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(54) Photographic elements containing ballasted couplers.

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DE-A- 1 547 803
DE-A- 2 355 115
DE-A- 2 456 076
DE-A- 2 529 991

(56) References cited :
GB-A- 2 029 977
GB-A- 2 038 808
US-A- 3 408 194
US-A- 3 880 661
US Serial No. 85140 (15.10.79), priority document of EP-A-0 028 099 (published 06.05.81)

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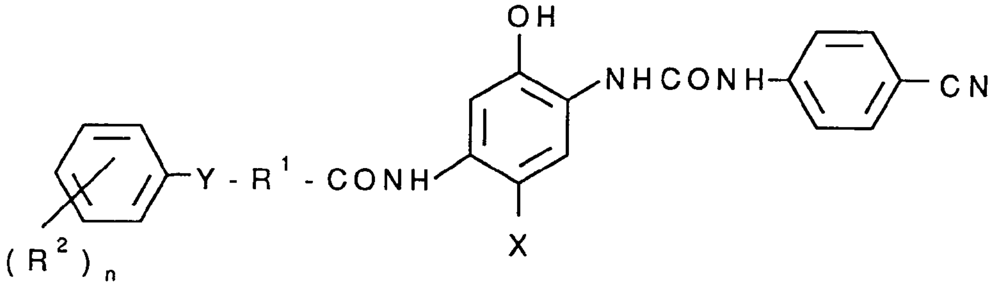
Description

This invention relates to photographic elements containing ballasted couplers.

Images are commonly obtained in the photographic art by a coupling reaction between the development product of a silver halide developing agent (i.e., oxidized aromatic primary amino developing agent) and a color forming compound commonly referred to as a coupler. The dyes produced by coupling are indoaniline, azomethine, indamine or indophenol dyes, depending upon the chemical composition of the coupler and the developing agent. The subtractive process of color formation is ordinarily employed in multicolor photographic elements and the resulting image dyes are usually cyan, magenta and yellow dyes which are formed in or adjacent silver halide layers sensitive to radiation complementary to the radiation absorbed by the image dye; i.e., silver halide emulsions sensitive to red, green and blue radiation.

Since this is a mature art, the patent and technical literature is replete with references to compounds which can be used as couplers for the formation of photographic images. Preferred couplers which form cyan dyes upon reaction with oxidized color developing agents are phenols and naphthols. Representative couplers are described in the following patents and publications: U.S. Patents 2,772,162; 2,895,826; 3,002,836; 3,034,892; 2,474,293; 2,423,730; 2,367,531; 3,041,236 and "Farbkuppler-ein Literaturubersicht", published in Agfa Mitteilungen, Band II, pp. 156-175 (1961).

US patent application serial no. 85 140 (filed 15 October 1979), priority document of EP-A-0 028 099 (published on 6 May 1981) describes photographic couplers which form cyan dyes having particularly desirable hues of narrow bandwidth. *Inter alia* the document discloses couplers having the general formula:



wherein

R^2 is a hydroxyphenylsulphonyl group;
X is hydrogen or a coupling-off group;
Y is oxygen or sulphur,
R^1 is a branched alkylene group of 2 to 20 carbon atoms; and
n is 1 to 3.

There is no disclosure on the subject of the reactivity of the couplers of this document.

Preferred couplers which form magenta dyes upon reaction with oxidized color developing agent are pyrazolones, pyrazolotriazoles, pyrazolobenzimidazoles and indazolones. Representative couplers are described in such patents and publications as U.S. Patents 2,600,788; 2,369,489; 2,343,703; 2,311,082; 2,673,801; 3,152,896; 3,519,429; 3,061,432; 3,062,653; 3,725,067; 2,908,573 and "Farbkuppler-eine Literaturübersicht", published in Agfa Mitteilungen, Band II, pp. 126-156 (1961).

Couplers which form yellow dyes upon reaction with oxidized color developing agent are acylacetanilides such as benzoylacetanilides and pivalylacetanilides. Representative couplers are described in the following patents and publications: U.S. Patents 2,875,057; 2,407,210; 3,265,506; 2,298,443; 3,048,194; 3,447,928 and "Farbkuppler-eine Literaturubersicht", published in Agfa Mitteilungen, Band II, pp. 112-126 (1961).

Also known are couplers which form black or neutral dyes upon reaction with oxidized color developing agent. Representative couplers are resorcinols and *m*-aminophenols such as are described in U.S. Patents 1,939,231; 2,181,944; 2,333,106; 4,126,461; German OLS 2,644,194 and German OLS 2,650,764.

Also known are compounds which react with oxidized color developing agent in the same way as couplers but which do not yield a dye. Such compounds are employed to modify the photographic image by competing with dye-forming coupler for oxidized color developing agent or by releasing a photographic reagent, such as a development inhibitor, as a result of the coupling reaction. While many such compounds are not commonly referred to as couplers, it is convenient to consider them as such in view of the similarities in the ways they and couplers react during photographic processing. For the purposes of the present invention, they are considered couplers. Representative couplers are described in such patents and published patent applications as U.S. Patents 3,632,345; 3,928,041; 3,938,996; 3.958,993; 3,961,959; 4,010,035; 4,029,503; 4,046,574; 4,049,455; 4,052,213; 4,063,950; 4,075,021; 4,121,934; 4,157,916; 4,171,223; 4,186,012 and 4,187,110; U.K. Patent Specifications 1,445,797; 1,504,094; 1,536,341 and 2,032,914A; Germany OLS's 2,448,063; 2,552,505; 2,610,546 and 2,617,310; and Belgian Patent 839,083.

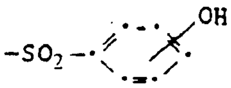
When intended for incorporation in photographic elements, couplers are commonly dispersed therein with the aid of a high boiling organic solvent, referred to as a coupler solvent. Couplers are rendered nondiffusible in photographic elements, and compatible with coupler solvents, by including in the coupler molecule a group referred to as a ballast group. This group is located on the coupler in a position other than the coupling position and imparts to the coupler sufficient bulk to render the coupler nondiffusible in the element as coated and during processing. It will be appreciated that the size and nature of the ballast group will depend upon the bulk of the unballasted coupler and the presence of other substituents on the coupler.

Although numerous couplers are known in the art, there is a continuing problem to improve, or optimize for particular applications, many properties of the coupler and the resultant dye.

It is an object of this invention to provide novel photographic elements that contain couplers that have improved stability, reactivity and compatibility with other components in the photographic element, the dyes derived from such couplers having efficient light absorption and good stability and hue.

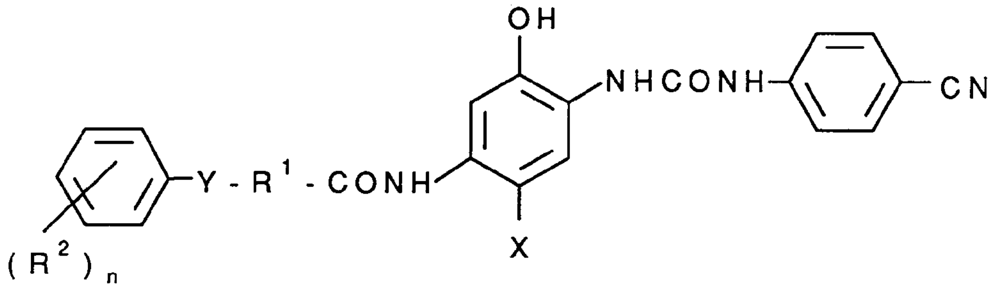
Such can be accomplished by a photographic element comprising a support, a photographic silver halide emulsion and associated therewith a non-diffusible photographic coupler which reacts with oxidized colour developing agent to give a compound which may or may not be an image dye, characterized in that the coupler contains a coupling group COUP-bonded at a position other than the coupling position to a ballast which is substituted with a hydroxyphenylsulfonyl or hydroxyphenylsulfinyl group.

Although substituents of formula



have been suggested for inclusion in photographic dye-forming couplers at other than the coupling position - see for example U.K. Patent Appliation 2,029,977A - they have not been suggested as constituents of ballast groups.

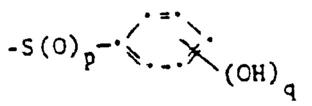
The coupling group COUP- of the couplers used in the photographic elements of the invention can be any coupling group known or used in the art to form a colored or colorless reaction product with oxidized color developing agent. The ballast group of the couplers used in the invention can be any ballast, or portion thereof, which is substituted with a hydroxyphenylsulfonyl group or hydroxyphenylsulfinyl group with the exception of couplers of the formula:



wherein

R^2 is a hydroxyphenylsulphonyl group;
X is hydrogen or a coupling-off group;
Y is oxygen or sulphur,
R^1 is a branched alkylene group of 2 to 20 carbon atoms; and
n is 1 to 3.

Preferred ballast groups used in the invention am substituted with a group of the structural formula:

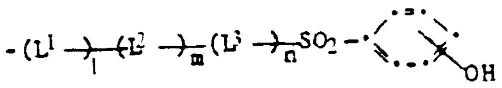


I

where
p is 1 or 2; and
q is 1 to 3.

The substituted group can be joined to the coupling group COUP- at any position, other than the coupling position, where ballast groups commonly are joined. The coupling position of the coupling group can be unsubstituted, or substituted with a coupling off group which can modify the equivalency of the coupler, its reactivity, its dispersibility or which, upon release from the coupler, interacts with other components of the element. The coupling group can include substituents in other positions.

Particularly preferred ballast groups used in the invention have the structural formula:

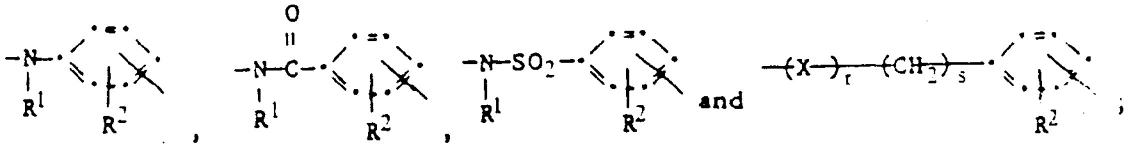


II

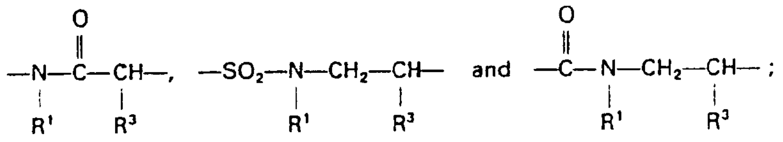
where

l, m and n are each individually 0 or 1, at least one of l, m and n being 1;

L^1 represents a bivalent group selected from

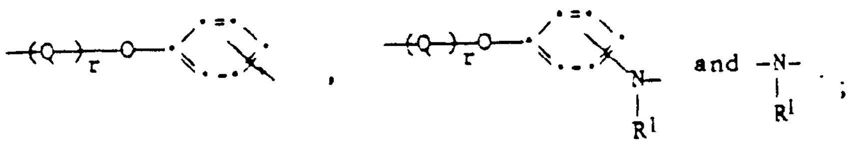


L^2 represents a bivalent group selected from



$$-N(R^1)-C(=O)-CH(R^3)-,\quad -SO_2-N(R^1)-CH_2-CH(R^3)-\quad \text{and}\quad -C(=O)-N(R^1)-CH_2-CH(R^3)-;$$

L^3 represents a bivalent group selected from

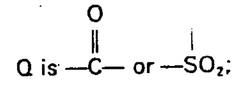


wherein the combination of L^1, L^2 and/or L^3 forms a ballast group;

R^1 and R^3 are each individually hydrogen, alkyl of 1 to 20 carbon atoms or aryl of 6 to 20 carbon atoms

R^2 is hydrogen or one or more halogen, alkyl or alkoxy substituents;

X is -O- or -S-;

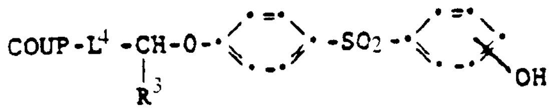


$$Q \text{ is } -C(=O)- \text{ or } -SO_2-;$$

r is 0 or 1; and
s is 0 or 10.

The bivalent linking group represented by L^1, L^2 and L^3 can be any of the groups found in ballast groups, such as alkylene of up to 10 carbon atoms, arylene of 6 to 10 carbon atoms, heterocyclene of 5 to 10 carbon atoms, may include oxygen, sulfur, amino, amido, sulfonamido, carbamoyl, sulfamoyl, and combinations of such linking groups, e.g. alkarylene, aralkylene, aminoarylene, aminoalkylene, amidoarylene, amidoalkylene, ureido, alkarylamido, amidoarylsulfamoyl, aminoarylamido and aminoarylsulfamoylalkyl.

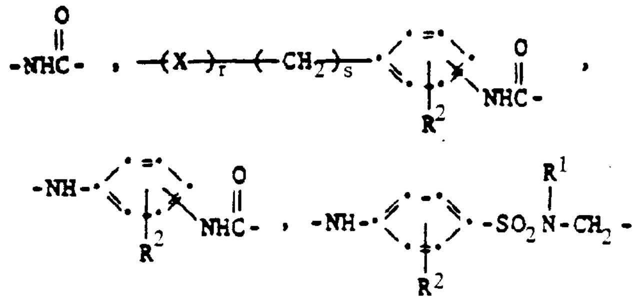
Particularly preferred couplers used in the invention have the structural formula:



III

where:

L^4 represents a bivalent group selected from



and

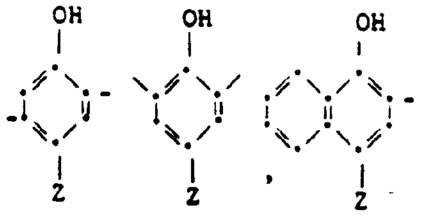
COUP, R^1, R^2, R^3, r and s are as defined above.

