



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

0 296 793
A2

⑫

EUROPEAN PATENT APPLICATION

⑲ Application number: 88305631.9

⑤① Int. Cl.⁴: G03C 7/36 , //C07C147/10

⑳ Date of filing: 22.06.88

⑳ Priority: 25.06.87 GB 8714866

④③ Date of publication of application:
28.12.88 Bulletin 88/52

⑤④ Designated Contracting States:
DE FR GB IT NL

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

⑤④ DE FR IT NL

⑦① Applicant: KODAK LIMITED
P.O. Box 66 Station Road
Hemel Hempstead Herts, HP1 1JU(GB)

⑤④ GB

⑦② Inventor: Clark, Bernard Arthur James
22 New Road
Holloport Maidenhead Berks(GB)
Inventor: Milner, Nigel Edgewick
23 Valley Walk
Croxley Green Watford Herts(GB)
Inventor: Stanley, Paul Louis Reginald
69 Archery Close
Wealdstone Harrow Middlesex(GB)

⑦② Representative: Baron, Paul Alexander
Clifford et al
Kodak Limited Patent Department Headstone
Drive
Harrow Middlesex HA1 4TY(GB)

⑤④ Colour photographic silver halide materials and process.

⑤⑦ A new non-diffusible yellow dye-forming para-R-oxybenzoylacetanilide coupler has a combination of (a) a para-hydroxyphenylsulphonylphenoxy coupling-off group in the coupling-position, (b) a chloro or trifluoromethyl group in the ortho position on the anilide moiety, and (c) a group on the anilide moiety that is selected from (i) a sulphamoyl group (ii) an aliphatic hydrocarbon group that is bonded to the anilide moiety directly or through a linking group as described in the application, (iii) chlorine and (iv) trifluoromethyl; wherein the coupler contains at least one ballast group on at least one of the anilide and para-R-oxybenzoyl moieties; and wherein R is an unsubstituted or substituted cyclic or non-cyclic aliphatic hydrocarbon group. These couplers are useful in color photographic silver halide materials and processes to produce image dyes that have excellent hue and high extinction coefficient.

EP 0 296 793 A2

COLOUR PHOTOGRAPHIC SILVER HALIDE MATERIALS AND PROCESS

This invention relates to novel acylacetanilide photographic colour couplers and photographic elements containing them.

It is well established in the photographic art that colour images may be obtained from imagewise exposed silver halide emulsions by developing them with a primary aromatic amine colour developing agent in the presence of a colour coupler. The oxidized colour developing agent formed in the areas of silver halide development couples with the coupler to form a dye. The coupler may be present in the developer solution but is normally incorporated in the sensitive photographic material.

For image dye-forming couplers to be practically useful, they must react both efficiently and at a suitable rate with oxidized developer to produce the dye. In addition, the dyes thus formed must possess acceptable hue and exhibit adequate stability over a wide range of keeping conditions.

Most of the examples of yellow image dye-forming couplers which have been used in commercial photographic products are drawn from two classes of acylacetanilide, namely pivaloylacetanilides and benzoylacetanilides. Historically, benzoylacetanilide couplers exhibit greater reactivity with oxidized developer than their pivaloylacetanilide analogues and furthermore, the extinction coefficient of their derived dyes can be greater. However, the hue of these dyes is generally deeper, and their stability on exposure to light, heat and humidity is generally poorer. Benzoylacetanilides are also more prone to crystallize either in coupler solvent or in photographic coatings.

Benzoylacetanilides have been largely superseded by pivaloylacetanilides over the last thirty years owing to the superior dye characteristics imparted by the latter. However, the present invention relates specifically to the use of benzoylacetanilides as yellow image dye-forming couplers.

European Patent Application 0126433 is largely concerned with pivaloylacetanilide couplers but three benzoylacetanilides (Compounds 4, 10 and 11) are disclosed; these compounds however do not fall within the claims of the present specification. US Patent 4,587,207 in its general description covers both pivaloylacetanilide and benzoylacetanilide but its specific disclosure is restricted to pivaloylacetanilides. Compound 17 of this patent has structural features in common with the couplers of the present invention but has the ballast group attached in a different position and its properties are not reported.

