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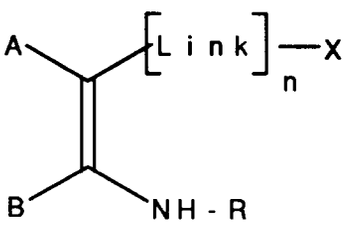
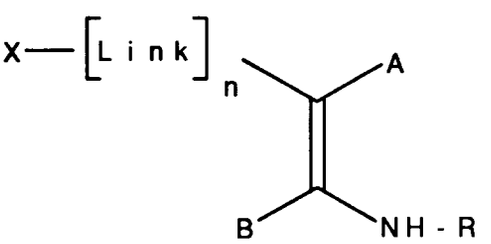
(54) Colour photographic materials containing couplers and phenotic solvents.

(57) A photographic element comprising a support, at least one photosensitive silver halide layer and in or adjacent said silver halide layer a colour coupler of the general formulae:



(1)



(2)

wherein A and B represent the same or different electron-withdrawing group,
X is H or a group which splits off on coupling with oxidised colour developer,
R is an alkyl, cycloalkyl, aryl or heterocyclic group any of which may be substituted, -COR[1], -CSR[1], SOR[1],

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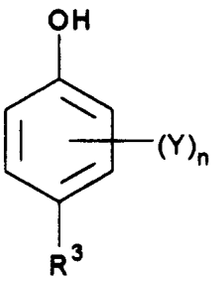
SO_2R^1, $-NHCOR^1$, $-CONHR^1$, $-COOR^1$, $-COSR^1$, $-NHSO_2R^1$ wherein R^1 is an alkyl, cycloalkyl, or aryl group any of which are optionally substituted,

and wherein two or more of A, B, R, and X optionally form part of a ring,

Link is a linking group and

n is 0, 1 or 2,

characterised in that the coupler is dissolved in droplets of a phenolic solvent having the formula:



(3)

wherein R^3 and each Y is, individually, an alkyl, alkoxy cycloalkyl, aryl, aryloxy or heterocyclic group any of which may be substituted, $-COR^1$, $-OCOR^1$ $-SOR^1$, $-SO_2R^1$, $-NHCOR^1$, $-CONHR^1$, $-COOR^1$, $-NHSO_2R^1$, $-SO_2NHR^1$ or $-NR^1R^2$, n is 0 to 4, or R^3 and a Y can, together with the atoms to which they are attached, complete a carbocyclic or heterocyclic ring which may be substituted,

where R^1 is as defined above and R^2 can have any of the meanings for R^1 or hydrogen.

Field of the Invention

The invention relates to photographic silver halide colour materials containing colour couplers of enhanced activity.

Background of the Invention

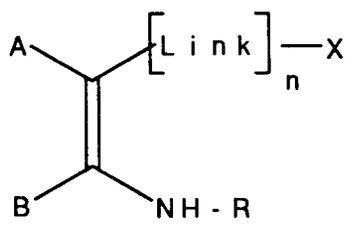
In our PCT application published as WO 93/07534 there is described a class of activated enamine couplers capable of forming magenta dye images of excellent spectral and other properties.

Problem to be Solved by the Invention

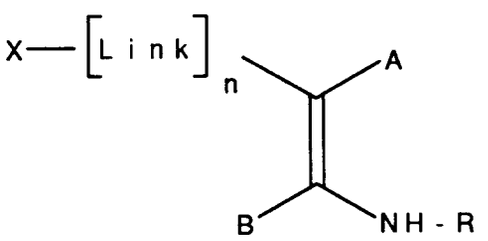
It is always desirable to increase the activity of a photographic colour coupler. The benefit can be taken as using a smaller quantity of coupler, improvement in granularity, etc.