In an especially preferred embodiment, the hydroxy group in structural formulae II and III is in the para position.

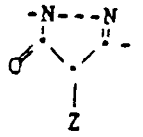
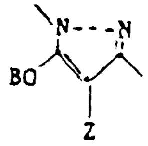
In the above structural formulae the alkyl, alkylene, aryl, arylene and heterocyclene groups can be unsubstituted or substituted with one or more groups such as halogen, nitro, amino, carboxy, alkyl, alkoxy, aryl, aryloxy, heterocyclyl, carbamoyl, amido, sulfamoyl and sulfonamido.

As indicated above, common yellow dye-forming couplers are acylacetanilides such as pivalylacetanilides and benzoylacetanilides. Common magenta dye-forming couplers are pyrazolones, pyrazolotriazoles, pyrazolobenzimidazoles and indazolones. Common cyan dye-forming couplers are phenols and naphthols, common neutral dye-forming couplers are resorcinols and *m*-aminophenols. Common non-dye-forming couplers are acyclic and cyclic compounds in which the active position, corresponding to the coupling position, is adjacent to or in conjugation with a carbon group or an imino group, such as α- or γ-substituted ketones or imines, e.g. cyclopentanones, cyclohexanones, indanones, indanoimines, oxyindoles and oxazolinones. These couplers can form the coupling group COUP in the above formulae. Structures of representative coupling groups are shown below. In these structures Z represents hydrogen or a coupling-off group and the unsatisfied bond, or bonds, indicates the preferred position, or positions, at which there can be attached the remainder of the molecule shown in the above structures; it being recognized that the coupling group can contain other substituents. Typical suitable coupling groups that can be used in the photographic elements of the invention are set out below.

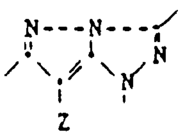
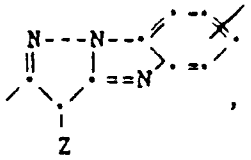
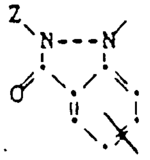
Cyan dye-forming coupling groups:



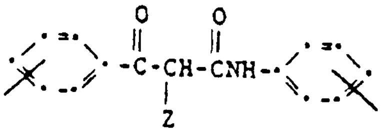
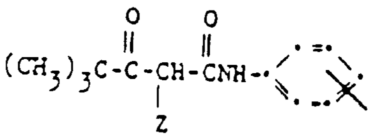
Magenta dye-forming coupling groups:

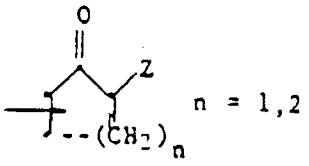
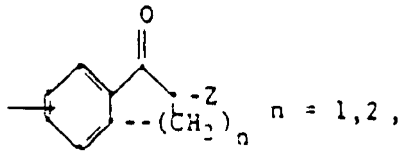
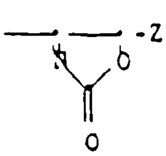
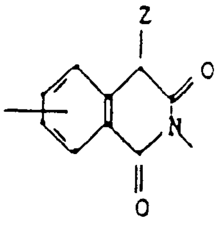
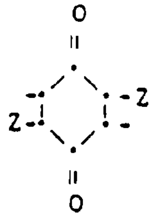
(B represents a blocking group capable of being removed during processing, e.g., by alkaline cleavage or coupling)

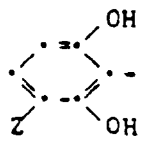
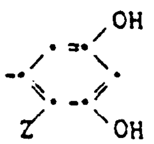
Yellow dye-forming coupling groups:

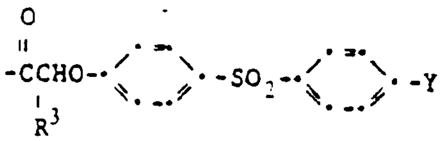
Non-dye-forming coupling groups:

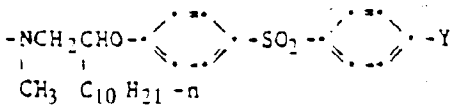
Neutral dye-forming coupling groups:

Specific couplers used in the invention, which are shown below, contain ballasts of general structures B^1 through B^6, where Y is -OH.

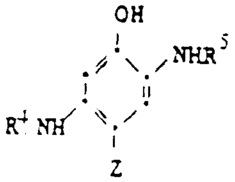


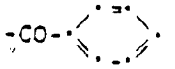
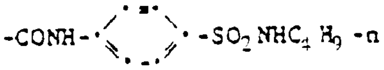
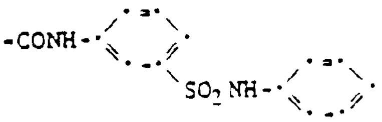
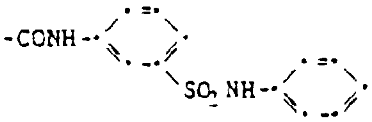
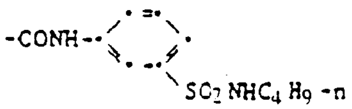
B¹: $R^3 = C_4H_9$-n
B²: $R^3 = C_{10}H_{21}$-n
B³: $R^3 = C_{12}H_{25}$-n

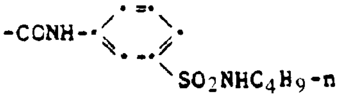
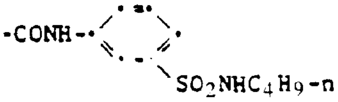
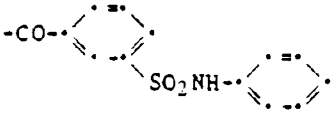
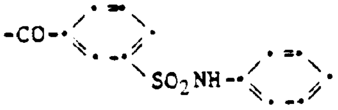
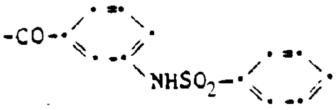
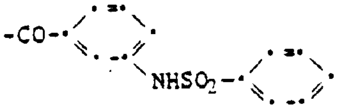
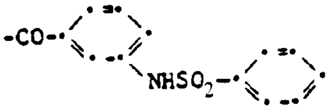
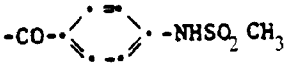
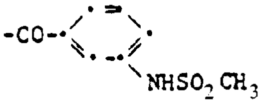
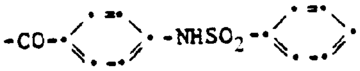
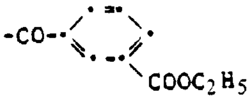


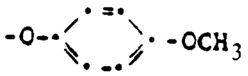
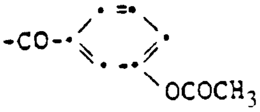
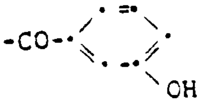
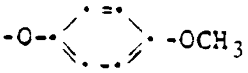
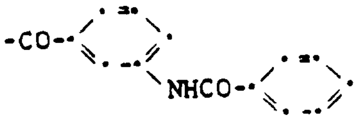
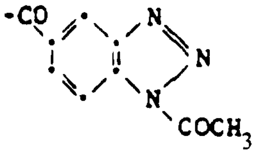
B⁵

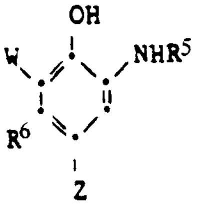
Cyan dye-forming couplers used in the invention including the following; the group Y in B², B³ and B⁴ being -OH:



Coupler No.	R_4	R_5	Z
C-1	n-C_3H_7CO—	—B³	—H
C-2	B³—	—COC_3H_7-n	—H
C-3	B³—	—$COCF_3$	—H
C-4	B³—	—COC_3F_7-n	—H
C-5	B²—		—Cl
C-6	B⁴—		—Cl
C-9	B²—		—H
C-10	B²—		—H
C-11	B²—		—OC_6H_5
C-12	B²—		—H

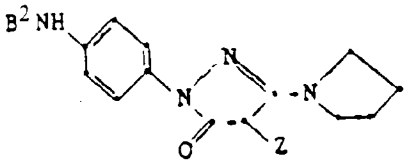
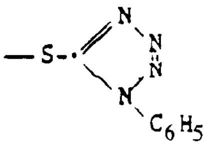
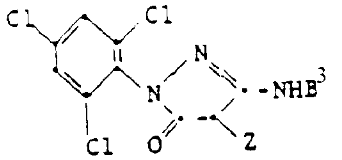
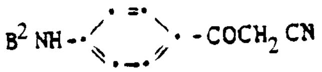
Coupler No.	R_4	R_5	Z
C-13	B^2—		—OCH_3
C-14	B^2—		—OC_6H_5
C-15	B^2—		—Cl
C-16	B^2—		—OC_6H_5
C-17	B^2—		—Cl
C-18	B^2—		—OC_6H_5
C-19	B^4—		—OC_6H_5
C-20	B^2—		—OC_6H_5
C-21	B^2—		—OC_6H_5
C-22	B^2—		—OC_6H_5
C-23	B^2—		—OC_6H_5

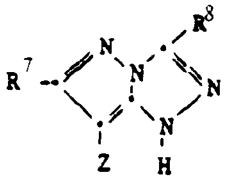
Coupler No.	R_4	R_5	Z
C-24	B^2—		
C-25	B^2—		$—OC_6H_5$
C-26	B^2—		
C-27	B^2—		$—OC_6H_5$
C-28	B^2—		$—OC_6H_5$

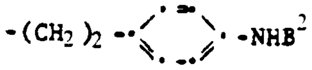
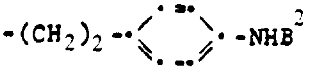
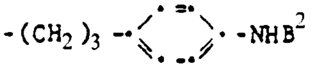
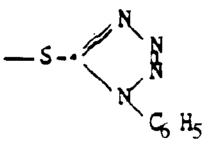


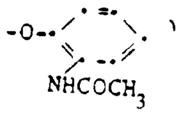
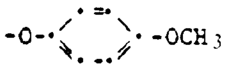
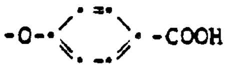
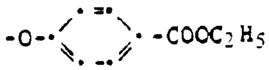
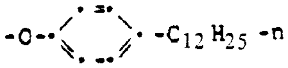
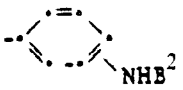
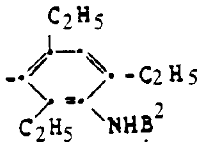
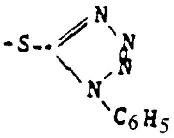
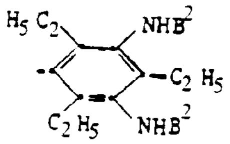
Coupler No.	R^6	R^5	W	Z
29	CH_3—	$—B^3$	—H	—H
30	CH_3—	$—B^2$	—H	—H
31	C_2H_5—	$—B^2$	—Cl	—Cl

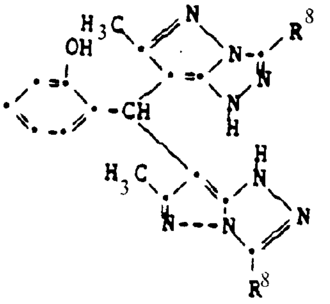
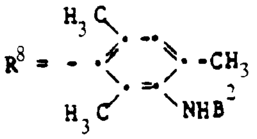
Magenta dye-forming couplers used in the invention including the following, the group Y in B^2 or B^3 being OH:

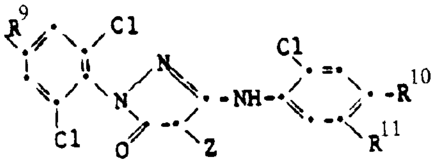
Coupler No.		Z
M-1		—H
M-2		
M-3		—H
M-4		

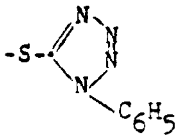


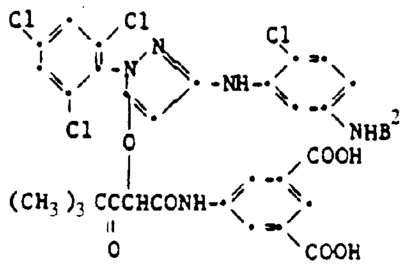
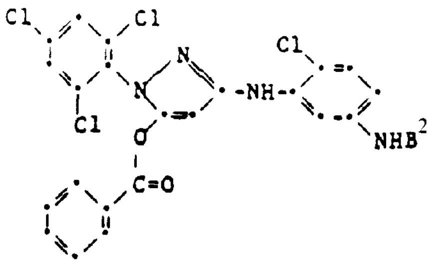
Coupler No.	R^7	R^8	Z
M-5	CH_3—		—Cl
M-6	CH_3—		—OC_6H_5
M-7	CH_3—		—Cl
M-8	CH_3—		—H
M-9	CH_3—	〃	—Cl
M-10	CH_3—	〃	—SC_7H_{15}-n
M-11	CH_3—	〃	
M-12	CH_3OCH_2—	〃	—Cl

Coupler No.	R^7	R^8	Z
M-13	CH_3—	〃	—OC_6H_5
M-14	CH_3—	〃	—$SCH_2CH_2N(CH_3)_2$
M-15	CH_3—	〃	
M-16	CH_3—	〃	
M-17	CH_3—	〃	
M-18	CH_3—	〃	
M-19	CH_3—	〃	
M-20	CH_3—	〃	
M-21	CH_3—		—H
M-22	CH_3—		
M-23	CH_3—	〃	—H
M-24	CH_3—	〃	—Cl
M-25	CH_3—		—Cl

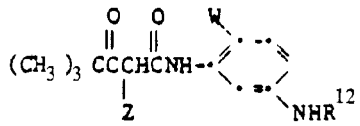
Coupler No.	R^7	R^8	Z
M-26			

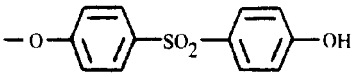
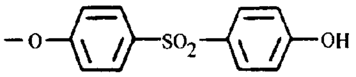
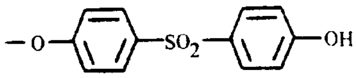
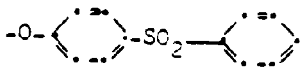
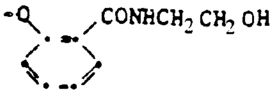