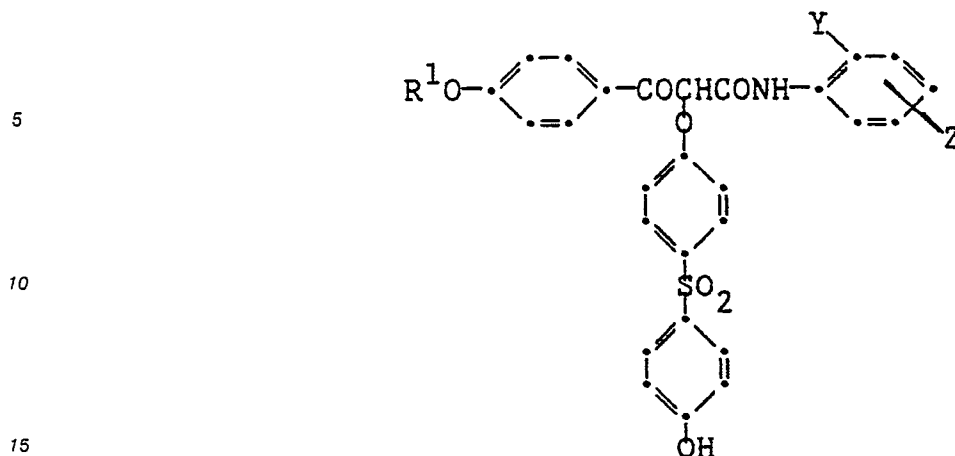
A continuing need has existed for acylacetanilide yellow dye-forming couplers that, in a photographic silver halide material and process, provide excellent dye density and image contrast characteristics and provide image dyes of excellent hue and high extinction coefficients. A need also has existed for such couplers that enable improved dark keeping characteristics.

We have found that such characteristics are provided in a colour photographic silver halide element comprising a support bearing at least one photographic silver halide emulsion layer and a non-diffusible yellow dye-forming para-R-oxybenzoylacetanilide coupler that has a combination of (a) a para-hydroxyphenylsulphonylphenoxy coupling-off group in the coupling-position, (b) a chloro or trifluoromethyl group in the ortho position on the anilide moiety, and (c) a group on the anilide moiety that is selected from (i) a sulphamoyl group, (ii) an aliphatic hydrocarbon group that is bonded to the anilide moiety directly or through a linking group that is a carbamoyl (-CONH-), oxycarbonyl (-CO-O-), carbonyloxy (-O-CO-), sulphonate (-O-SO₂-), sulphamoyl (-SO₂NH-), phosphate (-O-PO₂-) or alkylene, (iii) chlorine, and (iv) trifluoromethyl; wherein the coupler contains at least one ballast group on at least one of the anilide and para-R-oxybenzoyl moieties; and, wherein R is an unsubstituted or substituted cyclic or non-cyclic aliphatic hydrocarbon group.

Useful non-diffusible colour couplers have the formula:

45

50



wherein R¹ is an cyclic or non-cyclic aliphatic hydrocarbon group which may be substituted or unsubstituted and may comprise a ballast group,

Y is chloro or trifluoromethyl,

Z is -L-R² or -SO₂NR³R⁴,

where R² is an aliphatic hydrocarbon group which may be substituted or unsubstituted,

R³ and R⁴ are each hydrogen or an aliphatic hydrocarbon group which may be substituted or unsubstituted, or R³ and R⁴ together form a ring, or, if R¹ comprises a ballast group, Z may also be halogen or trifluoromethyl, and L is a direct bond or a carbamoyl (-CONH-), oxycarbonyl (-CO-O-), carbonyloxy (-O-CO-), sulphamate, (-O-SO₂-), sulphamoyl (-SO₂NH-), phosphate (-O-PO₂-) or alkylene group,

and wherein Z may comprise a ballast group, at least one of R¹ and Z contains a ballast group.

The benzoylacetyl anilide image dye-forming couplers of the invention are readily soluble in common coupler solvents and, when incorporated into a color negative photographic material, exhibit excellent dye density and contrast characteristics. Furthermore, these couplers produce dyes of excellent hue and high extinction coefficient which are stable under a wide range of conditions, particularly dark keeping which is of fundamental importance for colour negative materials.

Examples of the groups which R¹ may represent are alicyclic groups of 4 to 6 carbon atoms, and non-cyclic groups of 1-20 carbon atoms which may be substituted or unsubstituted, saturated or unsaturated, e.g. methyl, ethyl, n-butyl, n-dodecyl, n-hexadecyl, and n-undecyl.