Summary of the Invention

According to the present invention there are provided photographic elements comprising a support, at least one photosensitive silver halide layer and in or adjacent said silver halide layer a colour coupler of the general formulae:

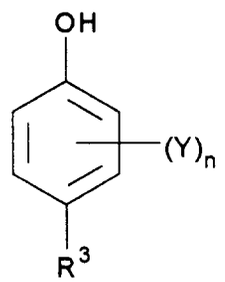


(1)



(2)

wherein A and B represent the same or different electron-withdrawing group,
X is H or a group which splits off on coupling with oxidised colour developer,
R is an alkyl, cycloalkyl, aryl or heterocyclic group any of which may be substituted, -COR^1, -CSR^1, -SOR^1, -SO_2R^1, -$NHCOR^1$, -$CONHR^1$, -$COOR^1$, -$COSR^1$, -$NHSO_2R^1$ wherein R^1 is an alkyl, cycloalkyl, or aryl group any of which are optionally substituted,
and wherein two or more of A, B, R, and X optionally form part of a ring,
Link is a linking group and
n is 0, 1 or 2,
characterised in that the coupler is dissolved in droplets of a phenolic solvent having the formula:



(3)

wherein R^3 and each Y is, individually, an alkyl, alkoxy cycloalkyl, aryl, aryloxy or heterocyclic group any of which may be substituted, -COR^1, -$OCOR^1$ -SOR^1, -SO_2R^1, -$NHCOR^1$, -$CONHR^1$, -$COOR^1$, -$NHSO_2R^1$, -SO_2NHR^1 or -NR^1R^2, n is 0 to 4, or R^3 and a Y can, together with the atoms to which they are attached, complete a carbocyclic or heterocyclic ring which may be substituted,

where R^1 is as defined above and R^2 can have any of the meanings for R^1 or hydrogen.

Advantageous Effect of the Invention

The substitution of phenolic coupler solvents for conventional ester coupler solvents leads to an increase in coupler activity without any large changes in dye hue. This is in contrast to the behaviour of conventional magenta couplers in phenolic solvents.

Detailed Description of the Invention

In one embodiment A and B together complete an electron-withdrawing heterocycle which may be substituted. In another embodiment R and X together complete a heterocyclic ring which is optionally substituted.

It is noted that formulae (1) and (2) represent geometric isomers (cis and trans versions) of the same compound.

The advantages of the present invention include the increase in the activity of the couplers compared to when they are dissolved in conventional ester solvents without shifting the spectral characteristics of the dye formed on colour development such as maximum wavelength (λ_{max}).

In one embodiment of the present invention the couplers contain a ballasting group of such size and configuration to render the coupler non-diffusible in the photographic material.

A and B may each individually represent an electron withdrawing group wherein the value of the Hammett substituent constant σ_p ($SIGMA_p$ as defined by Hansch et al, J. Med. Chem.,1973, 16, 1207; and ibid. 1977, 20, 304) is 0.03 or greater, preferably 0.35 or greater and more preferably 0.5 or above.

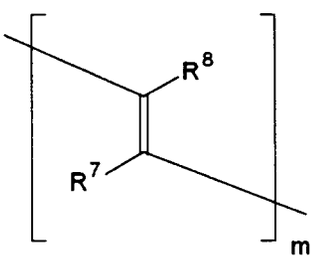
A substituent or atom wherein the value of the σ_p is 0.03 or above includes a fluorine atom, a chlorine atom, a bromine atom, an iodine atom, a substituted alkyl group (eg. trichloromethyl, trifluormethyl, chloromethyl and perfluorobutyl), a nitrile group, an acyl group (eg. formyl, acetyl and benzoyl), a carboxyl group, a substituted or unsubstituted carbamoyl group (eg. methylcarbamoyl) an aromatic group substituted by another electron attractive group (eg pentachlorophenyl, pentafluorophenyl), a heterocyclic group (eg. 2-thienyl, 2-benzoxazolyl, 2-benzthiazolyl, 1-tetrazolyl and 1-phenyl-2-benzimidazolyl), a nitro group, an azo group (eg. phenylazo), an amino group substituted by another electron attractive group (eg. ditrifluoromethylamino), an alkoxy group substituted by another electron attractive group (eg. trifluoromethoxy), an alkylsulphonyloxy group (eg. methanesulphonyloxy), an acyloxy group (eg. acetyloxy, benzoyloxy), an arylsulphonyloxy group (eg. benzenesulphonyloxy), a phosphoryl group (eg. dimethoxyphosphoryl and diphenylphosphoryl), a thioalkyl group substituted by another electron attractive group (eg. trifluoromethyl), a sulphamoyl group, a sulphonamide group, a sulphonyl group (eg. methanesulphonyl, benzenesulphonyl), a thiocyanate group and a sulphoxide group.