Coupler No.	R^9	R^{10}	R^{11}	Z
M-27	Cl—	—H	$—NHB^3$	—H
M-28	Cl—	—H	$—NHB^2$	—H
M-29	Cl—	—H	$—NHB^2$	$—SC_7H_{15}$-n
M-30	Cl—	—H	$—NHB^2$	$—SC_6H_5$
M-31	Cl—	—H	$—NHB^2$	
M-32	$(CH_3)_2NSO_2$—	$—SO_2B^5$	—H	—H
M-33	B^2NH—	—Cl	—H	—H
M-34	B^2NH—	$—SO_2NHCH_3$	—H	—H
M-35	B^2NH—	$—SO_2N(CH_3)_2$	—H	—H
M-36	B^4NH—	$—SO_2N(CH_3)_2$	—H	—H
M-37	B^2ONH— or $B^2N(OH)$—	$—SO_2N(CH_3)_2$	—H	—H

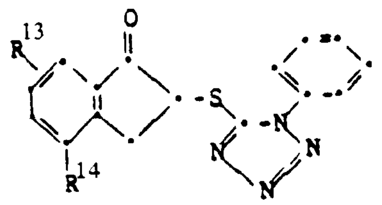
Coupler No.	R^9	R^{10}	R^{11}	Z
M-38				
M-39				

Yellow dye-forming couplers used in the invention include the following, the group Y in B^1, B^2 or B^6 being -OH:



Coupler No.	W	R^{12}	Z
Y-1	Cl—	$—B^1$	
Y-2	H—	$—B^1$	
Y-3	Cl—	$—B^2$	
Y-4	Cl—	$—B^2$	—H
Y-5	CH_3O—	$—B^2$	
Y-6	Cl—	$—B^2$	
Y-7	CH_3O—	$—B^2$	

Noncolor forming couplers used in the invention include the following:



Coupler No.	R^{13}	R^{14}
U-1	B^2NH—	H—
U-2	H—	B^2NH—

Couplers used in the invention can be prepared by attaching a blocked hydroxyphenylsulfonyl or blocked hydroxyphenylsulfinyl group directly to the coupling group or by attaching such a group to the remainder of the ballast group after which the ballast group is attached to the coupling group. Thereafter the blocking group is removed. Conventional condensation reactions can be employed in joining the various groups which ultimately form the coupler. For many of the couplers used in the invention it is convenient to provide the hydroxyphenylsulfonyl group using a 4,4'-sulfonyldiphenol mono ether (e.g. benzyl ether) or mono ester (e.g. acetyl ester.) Conventional reaction techniques can be employed to attach such a compound to the remainder of the ballast group and the thus formed ballast group to the coupling group. Thereafter, the blocking group can be removed by hydrogenation (in the case of the ether) or alkaline hydrolysis (in the case of an ester). When the coupler, or the remainder of the ballast group, has an amino group available for reaction, it is convenient to react that amino group with a blocked hydroxybenzenesulfonyl chloride after which the blocking group is removed.

The couplers used in the invention can be used in the ways and for the purposes that nondiffusible 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 the photographic elements of the invention. Alternatively, the couplers can be incorporated in photographic layers adjacent a silver halide emulsion layer 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 or in an adjacent location where, during processing, it will come into reactive association with silver halide development products.

The photographic elements of the invention 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 photographic 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 Belgian Patent 881,513.

A typical multicolor photographic element of the invention 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 couplers in the element being a coupler as described above. The element can contain additional layers, such as filter layers, interlayers, overcoat layers, subbing layers, and the like.

In the following discussion of suitable materials for use in the emulsions used in the invention, reference will be made to *Research Disclosure*, December 1978, Item 17643. This publication will be identified hereafter by the term "Research Disclosure".

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

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

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

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

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

Preferred color developing agents are p-phenylene diamines. Especially preferred are 4-amino-N,N-diethyl-aniline hydrochloride, 4-amino-3-methyl-N,N-diethylniline hydrochloride, 4-amino-3-methyl-N(ethyl-N-β-(methanesulfonamido) ethylaniline sulfate hydrate, 4-amino-3-methyl-N-ethyl-N-β-hydroxyethylaniline sulfate, 4-amino-3-β-(methanesulfonamido)ethyl-N,N-diethyl-aniline hydrochloride and 4-amino-N-ethyl-N-(2-methoxy ethyl)-m-toluidine di-p-toluene sulfonic acid.

With negative working silver halide this processing step leads to a negative image. To obtain a positive (or reversal) image, this step can be preceded by developing exposed silver halide with a non-chromogenic developing agent without forming a dye, and then uniformly fogging the element to render unexposed silver halide developable. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

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

The following examples are included for a further understanding of this invention.

Preparative Example 1

Preparation of ballast Group Intermediate B^2Cl, where Y = OBz (Bz is benzyl)

To a solution of 90 g (0.31 mol) methyl 2-bromododecanoate and 104.4 g (0.31 mol) 4,4'-sulfonyl-diphenol monobenzyl ether in 0.35 l dry acetone were added 1 g sodium iodide and 214.2 g (1.55 mol) potassium carbonate. After refluxing the mixture 20 h, solids were removed by filtration and the filtrate concentrated to a waxy solid. Recrystallization from methanol gave a white solid (B^2OCH_3, Y = OBz), mp 73-75°C, with the correct elemental analysis and expected NMR spectrum. A solution of 120 g (0.21 mol) of this product in 0.8 l dimethylformamide was added with stirring to 0.5 l of 2.3 mol aqueous potassium hydroxide solution, water was added and the cloudy solution stirred 0.5 h before pouring into acidic ice-water. The resulting solid was collected, dissolved in dichloromethane, and the solution washed, dried over magnesium sulfate, and concentrated. Recrystallization from acetonitrile yielded 67 g white solid (B^2OH, Y = OBz), mp 119-121°C, with the expected NMR spectrum and elemental analysis. This acid was converted to the acid chloride by dissolving 67 g (0.12 mol) in 0.4 l thionyl chloride and stirring 5 h. Excess thionyl chloride was removed under vacuum and the product recrystallized from dry acetonitrile to give a white solid (B^2Cl, Y = OBz), mp 84-85°C, with the expected NMR spectrum and elemental analysis.

Preparative Example 2

Preparation of ballast Group Intermediate B^2Cl, where Y = OAc

A solution of 455 g (0.82 mol), B^2OCH_3, Y = OBz in 1.6 l tetrahydrofuran and 0.4 l acetic acid was hydrogenated 12 h at 50 psi and 50°C over 45 g 5% palladium on charcoal catalyst. The catalyst was removed by filtration and the concentrated filtrate drowned in water. An ethyl acetate solution of resulting white solid was washed, dried, concentrated, and the product recrystallized from acetonitrile to give 340 g (0.74 mol) white solid (B^2OCH_3, Y = OH), 63-65°C with the expected elemental analysis. Hydrolysis of this ester was accomplished by slowly adding an aqueous solution containing 40 g (1 mol) sodium hydroxide to a stirred solution of the ester in 1 l dimethylformamide, stirring 2 h then pouring into acidified ice-water. The resulting gummy solid dissolved in ethyl acetate was washed with dilute hydrochloric acid, dried, and concentrated. Recrystallization from acetonitrile yielded a white solid (B^2OH, Y = OH), mp 116-117°C. This phenolic acid was acetylated by dissolving in 70 ml acetic anhydride and 7 ml concentrated surfuric acid, stirring 30 minutes at 20°C., then on a steam bath for 30 minutes, cooling, and pouring into 81 water. The product was recrystallized from methanol to give a white solid (B^2OH, Y = OAc), mp 73-75°C. Refluxing 35 g (0.07 mol) of this acid in excess thionyl chloride for 5 h and concentrating yielded a colorless oil, which on trituration in ligroin gave 22 g white solid (B^2Cl, Y = OAc), mp 66-69°C.

Preparative Example 3

Preparation of ballast Group Intermediates B^3Cl, where Y = OBz

The procedural steps were similar to those for preparation of B^3Cl in Preparative Example 1, except that ethyl 2-bromotetradecanoate was the starting material. Intermediates included white solids $B^3OCH_2CH_3$, Y = OBz (mp 55-61°C); B^3OH, Y = OBz (mp 117-118°C); and B^3Cl, Y = OBz (mp 81-84°C).

Preparative Example 4

Preparation of ballast Group intermediate B^1Cl where Y = OBz

The procedural steps were similar to those for preparation of B^3Cl in Preparative Example 1, except that ethyl 2-bromohexanoate was the starting material. Intermediates included white solids $B^1OCH_2CH_3$, Y = OBz (mp 102-105°C); B^1OH, Y = OBz (mp 147.5-148.5°C); and B^1Cl, Y = OBz (mp 40°C).

Preparative Example 5

Preparation of ballast Intermediate B^4Cl where Y = OBz

A solution of 10.2 g (0.029 mol) methyl 2-p-nitrophenoxy)dodecanoate in 100 ml tetrahydrofuran was shaken 6 h under 40 psi hydrogen in the presence of 0.7 g 10% palladium on charcoal catalyst to reduce the nitro group. Then 6.3 ml (0.04 mol) N,N-dimethylaniline and 8.2 g (0.029 mol) p-benzyloxybenzenesulfonyl chloride were added and the mixture stirred 15 hours at 20°C. The catalyst was removed by filtration and the filtrate poured into cold dilute hydrochloric acid. Ethyl acetate extraction, washing, drying, concentration, and purification through silica gel yielded 14 g colorless oil (B^4OCH_3, Y = OBz). This was dissolved in 60 ml tetrahydrofuran and 40 ml methanol, stirred 0.5 h with 20 ml aqueous sodium hydroxide solution and poured into cold dilute hydrochloric acid. Ethyl acetate extraction, washing, drying, concentration, ligroin trituration yielded 12 g white crystals (B^4OH, Y = OBz), mp 100-101°C, with the correct elemental analysis. To a stirred solution of 10 g (0.018 mol) of this acid in 50 ml tetrahydrofuran was added 1.8 ml (0.022 mol) oxalyl chloride and 5 drops dimethyl formamide. After 1.5 h concentration gave 0.018 mol of brown oil B^4Cl, Y = OBz.

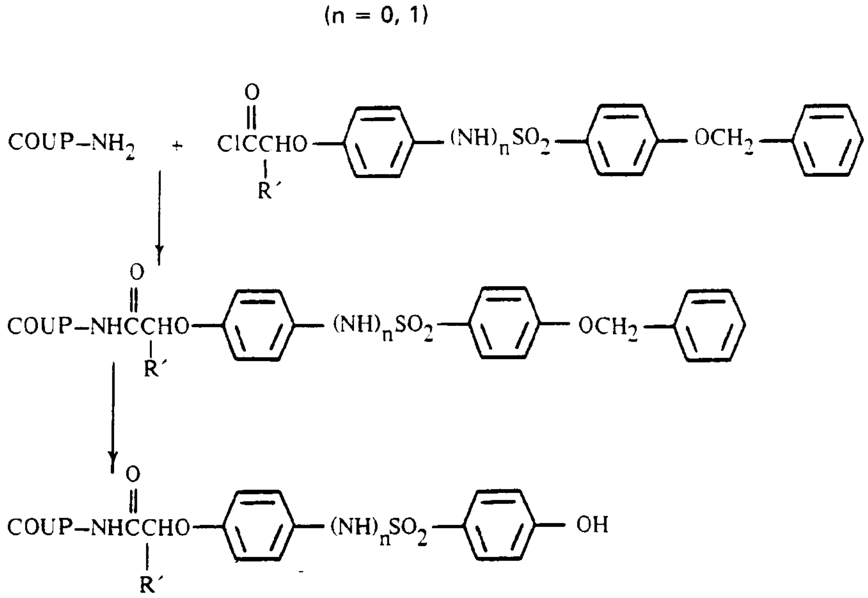
Preparative Example 6

Preparation of ballast Intermediate B^5 H·HCl where Y = OH

To a solution of 24 g (0.043 mol) acid chloride B^2Cl, Y = OBz in 400 ml tetrahydrofuran was a 40% aqueous solution containing 10 g (0.125 mol) methylamine. After 0.5 h stirring, the mixture was poured over acidified ice-water, extracted with diethyl ether, and the organic layer washed, dried and concentrated to yield, after further purification on a 50:50 silica gel/Fluorisil (trade mark) column, a clear colorless oil (B^2NHCH_3, Y = OBz). Reduction was accomplished by refluxing 16 g (0.029 mol) of this amide product and 16 ml 2 M borane-methyl sulfide complex in 400 ml tetrahydrofuran for 3 h. The cooled reaction mixture was slowly acidified with 50% hydrochloric acid solution, then extracted with diethyl ether. Acidification and concentration of the washed and dried organic layer gave 14 g of white solid ($B^5H{\cdot}HCl$, Y = OH).