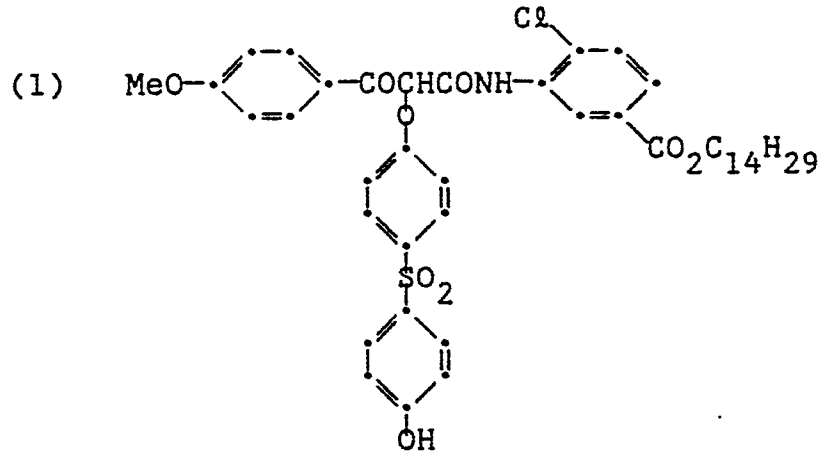
The ballast group may form part of R¹ in which case R¹ may be an alkyl group of 10-16 carbon atoms.

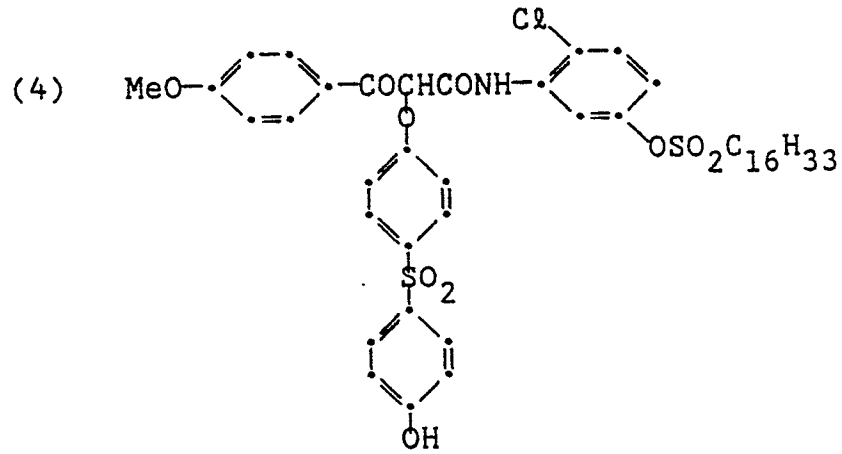
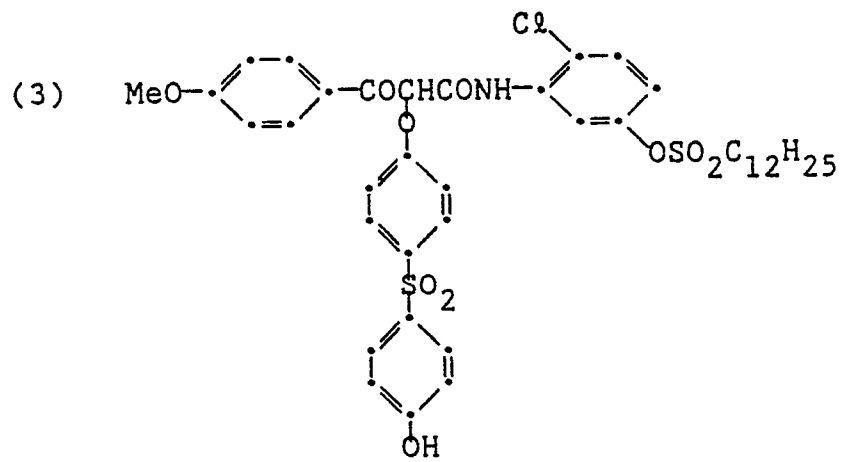
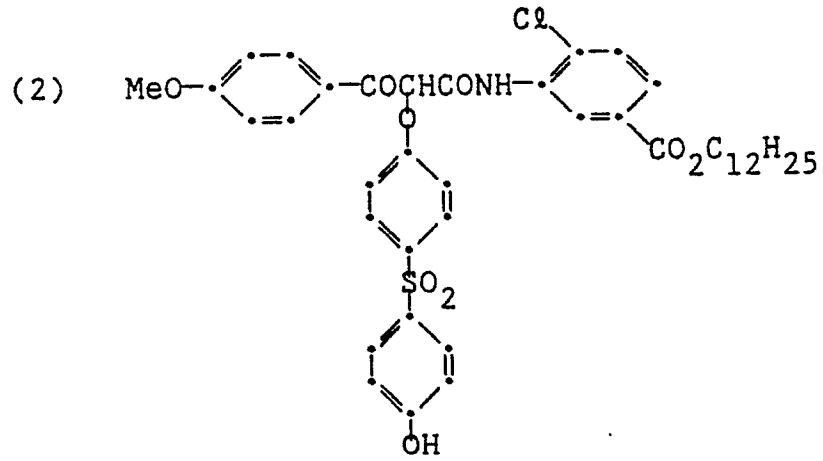
The ballast can also be attached via substituent Z. In such cases, the group which links the ballast to the anilide ring has a strong influence on the solubility of the coupler in coupler solvent and also its propensity to crystallize in photographic coatings. Linking groups or atoms which have been found to confer favorable solubility characteristics on the coupler include carbamoyl, oxycarbonyl, sulphamate, sulphamoyl, phosphate and alkyl. It is noted that linking groups or atoms which may give rise to coupler crystallinity problems include amide, sulphonamide and oxygen.