Examples of electron-withdrawing groups which A and B may represent are halogen, -CN, $-NO_2$, $-OR^4$, $-SR^4$, $-SO_2R^1$, $-OSO_2R^1$, $-SOR^1$, $-NHCOR^1$, $-CONHR^1$, $-OCONHR^1$, $-NHCO-OR^1$, $-SO_2NH-R^1$, $-NHSO_2R^1$, $-NHSO_2NHR^1$, $-NHNH-SO_2-R^1$, -COOH, $-COOR^1$, $-O-COR^1$, $-COR^1$, $-CSR^1$, $-CONHNHR^1$, $-CF_3$, silyloxy, aryl, aralkyl, alkyl, cycloalkyl, ureido, imido, or a heterocycle,

wherein R^1 is as defined above, and R^4 is an alkyl, cycloalkyl, aryl or heterocyclic group any of which are optionally substituted,

and wherein the nature of the groups R^1 and R^4 and the substituents thereon are such that the group is electron-withdrawing.

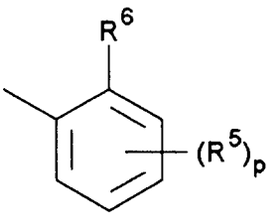
The groups A and B may be also be any of the above groups joined by way of a group that will extend the conjugated path from A or B to the -NH-R group while leaving the whole group electron-withdrawing. Such a group may have the formula:



wherein R^7 and R^8 are each hydrogen, halogen, or an alkyl or aryl group that may be substituted, or R^7 and R^8 may complete a carbocyclic or heterocyclic ring, and
m is 1 or 2.

The ballast group may be located as part of A, B, X or R. Preferably the ballast group is part of R.

A preferred class of groups R have the general formula:



wherein p is 0, 1, 2, 3 or 4 and each R^5 is preferably in a *meta* or *para* position with respect to R^6 (if vacant);

each R^5 is individually a halogen atom or an alkyl, alkoxy, aryloxy, carbonamido, carbamoyl, sulphonamido, sulfamoyl, alkylsulphoxyl, arylsulphoxyl, alkylsulphonyl, arylsulphonyl, alkoxycarbonyl, aryloxycarbonyl, acyloxy, ureido, imido, carbamate, cyano, nitro, acyl, trifluoromethyl, alkylthio, carboxyl or heterocylic group; and

R^6 is a hydrogen or halogen atom or an alkyl, alkoxy, aryloxy, alkylthio, arylthio, carbonamido, carbamoyl, sulphonamido, sulphamoyl, alkylsulphonyl, arylsulphonyl, alkoxycarbonyl, acyloxy, acyl, cyano, nitro, or trifluoromethyl group.

The ballast group or X may have water-solubilising substituents thereon and, in particular, those groups which will increase the activity of the coupler.

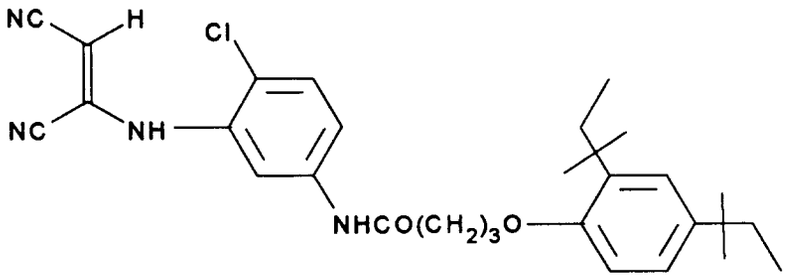
The coupling-off group X may comprise the radical of a photographically useful group, for example a developer inhibitor or accelerator, a bleach accelerator, etc. Such groups are referred to in the Research Disclosure article referred to below.

Link may be a timing group which can be used to speed or slow release of a photographically useful group. Two timing groups may be used in circumstances where staged release is required.

Specific examples of couplers of formula (1) or (2) are listed in PCT specification WO 93/07534 mentioned above whose disclosure is incorporated herein by reference.