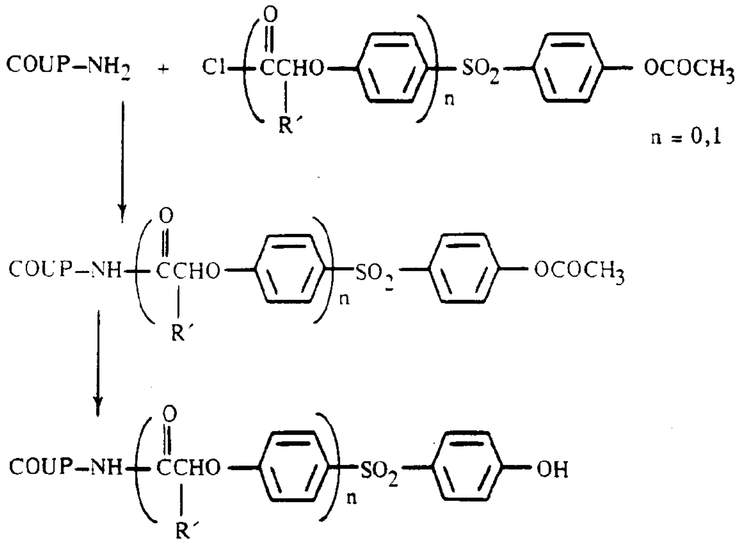
Final steps in the synthetis of couplers used in this invention generally involved the attachment of the ballast group and the removal of the ballast blocking group, if any. For example, in Scheme I an amino-substituted coupling group, COUP-NH_2, is allowed to react with an acid chloride ballast group and the resulting intermediate is converted to the desired coupler by hydrogenation to remove the benzyl group.

Scheme I



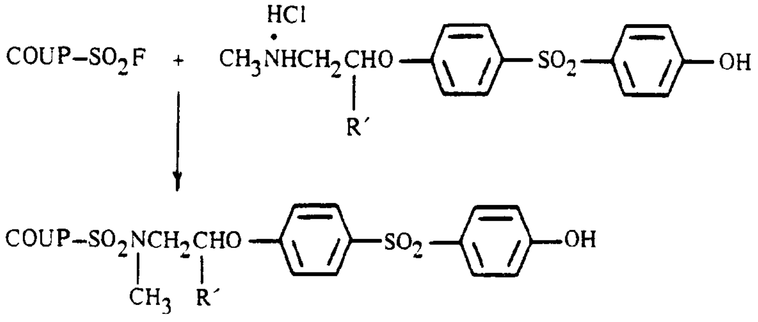
Where the blocking group is acetyl, as in Scheme II, it is removed by alkaline hydrolysis:

Scheme II



Alternatively, if the coupler is substituted with an acidic function, a ballast group containing an amine function may be attached according to Scheme III:

Scheme III



Preparative Example 7

Preparation of Coupler C-8 by Scheme I

A suspension of 5.4 g (0.018 mol) 2-(p-cyanophenylureido)-5-nitrophenol in 200 ml tetrahydrofuran was shaken overnight under 40 psi hydrogen with 1.6 10% palladium on charcoal catalyst and 0.3 ml acetic acid. Then 0.018 mol of the acid chloride B^4Cl prepared in Preparative Example 5 and 6.8 ml dimethylaniline were added under nitrogen and the mixture stirred 0.5 h before removing the catalyst by filtration and pouring the filtrate into cold dilute hydrochloric acid. Ethyl acetate extraction, washing, drying, concentration, and crystallization from acetonitrile yielded 10.2 g of the pale white solid benzyl ether of the desired coupler. A solution of this product in 100 ml tetrahydrofuran was shaken for 15 hours under 40 psi hydrogen with 2.5 g 10% palladium on charcoal catalyst and 0.5 ml acetic acid. The catalyst was removed by filtration and the reduction product concentrated and crystallized from acetonitrile to give 6.1 g white solid coupler C-8, mp 103-106°C, with an infrared spectrum and elemental analysis consistent with the desired structure.

Preparative Example 8

Preparation of Coupler M-28 by Scheme II

A solution of 50 g (0.115 mol) 3-(2-chloro-5-nitroanilino)-1-(2,4,6-trichlorophenyl)-2-pyrazolin-5-one in dimethylformamide and tetrahydrofuran was reduced with 35 psi hydrogen and Raney nickel catalyst. Removal of the catalyst by filtration and concentration of the filtrate gave 21 g (0.052 mol) light yellow solid 3-(2-chloro-5-aminoanilino-1-(2,4,6-trichlorophenyl)-2-pyrazolin-5-one. To an acetic acid solution containing 6.9 g (0.017 mol) of this amine and 9.5 g potassium acetate was added, in small portions, 9.5 g (0.019 mol) of the acid chloride B^2Cl prepared in Example 2. After stirring 15 hours, the mixture was concentrated to a third of its volume, poured into a large volume of water and extracted with diethyl ether. The organic layers were washed, dried, concentrated, and crystallized from methanol to give 14 g (0.016 mol) buff-colored solid acetate ester of the desired coupler, mp 115-116°C. To a solution of this product in dimethylformamide stirred under nitrogen was added an aqueous solution containing 2 g potassium hydroxide. After 15 minutes the mixture was acidified with hydrochloric acid, poured into dilute hydrochloric acid, extracted with diethyl ether, washed, dried, concentrated, and crystallized from methanol to give 9.2 g white crystalline coupler M-28, mp 127-130°C.

Preparative Example 9

Preparation of Coupler M-8 by Scheme I

A suspension of 10 g (0.035 mol) 6-methyl-3-[3-(p-nitrophenyl)-propyl]-1H-pyrazole[3,2-c]-5-triazole in 300 ml tetrahydrofuran was shaken about 2 h at 25°C with 35 psi hydrogen and a palladium on charcoal catalyst. Removal of the catalyst, concentration of the filtrate, and recrystallization from acetonitrile gave a buff-colored solid amine, mp 194-6°C. To a stirred acetic acid solution of 7.6 g (0.03 mol) of this amine product and 2 g potassium acetate was added, in small portions, 16.7 g (0.03 mol) of the acid chloride B^2Cl prepared in Preparative Example 1. After stirring 15 h, the mixture was poured into a large volume of water, extracted with diethyl ether, and the combined extracts then washed, dried, and concentrated to give the white solid benzyl ether of the desired coupler, mp 122-124°C. A concentrated solution of 7 g (0.009 mol) of the product in tetrahydrofuran was shaken 2 h under 40 psi hydrogen with a mixture of palladium on charcoal catalyst in ethanol. Removal of the catalyst by filtration, concentration, and recrystallization from acetonitrile gave 5.5 g cream-colored solid coupler M-8, mp 170-172°C, with an infrared spectrum and elemental analysis consistent with the desired compound.

Preparative Example 10

Preparation of Coupler M-32 by Scheme III

A mixture of 8 g (0.015 mol) 3-(2-chloro-4-fluorosulfonylanilino)-1-(2,6-dichloro-4-dimethylsulfamoyl phenyl)-2-pyrazolin-5-one and 5.5 g aluminum chloride in 175 ml 1,2-dichloroethane was refluxed 15 minutes. After cooling to 20°C, 7.25 g (0.015 mol) of the amine salt $B^5H \cdot HCl$ prepared in Example 6 in 25 ml pyridine was added and the mixture refluxed 2 h. Then a mixture of hydrochloric acid, ice, and diethyl ether was added and the organic layer washed, dried, concentrated, and triturated with hexane to give 14.2 g light tan solid coupler M-32 with the correct elemental analysis.

Preparative Example 11

Preparation of Coupler Y-1 by Scheme I

To a solution of 57.8 g (0.095 mol) α-pivalyl-α-[4-(p-benzyloxyphenylsulfonyl)-phenoxy]-2-chloro-5-amino acetanilide and 13 g quinoline, cooled to 0°C, was added in one portion 45 g (0.095 mol) of the acid chloride B^1 Cl prepared in Preparative Example 4. After stirring 1 h the reaction mixture was poured into 3 l cold water to produce 98 g (after oven drying) crude product. Recrystallization from toluene yielded 84.5 g (0.018 mol) white crystalline dibenzyl ether of the desired coupler. A suspension of 10.4 g (0.01 mol) of this product in 200 ml ethanol and 200 ml tetrahydrofuran was shaken 3 h under 35 psi hydrogen with palladium on charcoal catalyst. Removal of catalyst by filtration concentration of the filtrate and trituration in hot cyclohexane gave a good yield of coupler Y-1 with the correct elemental analysis.

Examples 1-14

Photographic elements of this invention and control elements were prepared and tested according to the procedures described below.

All photographic elements were prepared by coating a cellulose acetate butyrate film support with a photosensitive layer containing a silver bromo-iodide emulsion at 0.91 g Ag/m^2 (when the coupler is 4-equivalent) or 0.46 g Ag/m^2 (when the coupler is 2-equivalent), gelatin at 3.78 g/m^2, and one of the couplers identified in Table I dispersed in one-half its weight of the coupler solvent described and coated at 1.62×10^{-3} moles/m^2. The photosensitive layer was overcoated with a layer containing gelatin at 1.08 g/m^2 and bis-vinyl-sulfonylmethyl ether at 1.75 weight percent based on total gelatin.

Samples of each element were imagewise exposed through a graduated-density test object and processed at 40°C employing one of three color developing solutions identified below then stopped, bleached, fixed and washed.

In each element, well-defined, magenta dye images were produced which were evaluated by plotting dye density vs. log exposure sensitometric curves and recording the maximum dye density (D_{max}) and gamma (γ) i.e., the contrast determined by the slope of the straight line portion of the curve. Additionally, dye hues were evaluated from spectrophotometric curves by measuring the maximum absorption peak (λ_{max}) normalized to a density of 1.0 and the half band width (HBW). Halfband width is the width, in nanometers, of the spectrophotometric curve at one-half the difference between maximum density and stain. Similarly, the top-band width (TBW) and bottom-band width (BBW) of the curve were measured at three-fourths and one-fourth, respectively, of the normalized density. Curve shape factor (CSF) equals 100 × TbW/HBW and provides a ratio of the width near the top and bottom of the absorption curve. The greater this ratio, the steeper are the sides of the absorption peak, and the more efficient is the dye's absorption of light in its spectral region.

All results are recorded in Table I.

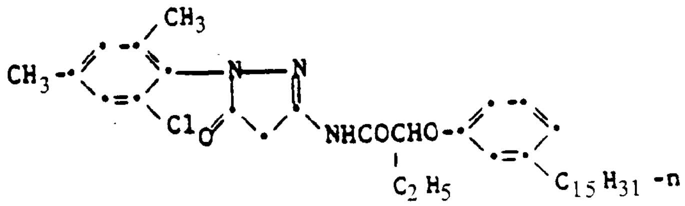
These results show that couplers of this invention have enhanced activity, which results in increased maximum dye density and gamma. In addition many of the dyes formed from couplers of this invention have absorption maxima at desirably longer wavelengths and have broader half band widths and larger curve shape factors, resulting in more efficient spectral absorption.

TABLE I

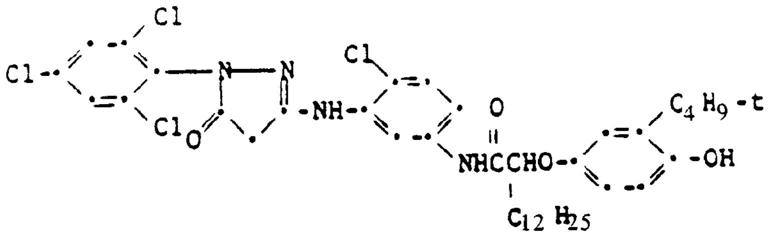
Example No.	Coupler No.(1)	Coupler Solvent(2)	Developer(3)	Activity		Hue		
				D-max	γ	λ-max	HBW	CSF
1	M-3	CS-1	D-1	3.70	1.12	546	96	46.0
	CC-1	CS-1	D-1	3.28	1.06	531	94	43.3
2	M-8	CS-2	D-3	4.21	2.03	550	86	50.5
	CC-3	CS-2	D-3	3.68	1.30	556	88	45.3
3	M-27	CS-1	D-1	4.40	2.14	545	91	47.0
	CC-1	CS-1	D-1	3.36	1.27	531	94	43.6
4	M-28	CS-1	D-1	4.32	2.01	549	92	46.7
	CC-1	CS-1	D-1	3.20	1.19	531	94	43.1
5	M-28	CS-2	D-2	4.12	1.65	541	93	46.5
	CC-2	CS-2	D-2	2.96	1.04	539	81	46.3
6	M-28	CS-2	D-3	4.98	1.88	549	94	46.4
	CC-3	CS-2	D-3	3.66	1.30	556	88	45.3
7	M-29	CS-2	D-2	4.53	2.92	540	88	46.7
	CC-2	CS-2	D-2	2.12	0.75	539	79	39.5
8	M-29	CS-2	D-3	4.87	3.14	545	90	40.9
	CC-2	CS-2	D-3	3.03	1.05	545	79	40.4
9	M-32	CS-2	D-2	3.15	1.32	549	82	40.9
	CC-2	CS-2	D-2	2.37	0.99	540	78	39.9
10	C-31	CS-3	D-2	3.25	1.14	675	160	47.0
	CC-4	CS-3	D-2	2.22	0.78	659	141	45.2
11	Y-1	CS-3	D-2	2.82	1.13	445	90	44.4
	CC-7	CS-3	D-2	1.92	0.55	445	85	45.2
12	Y-2	CS-3	D-2	1.89	0.62	441	93	44.4
	CC-8	CS-3	D-2	0.57	0.14	439	90	44.3
13	Y-3	CS-3	D-1	3.86	1.90	450	90	44.6
	CC-9	CS-3	D-1	3.69	1.48	450	87	43.8