If the ballast is in Z, R¹ preferably contains 1-4 carbon atoms.

The aliphatic hydrocarbon groups which R², R³ and R⁴ may represent can be any of the groups given as examples of R¹ or when R³ and R⁴ are taken together they may, for example, be the atoms required to complete a piperidine, pyrrolidine or morpholine ring.

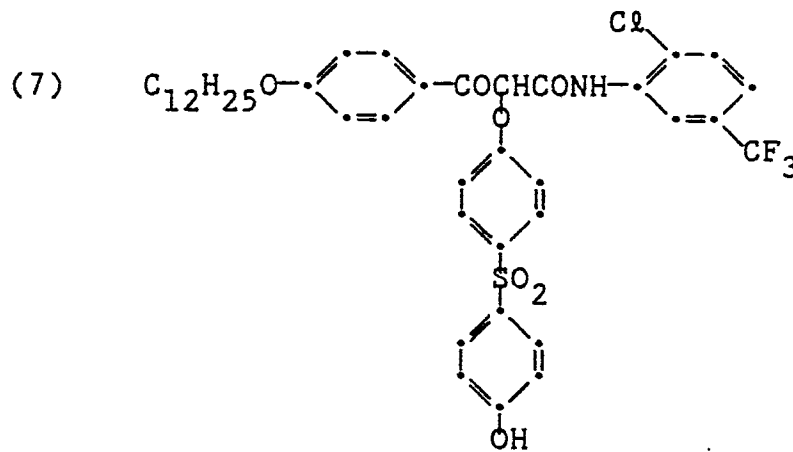
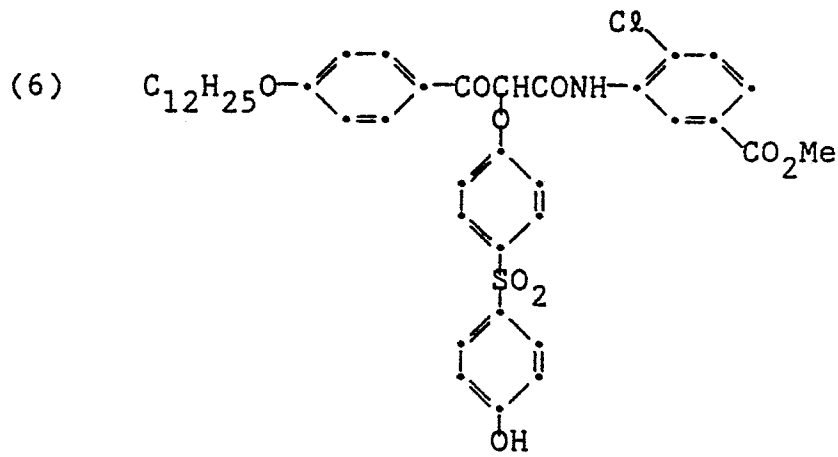
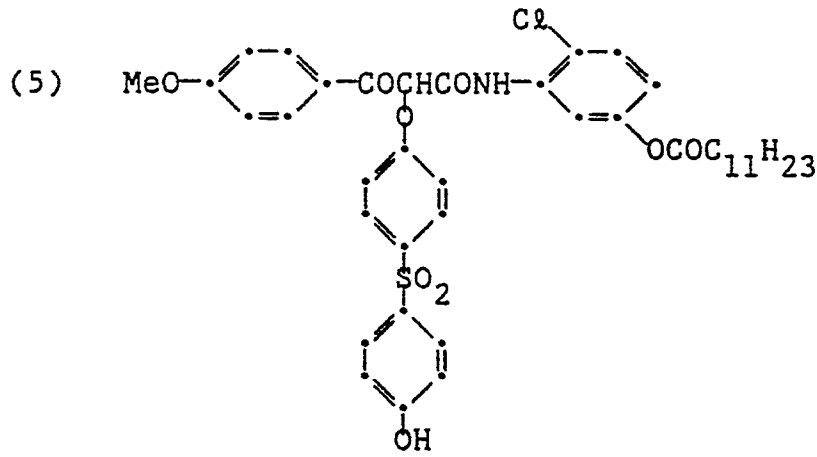
Benzoylacetyl anilide couplers 1 to 11 specified below are examples of couplers of the invention whose derived dyes exhibit exceptional dark/wet stability. Furthermore, these compounds display all the other characteristics required of an image dye-forming coupler for use in color negative photographic materials.

