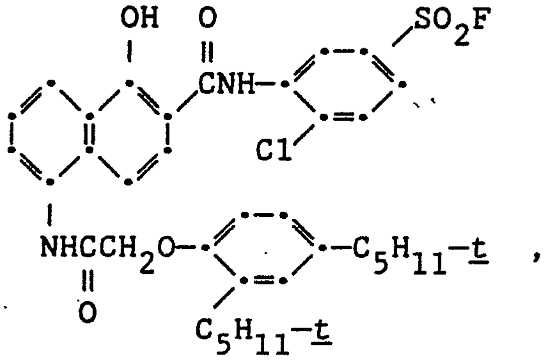


or

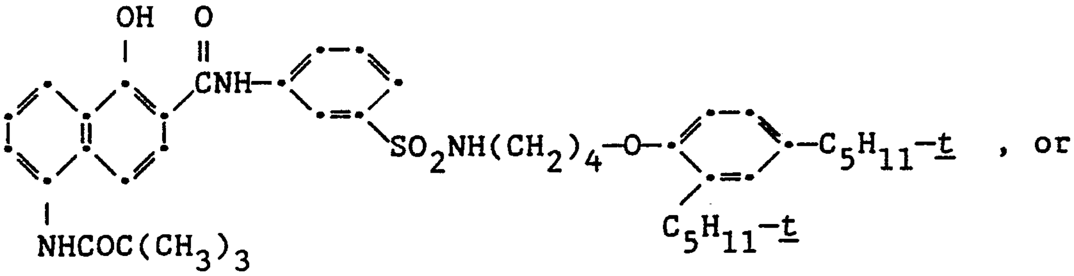


.

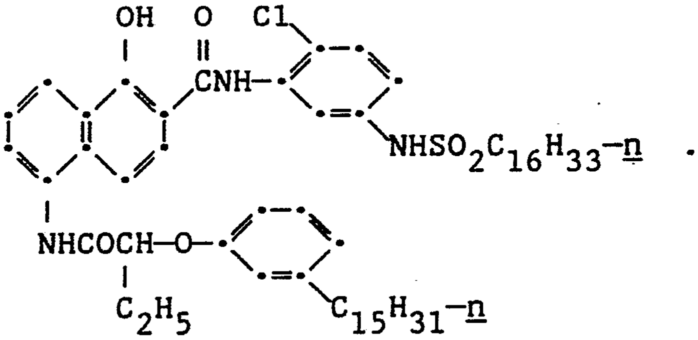
4. A photographic element as in claim 1 wherein said coupler is represented by the formula:



,



, or



.

5. A process of forming a dye image in an exposed photographic element as defined in any one of the preceding claims said process comprising the step of reacting said coupler with an oxidized color developing agent to form a red or infrared absorbing dye.

6. A process of developing an image in a photographic element comprising a support and a silver halide emulsion containing an imagewise distribution of developable silver halide grains, the process comprising the step of developing the element with a silver halide color developing agent in the presence of a red or infrared dye-forming coupler as defined in any one of claims 1 to 4.

7. A multicolor photographic element comprising a support bearing a cyan dye image-forming unit comprising at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta 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, and wherein the photographic element comprises at least one dye-forming coupler as defined in claims 1 - 4.

8. A photographic red or infrared dye-forming coupler as defined in any one of claims 1 to 4.