1) Comparison Couplers

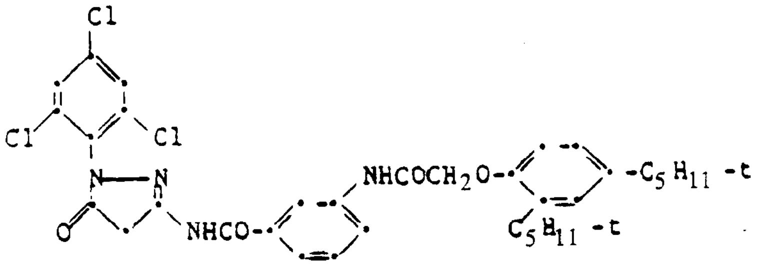
CC-1



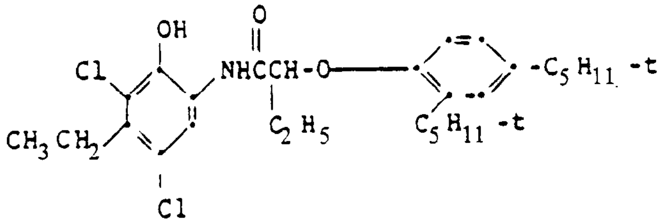
CC-2



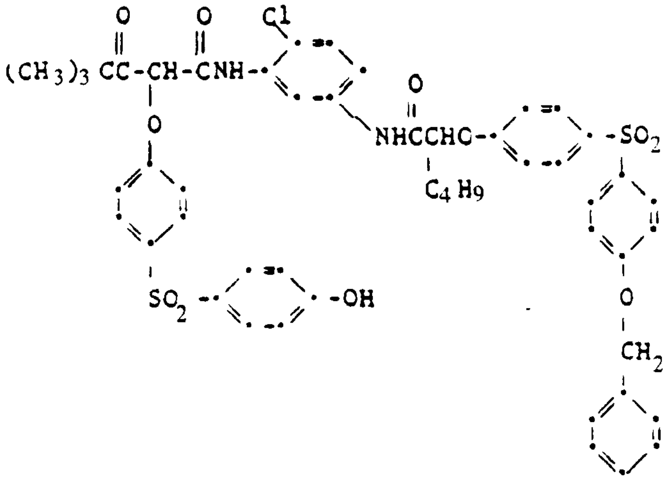
CC-3



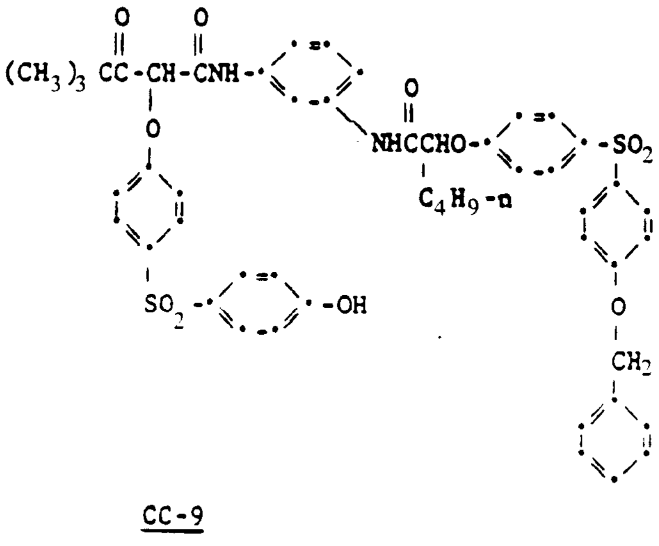
CC-4



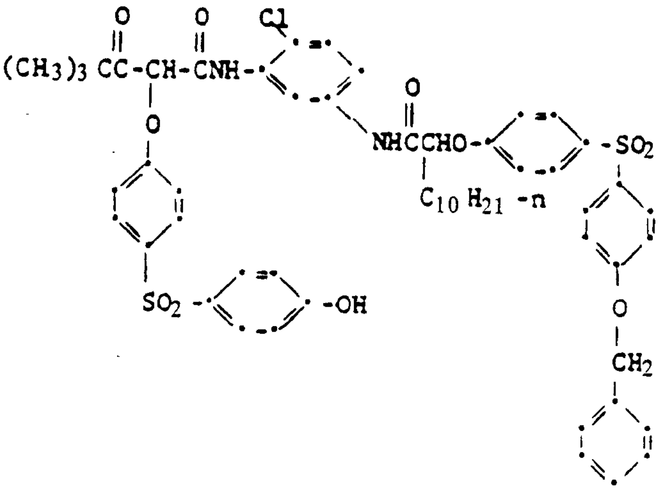
CC-7



CC-8


(CH3)3 CC-CH-CNH
O
NHCCHO
C4H9-n
SO2
SO2
OH
O
CH2

CC-9


(CH3)3 CC-CH-CNH
Cl
O
NHCCHO
C10H21-n
SO2
SO2
OH
O
CH2

(2) Coupler Solvents:

CS-1 - 1,4-Cyclohexylenedimethylene bis(2-ethyl-hexanoate)
CS-2 - Tri-cresyl phosphate
CS-3 - Dibutyl phthalate
CS-4 - 2,4-Di-t-pentylphenol

(3) Developer Formulations:

	D-1	D-2	D-3
4-Amino-3-methyl-N,N-di ethylaniline hydrochloride	2.45 g	—	—
4-Amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)-ethylaniline sulfate	—	5.0 g	—
4-Amino-3-methyl-N-ethyl-N-β-hydroxyethyl aniline sulfate	—	—	3.55 g
Potassium sulfite	2.0 g	2.0 g	2.0 g
Potassium carbonate (anhydrous)	30.0 g	30.0 g	30.0 g
Potassium bromide	1.25 g	1.25 g	1.25 g
Potassium iodide	0.6 mg	0.6 mg	0.6 mg
1% Solution in methanol of 5-nitro-1H-indazole	4.0 ml	—	—
Water to:	1.0 l	1.0 l	1.0 l
pH adjusted to:	10.0	10.0	10.0

Example 15

Photographic elements containing additional couplers were prepared, processed and evaluated as described above in connection with Examples 1-14. The results are reported in Table II below.

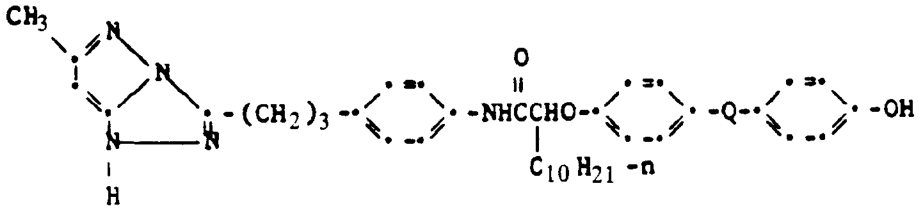
TABLE II

Coupler	Coupler Solvent	Dev.	D-max	α	λ-max (nm)	HBW (nm)	CSF %
C-2	CS-3	D-1	3.78	1.77	655	144	45.7
C-3	CS-3	D-2	3.30	1.28	659	161	47.8
C-13	CS-3	D-3	2.99	1.11	702	135	44.4
M-3	CS-1	D-1	3.70	1.12	546	96	45.7
M-9	CS-4	D-3	4.16	1.81	558	90	44.2
M-28	CS-2	D-3	4.58	1.88	549	94	42.6

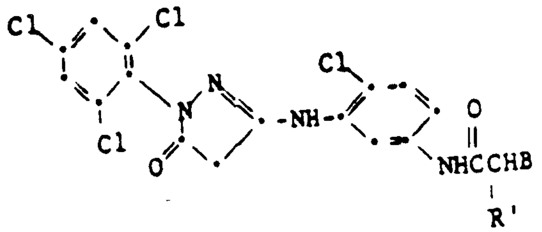
Example 16

For each of the couplers identified below, photographic elements were prepared as described above in connection with Examples 1-14. Four samples from each element were exposed as described above. One pair of the exposed elements was developed in developer D-2, described above, and the other pair was developed in this developer to which had been added 1.5 g/l of the soluble competing coupler citrazinic acid. The remaining processing for one element from each pair was stopping, bleaching, fixing and washing while for the second element from each pair the bleaching step was omitted so that the developed silver remained in the element. For those elements in which the silver remained, the amount of developed silver, in g/m^2 , was determined by x-ray fluorescence analysis and plotted against exposure. For those elements from which the developed silver had been removed, dye density vs exposure curves were generated. From the plots for pairs of elements developed with the same developer composition there was plotted, for each exposure step, dye density vs developed silver. The slope of the line for the elements developed in the absence of a competing coupler (Y_O in Table III, below) is a measure of the efficiency with which the coupler forms dye; the greater the slope the more efficient the coupler. The slope of the line for the elements developed in the presence of the competing coupler (Y_C in Table III, below) is a measure of the reactivity of the coupler, the greater the slope, the more reactive the coupler.

The couplers employed had the following structure:



Coupler	Q
M-8	$-SO_2-$
CC-10	$-C(CH_3)_2-$



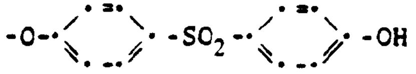
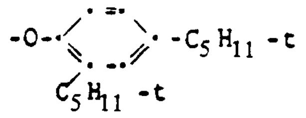
Coupler	R′	B
M-28	$-C_{10}H_{21}$-n	
CC-11	$-C_2H_5$	

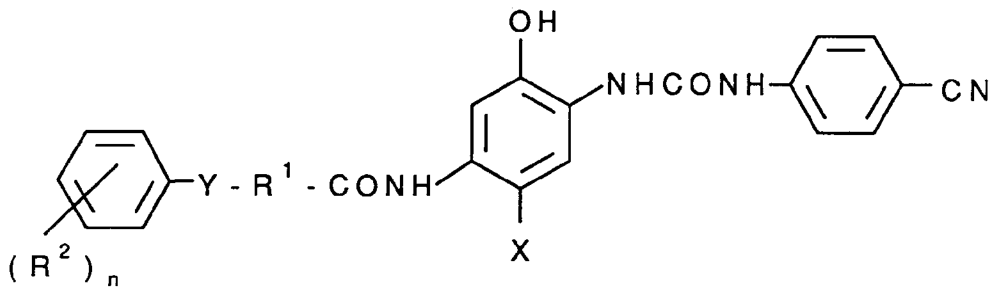
TABLE III

Coupler	Coupler Solvent	Y_o	Y_c	Y_c/Y_o
M-8	CS-4	5.55	1.73	0.312
CC-10	CS-4	1.62	0.21	0.130
M-28	CS-2	6.30	4.65	0.738
CC-11	CS-2	4.50	1.50	0.337

It is apparent from the values for Y_o and Y_c in Table III that the couplers used in the invention react more efficiently with oxidized developer to form image dye, in the presence or absence of a competing coupler, than do those couplers with ballasts not used in this invention.

Claims

1. A photographic element comprising a support, a photographic silver halide emulsion and associated therewith, a nondiffusable photographic coupler which reacts with oxidized color developing agent to give a compound which may or may not be an image dye characterized in that said coupler contains a coupling group COUP- bonded at a position other than the coupling position to a ballast groupwhich is substituted with a hydroxyphenylsulfonyl or hydroxyphenylsulfinyl group with the exception of couplers of the formula:



wherein

R^2 is a hydroxyphenylsulphonyl group;

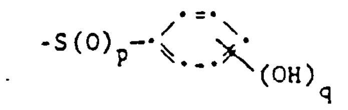
X is hydrogen or a coupling-off group;

Y is oxygen or sulphur,

R^1 is a branched alkylene group of 2 to 20 carbon atoms; and

n is 1 to 3.

2. A photographic element according to claim 1 wherein the ballast group is substituted with a group of the structural formula:



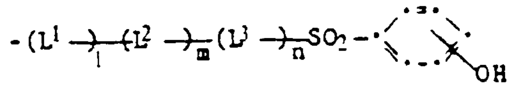
I

where:

p is 1 or 2; and

q is 1 to 3.

3. A photographic element according to claim 1 wherein the ballast group has the structural formula:

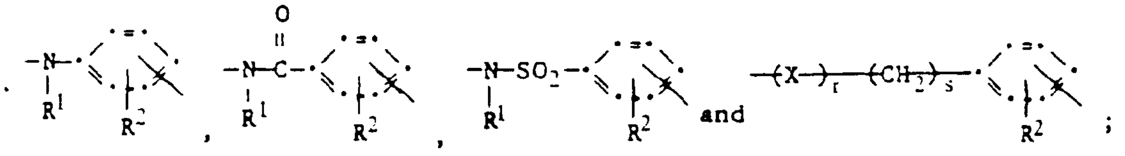


II

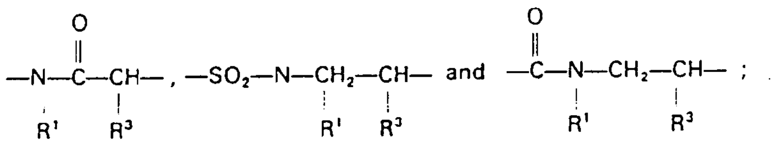
where:

l, m and n are each individually 0 or 1, at least one of l, m and n being 1;

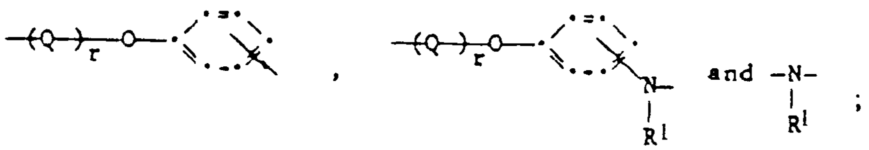
L^1 represents a bivalent group selected from



L^2 represents a bivalent group selected from



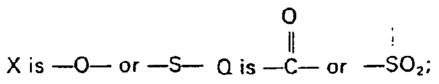
$-\underset{R^1}{N}-\overset{O}{\overset{\|}{C}}-\underset{R^3}{CH}-$, $-SO_2-\underset{R^1}{N}-CH_2-\underset{R^3}{CH}-$ and $-\overset{O}{\overset{\|}{C}}-\underset{R^1}{N}-CH_2-\underset{R^3}{CH}-$;



wherein the combination of L^1, L^2 and/or L^3 forms a ballast group;

R_1 and R^3 are each individually hydrogen, alkyl of 1 to 20 carbon atoms or aryl of 6 to 20 carbon atoms;

R^2 is hydrogen or one or more halogen, alkyl or alkoxy substituents;



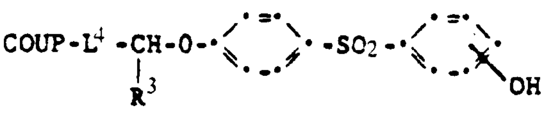
$$X \text{ is } -O- \text{ or } -S- \quad Q \text{ is } -\overset{\overset{\displaystyle O}{\|}}{C}- \text{ or } -SO_2;$$

r is 0 or 1; and

S is 0 to 10,

any alkyl, alkylene, aryl or arylene group possibly being substituted.