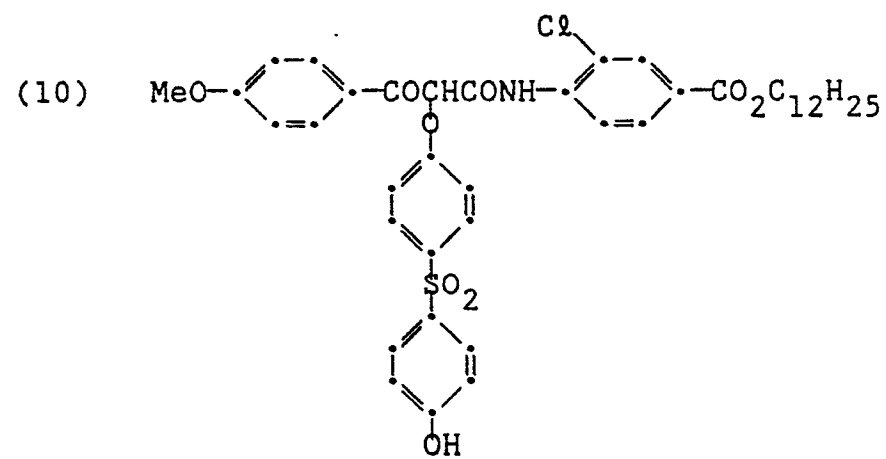
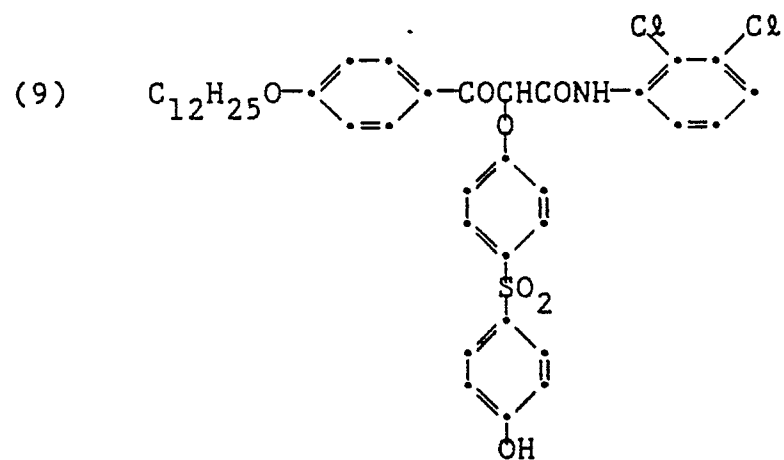
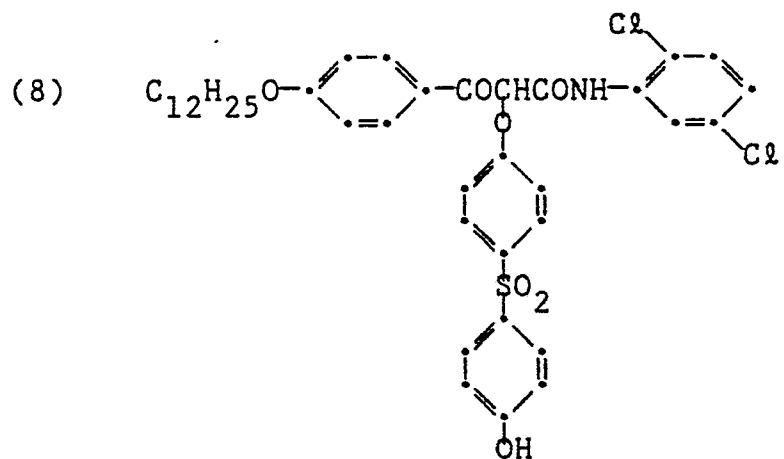