In addition to those, a specific example of a coupler to be used in the invention is:

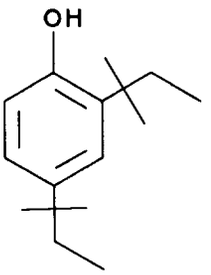
C1



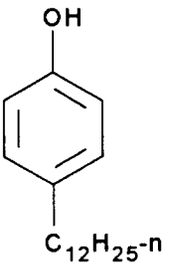
Examples of substituents R^3 and Y on the phenolic solvents of formula (3) are: butyl, t-butyl, n-octyl, s-octyl, t-octyl, amyl, t-amyl, n-dodecyl and methylsulphonylamino, methylsulphamoyl, methylacetyl and methoxy.

The couplers may be dissolved in the phenolic coupler solvent and then dispersed in a solution of a hydrophilic colloid using any means of dispersion. Preferably the ratio of coupler:phenol is within the range 1:0.1 to 1:10, with 1:0.2 to 1:4 being preferred.

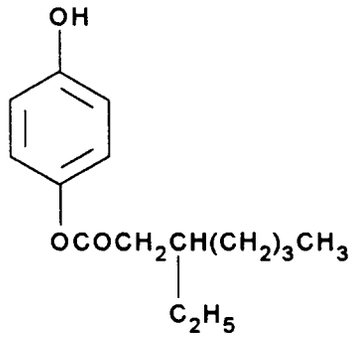
Specific examples of phenolic solvents of formula (3) are:



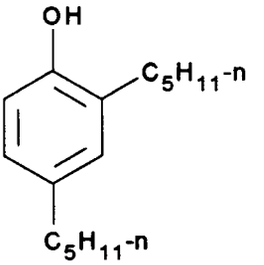
S1



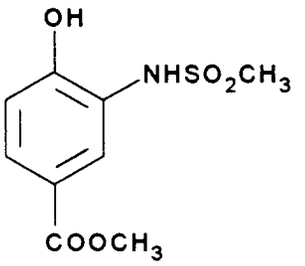
S2



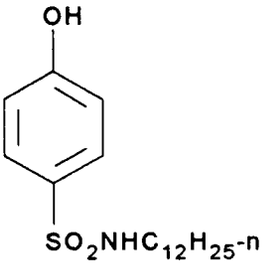
S3



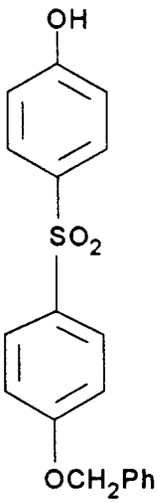
S4



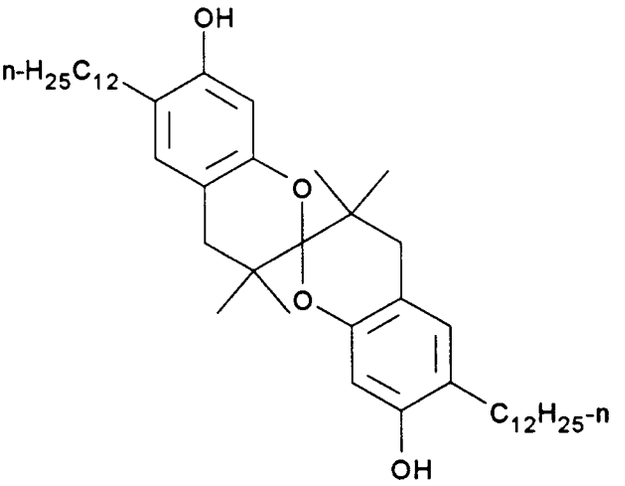
S5



S6



S7



S8

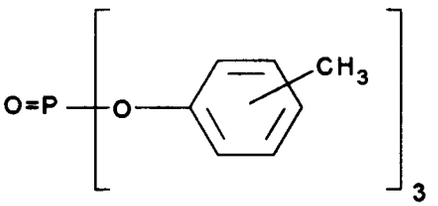
There may also be used another coupler solvent in combination with the phenolic solvent. Such a co-solvent may be an auxiliary volatile or water-miscible solvent which is removed from the dispersion before use. Such techniques are described in Research Disclosure Item 308119, December 1989 published by Kenneth Mason Publications, Emsworth, Hants, United Kingdom.