4. A photographic element according to claim 1 wherein the coupler has the structural formula:

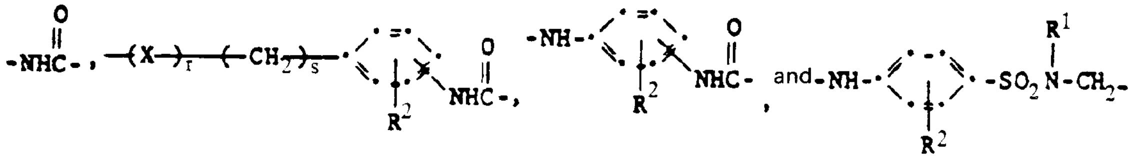


III

where:

COUP represents the coupling group

L^4 represents a bivalent group selected from



where:

R^1 and R^3 are each individually hydrogen, alkyl of 1 to 20 carbon atoms or aryl of 6 to 20 carbon atoms;

R^2 is hydrogen or one or more halogen, alkyl or alkoxy substituents,

X is -O- or -S-;

r is O or 1; and

s is 0 to 10,

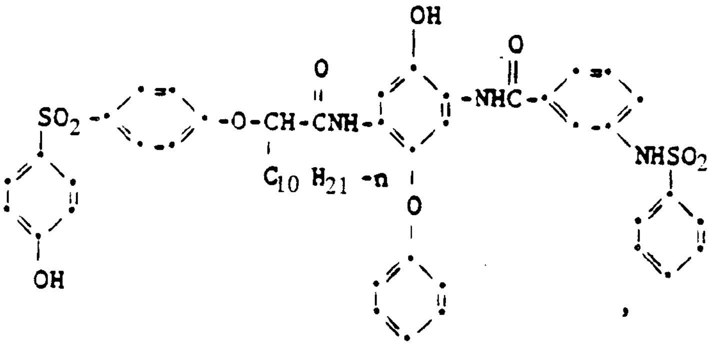
any alkyl, alkylene, aryl or arylene group possibly being substituted.

5. A photographic element according to claim 2, 3, or 4 wherein the coupler is a yellow dye-forming coupler and COUP is an acylacetanilide coupling group.

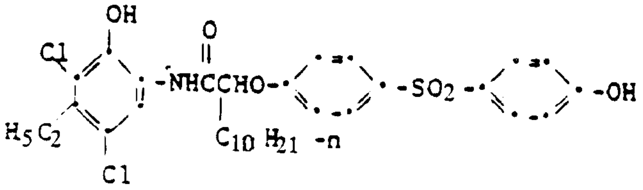
6. A photographic element according to claim 2, 3 or 4 wherein the coupler is a cyan dye-forming coupler and COUP is a phenol or naphthol coupling group.

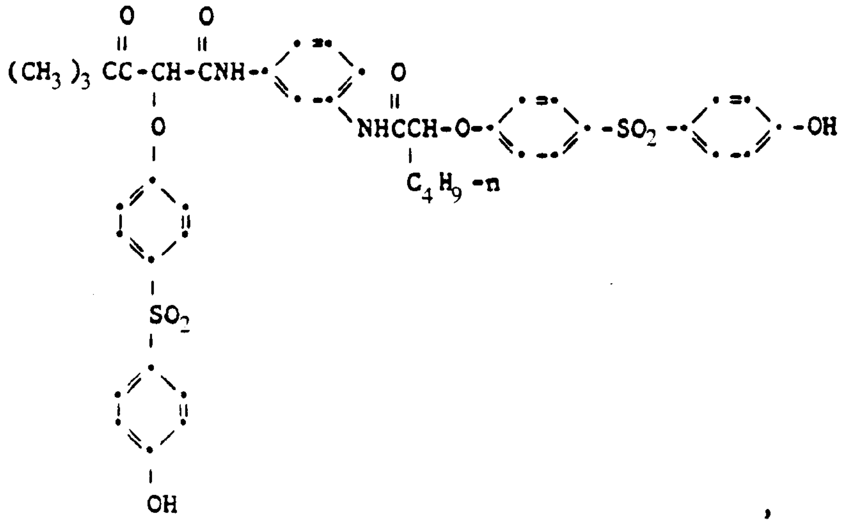
7. A photographic element according to claim 2, 3 or 4 wherein the coupler is a magenta dye-forming coupler and COUP is a pyrazolone, pyrazolo-triazole, pyrazolobenzimidazole or idazolone coupling group.

8. A photographic element according to claim 1 wherein the coupler has the structure:

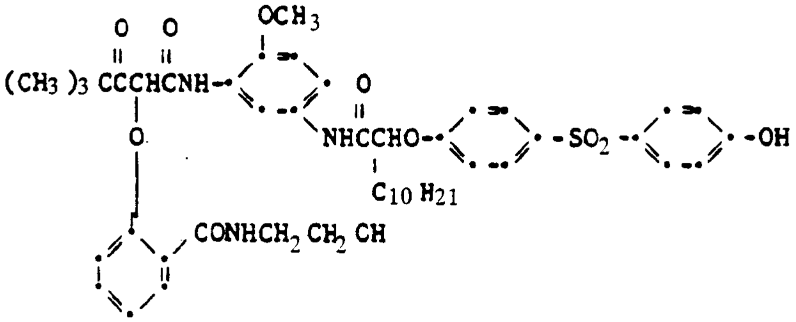

OH
O
O
SO2
-O-CH-CNH-
-NHC-
C10 H21 -n
NHSO2
O
OH

,

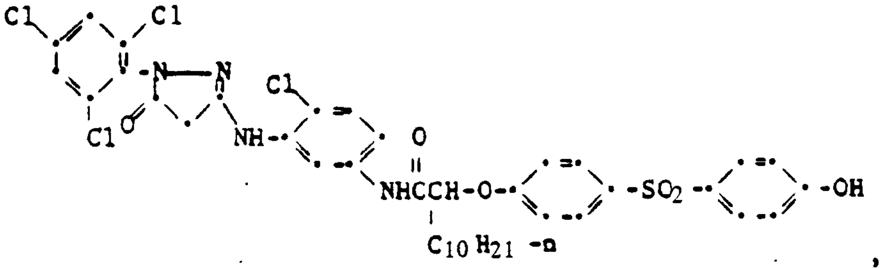

OH
O
Cl
-NHCCHO-
-SO2
-OH
H5C2
C10 H21 -n
Cl



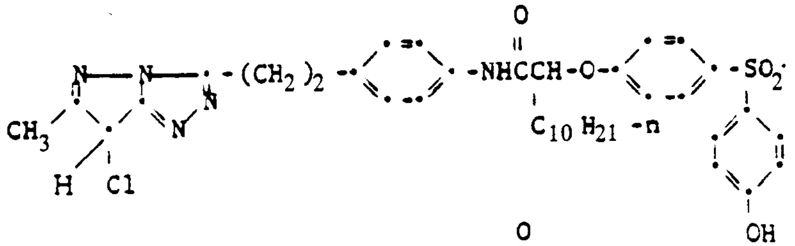
,



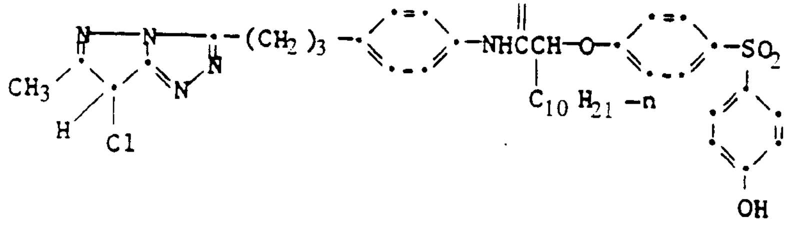
,



,



,

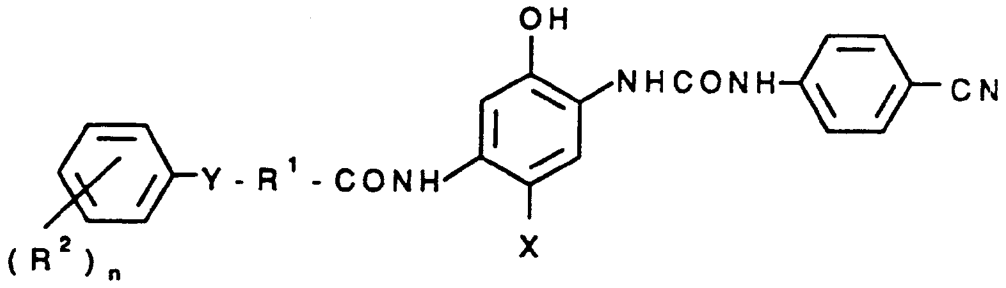


, or

Patentansprüche

1. Photographisches Element mit einem Träger, einer photographischen Silberhalogenidemulsion und ei-

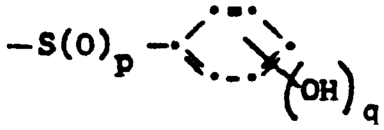
nem der Emulsion zugeordneten nicht-diffundierenden Kuppler, der mit oxidierter Farbentwicklerverbindung zu einer Verbindung reagiert, die ein Bildfarbstoff oder kein Bildfarbstoff sein kann, dadurch gekennzeichnet, daß der Kuppler eine kuppelnde Gruppe COUP- aufweist, die in einer von der Kupplungsposition verschiedenen Gruppe an eine Ballastgruppe gebunden ist, die durch eine Hydroxyphenylsulfonyloder Hydroxyphenylsulfinylgruppe substituiert ist, mit der Ausnahme von Kupplern der Formel:



worin

R^2 eine Hydroxyphenylsulfonylgruppe ist;
X Wasserstoff oder eine abkuppelnde Gruppe darstellt;
Y gleich Sauerstoff oder Schwefel ist;
R^1 eine verzweigtkettige Alkylengruppe mit 2 bis 20 Kohlenstoffatomen ist und
n gleich 1 bis 3 ist.

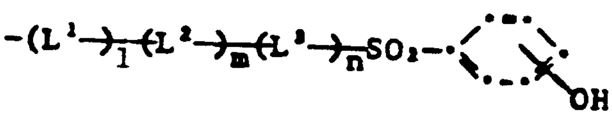
2. Photographisches Element nach Anspruch 1, dadurch gekennzeichnet, daß die Ballastgruppe durch eine Gruppe Der folgenden Strukturformel substituiert ist:



in der bedeuten:

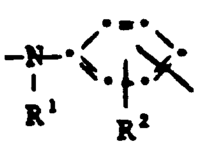
p = 1 oder 2 und
q = 1 bis 3.

3. Photographisches Element nach Anspruch 1,dadurch gekennzeichnet, daß die Ballastgruppe der folgenden Strukturformel entspricht:

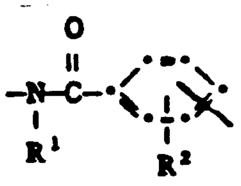


in der bedeuten:

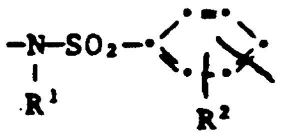
l, m und n einzeln jeweils 0 oder 1, wobei mindestens eines der Symbole l, m und n = 1 ist;
L^1 eine zweiwertige Gruppe ausgewählt aus:



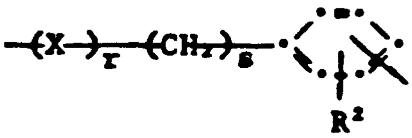
,



,

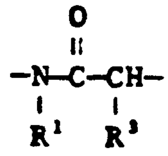


und

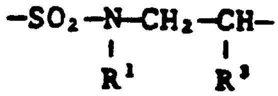


;

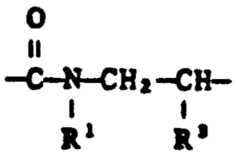
L² eine zweiwertige Gruppe ausgewählt aus:



$-\underset{R^1}{N}-\overset{O}{\overset{\|}{C}}-\underset{R^3}{CH}-$,

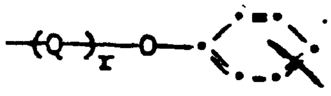


$-SO_2-\underset{R^1}{N}-CH_2-\underset{R^3}{CH}-$ und

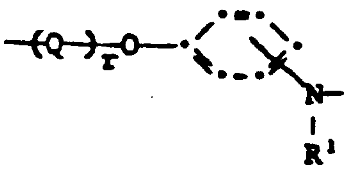


$-\overset{O}{\overset{\|}{C}}-\underset{R^1}{N}-CH_2-\underset{R^3}{CH}-$;

L³ eine zweiwertige Gruppe aususgewählt aus:



,



und

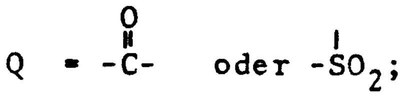
$-\underset{R^1}{N}-$;

wobei die kombination von L¹ , L² und/oder L³ eine Ballastgruppe bildet;

R¹ und R³ jeweils einzeln ein Wasserstoffatoom, eine Alkylgruppe mit 1 bis 20 Kohlenstoffatomen oder eine Alkylgruppe mit 6 bis 20 Kohlenstoffatomen;

R² ein Wasserstoffatom oder ein oder mehrere Halogen-, Alkyl- oder Alkoxysubstituenten;

X = O der -S-;



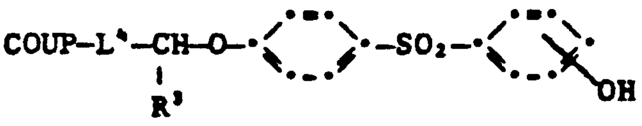
$$Q = -\overset{O}{\overset{\|}{C}}- \text{ oder } -\overset{|}{S}O_2;$$

r = 0 oder 1 und

s = 0 bis 10,

wobei gilt, daß jede Alkyl-, Alkylen-, Aryl- oder Arylengruppe gegebenenfalls substituiert sein kann.