The photographic elements can be single colour elements or multicolour elements. In a multicolour element, the dye-forming couplers of this invention which provide magenta dyes would usually be associated with a green-sensitive emulsion, although they could be associated with an emulsion sensitised to a different region of the spectrum, or with a panchromatically sensitised, orthochromatically sensitised or unsensitised emulsion. Multicolour elements contain dye image-forming units sensitive to each of the three primary regions of the spectrum. Each unit can be comprised of a single emulsion layer or of multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art.

A typical multicolour photographic element comprises a support bearing yellow, magenta and cyan dye image-forming units comprising at least one blue-, green- or red-sensitive silver halide emulsion layer having associated therewith at least one yellow, magenta or cyan dye-forming coupler respectively, at least one of the dye-forming couplers being a coupler of this invention. The element can contain additional layers, such as filter and barrier layers.

Photographic materials that may contain the present couplers in phenolic coupler solvent solution are described in the Research Disclosure article referred to above.

The following Example is included for a better understanding of the invention. In the Examples a conventional control coupler solvent having the formula is used:



S9

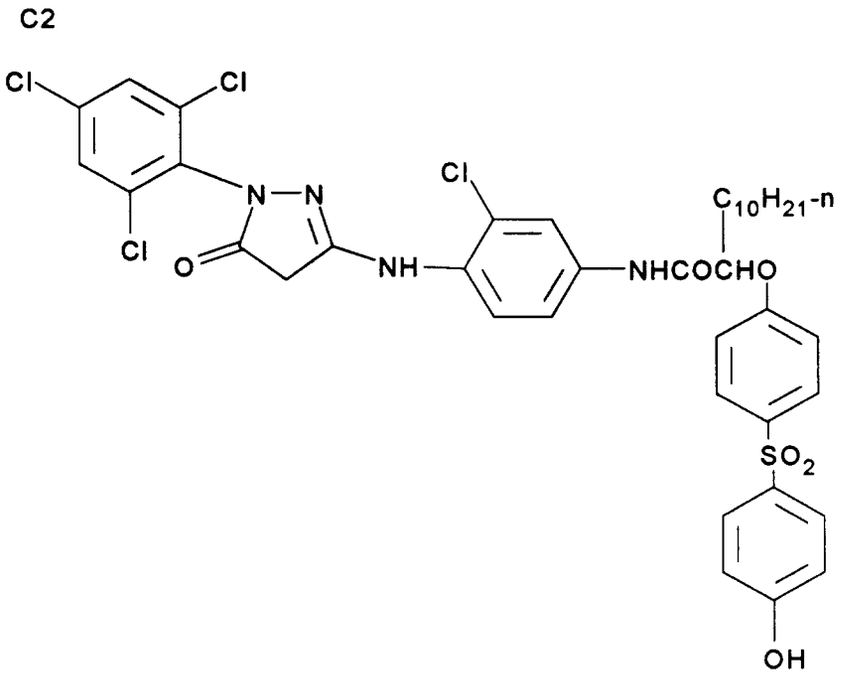
EXAMPLE

The compound of the invention (C1) was dispersed in a range of phenolic solvents (S1) and (S2) and incorporated into a photographic silver bromoiodide emulsion and coated in thefollowing format:-

Gel Supercoat	Gelatin	1.5 g/m^2
Emulsion Layer	Silver bromoiodide Test Coupler Gelatin Bis (vinylsulphonyl)-methane (hardener)	1.61 g/m^2 1.042 mmol/m^2 2.42 g/m^2 0.06 g/m^2
Support	Cellulose acetate	

The common pyrazolone coupler (C2) having the formula below was used as the control:

C2



was also dispersed in the same range of phenolic solvents and incorporated into photographic coatings having the same structure as described above.

The coupler dispersion used for both the test coupler and control (C2) contained 6% w/w gelatin, 8.8% coupler and coupler solvents in the ratio:

coupler : phenolic coupler solvent : 2-(2-butoxyethoxy)ethyl acetate = 1.0 : 0.5: 1.5.

Both the test coupler (C1) and the control coupler (C2) were coated using the commonly used ester coupler solvent (S9) (tri-cresyl phosphate) in place of the phenolic couplers solvent in the above formulation for comparison purposes.

The experimental photographic coatings prepared in this way were slit and chopped into 35mm test strips. These were exposed through a 0 - 4.0 neutral density step wedge (0.2 ND step increments) and Daylight V, Wratten 9 filters then processed through the following standard C-41 process:

Developer	2.5 minutes
Bleach	4 minutes
Wash	2 minutes
Fix	4 minutes
Wash	2 minutes.

For each test strip, step-wedge densities were measured using a spectral array automatic transmission densitometer. Measurements of maximum density (Dmax) are calculated from the D logE curves.

35mm test strips were also exposed through a 0 - 0.9 neutral density step wedge (0.3ND increments) and Daylight V and WR9 filters and the correct neutral density filters to give a density of *ca.* 1.0. The strips were then processed through a standard C-41 process as described above. Samples were then cut from the step with density closest to 1.0 and visible absorption spectra of the resultant magenta dyes obtained (normalised to a density of 1.0) using a Pye-Unicam SP8-100 spectrophotometer. Measurements of the wavelength of maximum absorption (λ-max) were obtained from the absorption spectra. The results from these measurements are shown in Table 1.

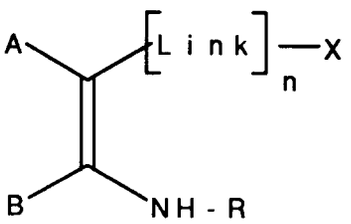
Table 1

Coupler	Solvent	Dmax	%Increase in Dmax	λ-max
(C2)	(S9)	2.81	0.0 (control)	547.0
(C2)	(S1)	2.83	0.0	552.0
(C2)	(S2)	2.93	4.0	552.0
(C1)	(S9)	2.41	0.0 (control)	549.0
(C1)	(S1)	2.96	23.0	548.5
(C1)	(S2)	2.89	20.0	548.0

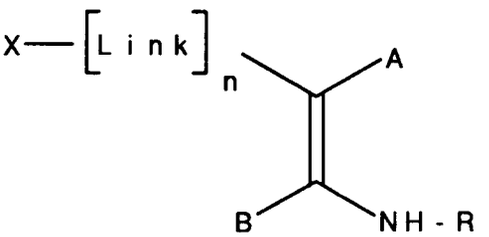
The data in Table 1 demonstrate that the activity of the enamine coupler (C1) is greatly enhanced by incorporation in phenolic solvents (S1) and (S2) relative to the commonly used ester solvent (S9) with no deleterious effect on the hue of the dye produced. By contrast, in phenolic coupler solvents, the common pyrazolone coupler (C2) shows no comparable activity enhancement. Furthermore an undesirable bathochromic shift in dye hue (*ca.* 5nm) is obtained.

Claims

1. A photographic element comprising a support, at least one photosensitive silver halide layer and in or adjacent said silver halide layer a colour coupler of the general formulae:



(1)



(2)

wherein A and B represent the same or different electron-withdrawing group,

X is H or a group which splits off on coupling with oxidised colour developer,

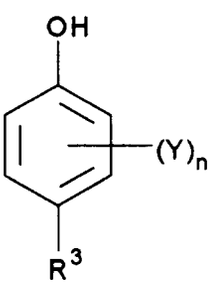
R is an alkyl, cycloalkyl, aryl or heterocyclic group any of which may be substituted, -COR^1, -CSR^1, SOR^1, SO_2R^1, -$NHCOR^1$, -$CONHR^1$, -$COOR^1$, -$COSR^1$, -$NHSO_2R^1$ wherein R^1 is an alkyl, cycloalkyl, or aryl group any of which are optionally substituted,

and wherein two or more of A, B, R, and X optionally form part of a ring,

Link is a linking group and

n is 0, 1 or 2,

characterised in that the coupler is dissolved in droplets of a phenolic solvent having the formula:



(3)

wherein R^3 and each Y is, individually, an alkyl, alkoxy cycloalkyl, aryl, aryloxy or heterocyclic group any of which may be substituted, -COR^1, -$OCOR^1$ -SOR^1, - SO_2R^1, -$NHCOR^1$, -$CONHR^1$,

-COOR^1, -NHSO$_2$R^1, -SO$_2$NHR^1 or -NR^{1}R^2, n is 0 to 4, or R^3 and a Y can, together with the atoms to which they are attached, complete a carbocyclic or heterocyclic ring which may be substituted,
where R^1 is as defined above and R^2 can have any of the meanings for R^1 or hydrogen.