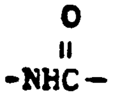
4. Photographisches Element nach Anspruch 1, dadurch gekennzeichnet, daß der Kuppler der folgenden Strukturformel entspricht:



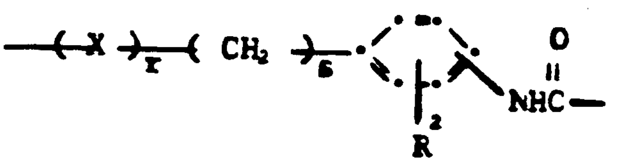
in der bedeuten:

COUP eine kuppelnde Gruppe;

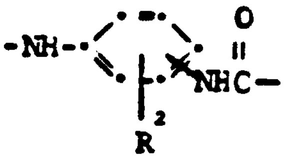
L⁴ eine zweiwertige Gruppe ausgewählt aus:



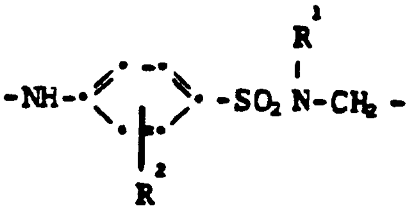
$$-NH\overset{O}{\overset{\|}{C}}-$$



,



und



.

worin bedeuten:

R¹ und R³ einzeln jeweils ein Wasserstoffatom, eine Alkylgruppe mit 1 bis 20 Kohlenstoffatomen oder eine Arylgruppe mit 6 bis 20 Kohlenstoffatomen;

R² ein Wasserstoffatom oder ein oder mehrere Halogen-, Alkyl- oder Alkoxysubstituenten;

X = -O- der -S-;

r = 0 oder 1 und

s = 0 bis 10,

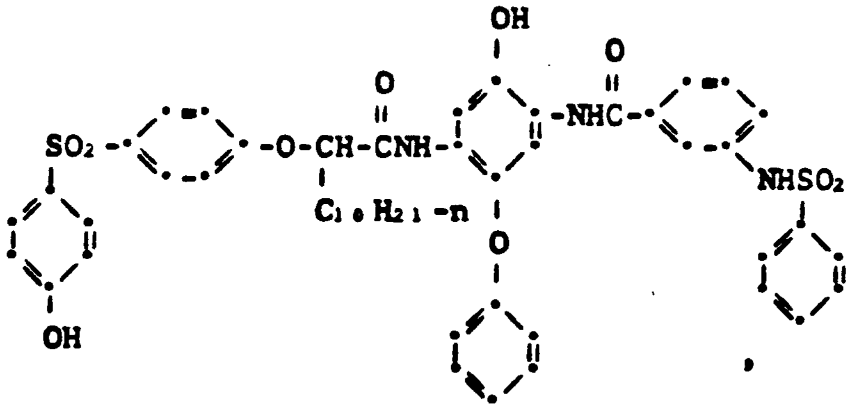
wobei gilt, daß jede Alkyl-, Alkylen-, Aryl- oder Arylengruppe gegebenenfalls substituiert sein kann.

5. Photographisches Element nach Anspruch 2, 3 oder 4, dadurch gekennzeichnet, daß der Kuppler ein einen gelben Farbstoff liefernder Kuppler ist und daß COUP eine kuppelnde Acylacetanilidgruppe ist.

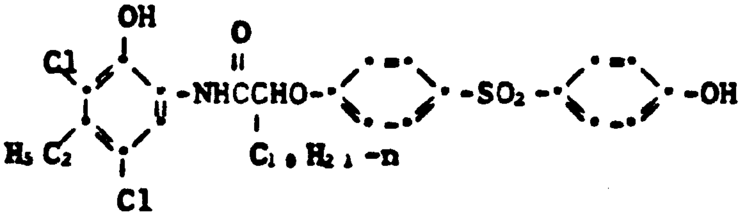
6. Photographisches Element nach Anspruch 2, 3 oder 4, dadurch gekennzeichnet, daß der Kuppler ein einen blaugrünen Farbstoff liefernde Kuppler ist und daß COUP eine kuppelnde Phenol- oder Naphtholgruppe ist.

7. Photographisches Element nach Anspruch 2, 3 oder 4, dadurch gekennzeichnet, daß der Kuppler ein einen purpurroten Farbstoff liefernder Kuppler ist und daß COUP eine kuppelnde Pyrazolon-, Pyrazolotriazol-, Pyrazolobenzimidazol- oder Indazolongruppe ist.

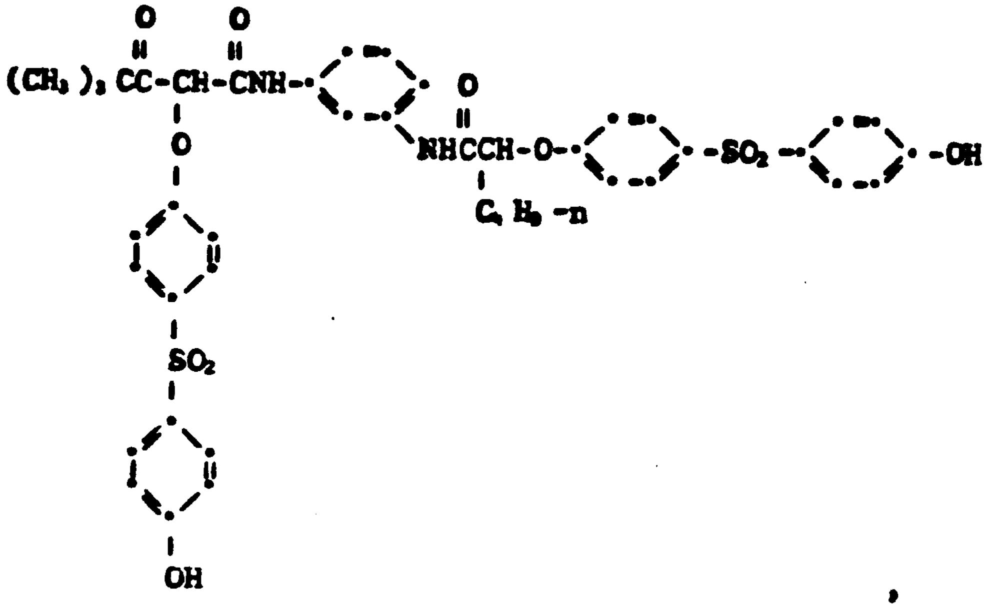
8. Photographisches Element nach Anspruch 1, dadurch gekennzeichnet, daß der Kuppler einer der folgenden Formeln entspricht:



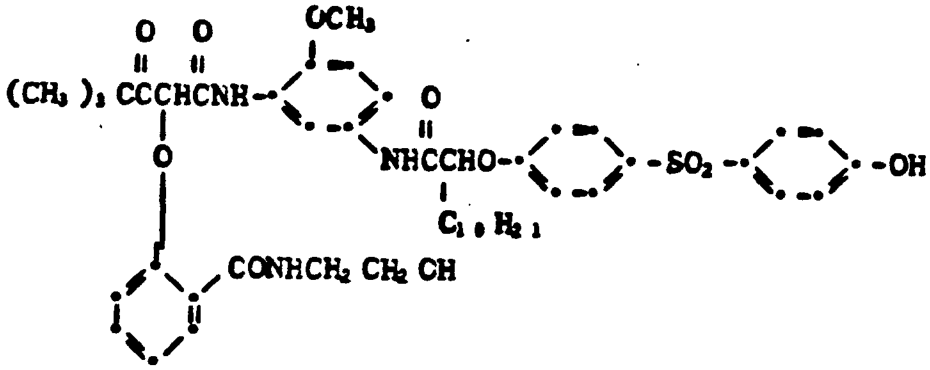
,


OH
Cl
H_5C_2
Cl
O
-NHCCHO-
$C_{10}H_{21}$-n
-SO$_2$-
-OH

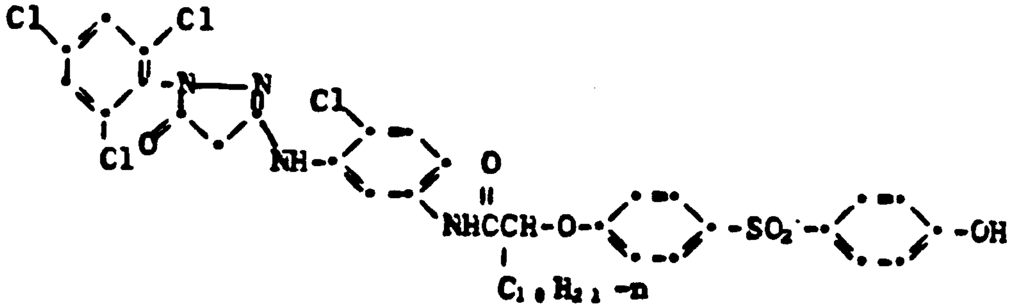
,



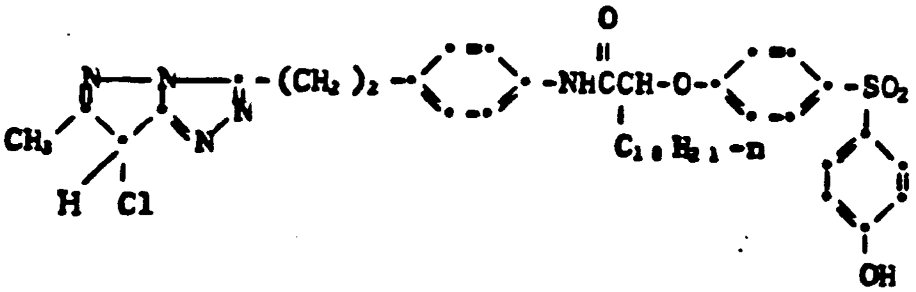
,



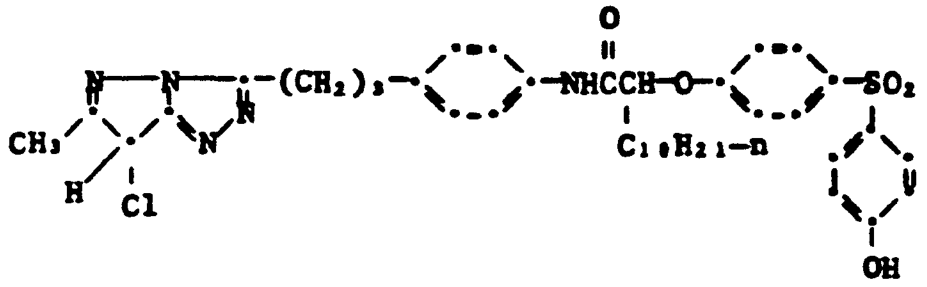
,



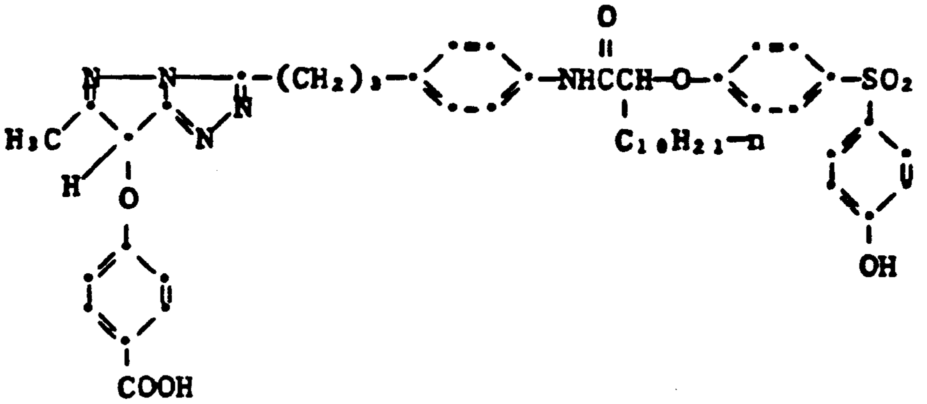
,



,

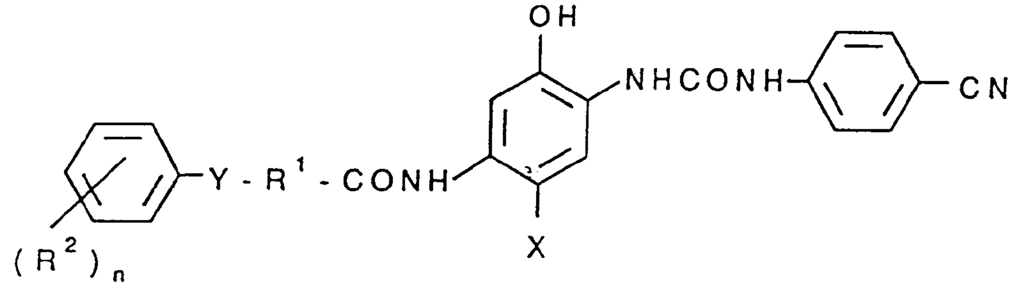


, oder



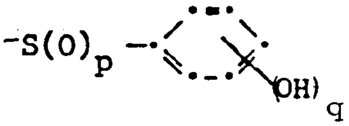
Revendications

1- Produit photographique comprenant un support, une émulsion photosensible aux halogénures d'argent à laquelle est associé un coupleur photographique non diffusible qui réagit avec l'agent développateur chromogène oxydé pour fournir un composé qui peut être un colorant d'image ou qui peut ne pas être un colorant d'image, caractérisé en ce que ce coupleur contient un groupement de couplage COUP- relié, en une position différente de la position de couplage, à un groupe ballast qui est substitué par un groupement hydroxyphénylsulfonyle ou hydroxyphénylsulfinyle, excepté les coupleurs de formule :



où
R^2 est un groupe hydroxyphenylsulfonyle ;
X est l'hydrogène ou un groupe se séparant par couplage ;
Y est l'oxygène ou le soufre ;
R^1 est un groupe alkylène branché de 2 à 20 atomes de carbone ; et
n est un nombre de I à 3.

2- Produit photographique conforme à la revendication I, dans lequel le groupe ballast est substitué par un groupement correspondant à la formule structurale suivante :

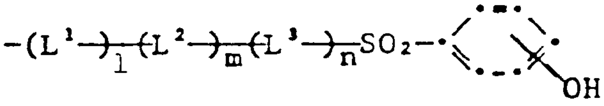


où :

p est l ou 2, et,

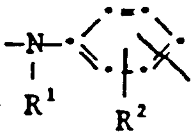
q est l à 3.

3- Produit photographique conforme à la revendication 1, dans lequel le groupe ballast correspond à la formule structurale suivante :

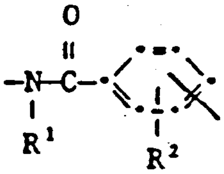


où :

l, m et n représentent chacun séparément 0 ou l, au moins l'une des valeurs l, m et n étant égale à l, L' représente un groupe bivalent choisi parmi ceux qui correspondent aux formules suivantes :



,



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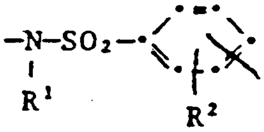
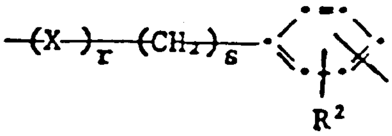
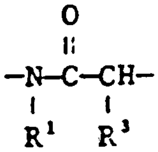


et

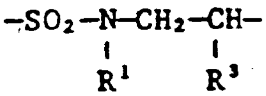


;

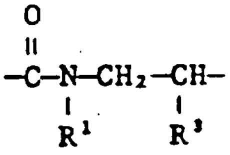
L^2 représente un groupe bivalent choisi parmi ceux qui correspondent aux formules suivantes :



$-N(R^1)-C(=O)-CH(R^3)-$,

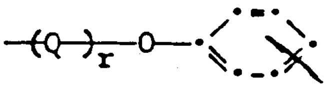


$-SO_2-N(R^1)-CH_2-CH(R^3)-$ et

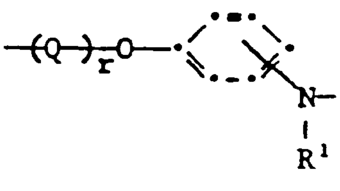


$-C(=O)-N(R^1)-CH_2-CH(R^3)-$;

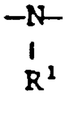
L^3 représente un groupe bivalent choisi parmi ceux qui correspondent aux formules suivantes :



,



et



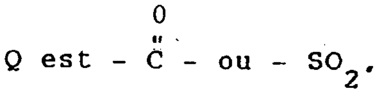
$-N(R^1)-$;

où l'association de L', L^2 et/ou L^3 forme un groupe ballast.

R^l et R^3 représentent chacun séparément l'hydrogéne, un groupe alkyle de I à 20 atomes de carbone ou un groupe aryle de 6 à 20 atomes de carbone.

R^2 représente l'hydrogène ou un ou plusieurs radicaux halogéno, alkyle ou alcoxy,

X est - O - ou - S -,



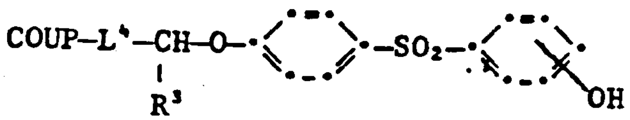
Q est $-\overset{O}{\overset{\|}{C}}-$ ou $-SO_2$,

r est O ou I, et,

s est à I0,

n'importe quel groupe alkyle, alkylène, aryle ou arylène pouvant être substitué.

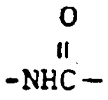
4- Produit photographique conforme à la revendication I, dans lequel le coupleur correspond à la formule structurale suivante :



où :

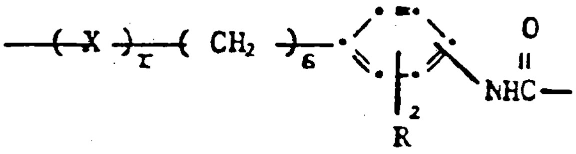
COUP représente le groupe de couplage,

L^4 représente un groupe bivalent choisi parmi ceux qui correspondent aux formules suivantes :

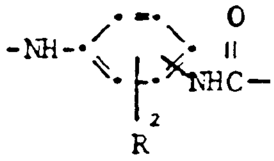


$-NH\overset{O}{\overset{\|}{C}}-$

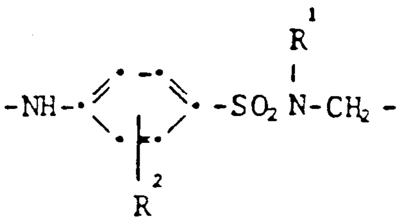
,



,



, et



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où :

R^l et R^3 représentent chacun séparement l'hydrogène, un groupé alkyle de I à 20 atomes de carbone ou un groupe aryle de 6 à 20 atomes de carbone,

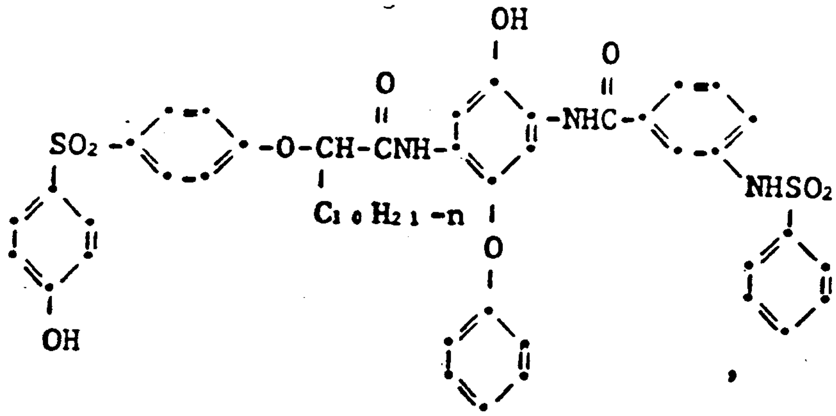
R^2 est l'hydrogène ou un ou plusieurs radicaux halogèno, alkyle ou alcoxy,
X est - O - ou - S -,
r est 0 ou l, et,
s est 0 à l0,
n'importe quel groupe alkyle, alkylène, aryle ou arylène pouvant être substitué.

5- Produit photographique conforme à la revendication 2, 3, ou 4, dans lequel le coupleur est un coupleur formateur de colorant jaune et COUP est un groupement de coupleur acylacétanilide.

6- Produit photographique conforme à la revendication 2, 3 ou 4 dans lequel le coupleur est un coupleur formateur de colorant cyan et COUP est un groupement de coupleur phénol ou naphtol.

7- Produit photographique conforme à la revendication 2, 3 ou 4, dans lequel le coupleur est un coupleur formateur de colorant magenta et COUP est un groupement de coupleur pyrazolone, pyrazolotriazole, pyrazolobenzimidazole ou indazolone.

8- Produit photographique conforme à la revendication l, dans lequel le coupleur correspond à l'une des structures suivantes :



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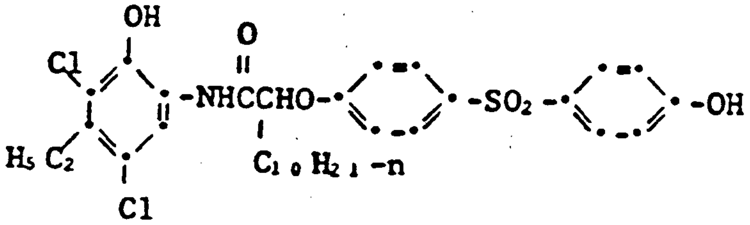

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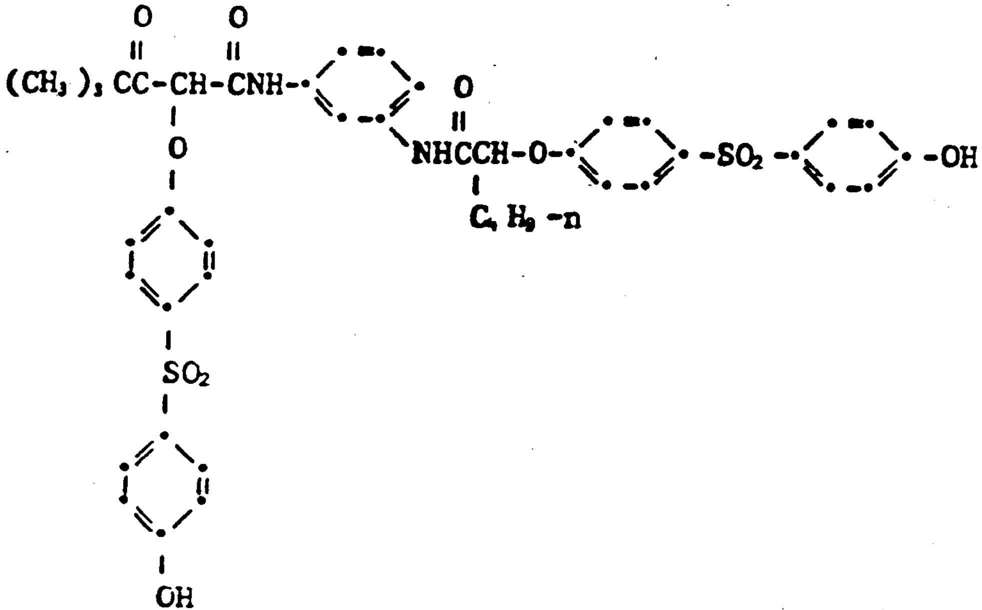

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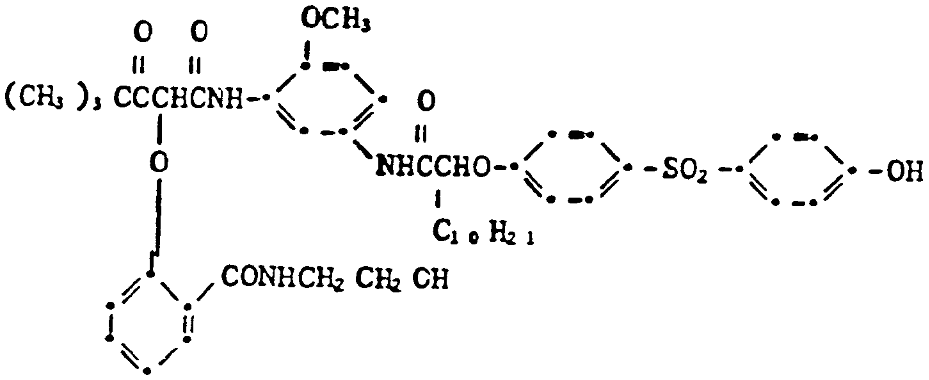

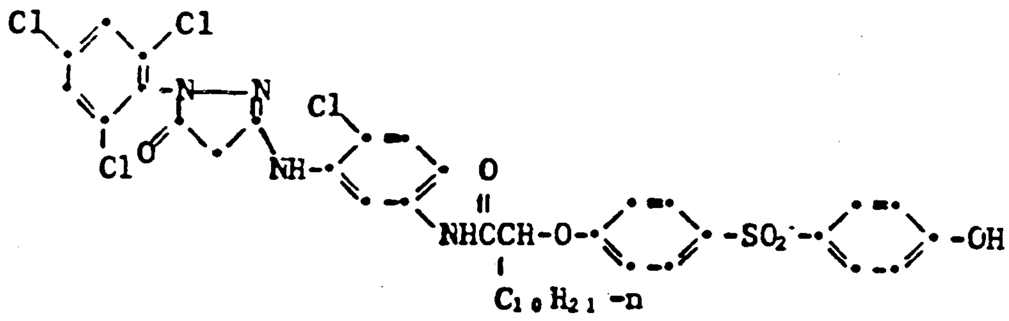

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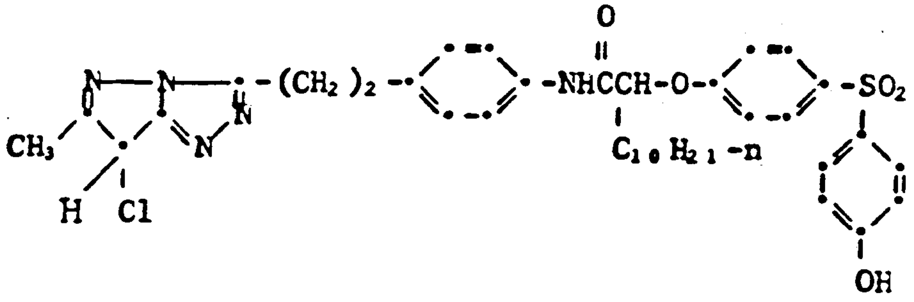

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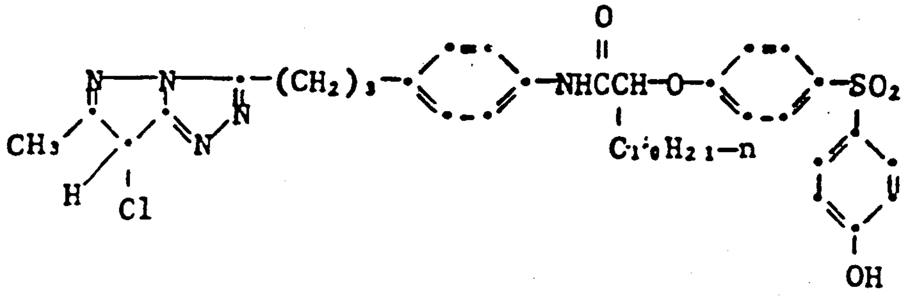

, ou