2. A photographic element as claimed in claim 1 wherein the ratio of coupler:phenol is within the range 1:0.1 to 1:10.

3. A photographic element as claimed in claim 1 wherein the ratio of coupler:phenol is within the range 1:0.2 to 1:4.

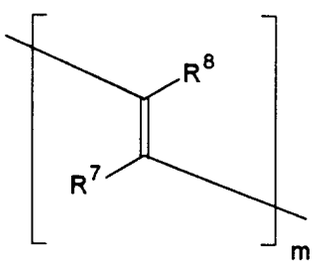
4. A photographic element as claimed in any of claims 1-3 wherein A and B of formulae (1) or (2) are each individually an electron-withdrawing group wherein the value of the Hammett substituent constant σ_p (SIGMA$_p$ as defined by Hansch et al, J. Med. Chem.,1973, 16, 1207; and ibid. 1977, 20, 304) is 0.03 or greater.

5. A photographic element as claimed in claim 4, wherein the value of the Hammett substituent constant is 0.35 or greater.

6. A photographic element as claimed in any of claims 1-5 wherein the group Y of formula (3) is a butyl, t-butyl, n-octyl, s-octyl, t-octyl, amyl, t-amyl, n-dodecyl, or methylsulphonylamino group.

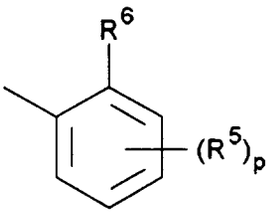
7. A photographic element as claimed in any of claims 1-6 wherein A and B are each individually a halogen, -CN, -NO$_2$, -OR^4, -SR^4, -SO$_2$R^1, -OSO$_2$R^1, - SOR^1, -NHCOR^1, -CONHR^1, -OCONHR^1, -NHCO-OR^1, -SO$_2$NH-R^1, -NHSO$_2$R^1, -NHSO$_2$NHR^1, -NHNH-SO$_2$-R^1, -COOH, -COOR^1, -O-COR^1, -COR^1, -CSR^1, -CONHNHR^1, -CF$_3$, silyloxy, aryl, aralkyl, alkyl, cycloalkyl, ureido, imido, or a heterocycle,
wherein R^1 is as defined in claim 1, and
R^4 is an alkyl, cycloalkyl, aryl or heterocyclic group any of which are optionally substituted, and wherein the nature of the groups R^1, and R^4
and the substituents thereon are such that the group is electron-withdrawing.

8. A photographic element as claimed in any of claims 1-7 wherein A and B are joined by way of a group of the formula:



that will extend the conjugated path from A or B to the -NH-R group while leaving the whole group A or B with its link electron-withdrawing group,
wherein R^7 and R^8 are each hydrogen, halogen, or an alkyl or aryl group that may be substituted, or R^7 and R^8 complete a carbocyclic or heterocyclic ring, and
m is 1 or 2.

9. **A photographic element as claimed in any of claims 1-8 wherein group R of formula (1) or (2) has the formula:**



wherein p is 0, 1, 2, 3 or 4 and each R^3 is preferably in a *meta* or *para* position with respect to R^6 (if vacant);

each R^5 is individually a halogen atom or an alkyl, alkoxy, aryloxy, carbonamido, carbamoyl, sulphonamido, sulfamoyl, alkylsulphoxyl, arylsulphoxyl, alkylsulphonyl, arylsulphonyl, alkoxycarbonyl, aryloxycarbonyl, acyloxy, ureido, imido, carbamate, cyano, nitro, acyl, trifluoromethyl, alkylthio, carboxyl or heterocylic group; and

R^6 is a hydrogen or halogen atom or an alkyl, alkoxy, aryloxy, alkylthio, arylthio, carbonamido, carbamoyl, sulphonamido, sulphamoyl, alkylsulphonyl, arylsulphonyl, alkoxycarbonyl, acyloxy, acyl, cyano, nitro, or trifluoromethyl group.

10. A photographic element as claimed in any of claims 1-9 in which the ballast group or X contains a water-solubilising group.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 20 0472

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,X D,Y	WO-A-93 07534 (KODAK) * the whole document * * table 7 *	1-9 1-9	G03C7/30 G03C7/388
Y	WO-A-91 18323 (KODAK) * page 3; claims; tables 2,3 *	1-9	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	31 March 1995	Heywood, C

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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