50

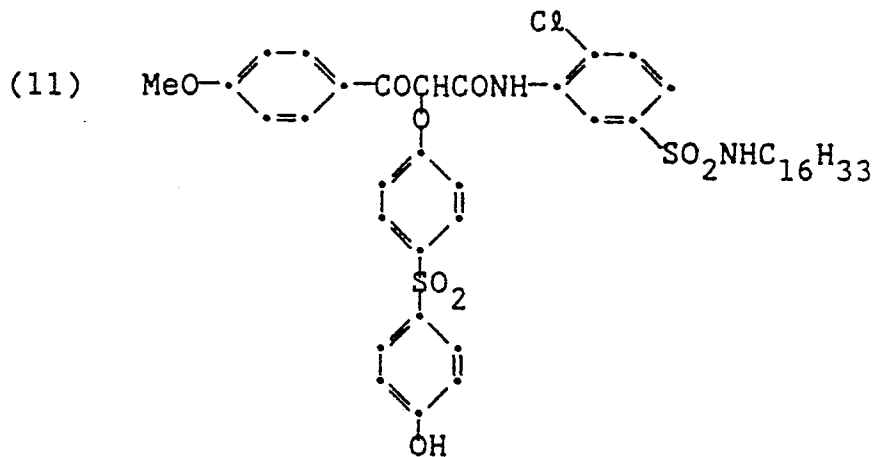
55





50

55

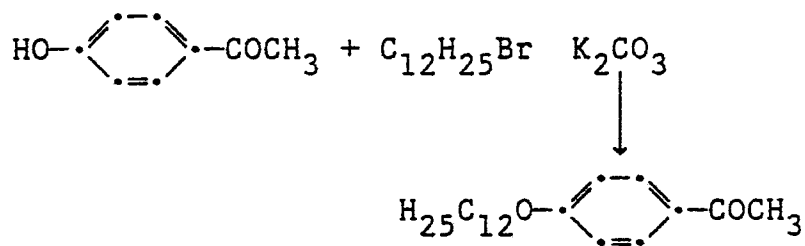


Me herein means CH₃-.

The present couplers may be prepared by methods, in themselves, known. The following synthetic procedure for coupler 6 is illustrative for all the compounds of the invention.

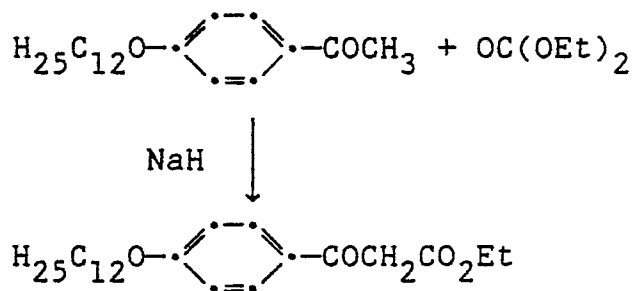
Preparation of coupler 6

1) 4-Dodecyloxyacetophenone



A stirred mixture of 4-hydroxyacetophenone (54.5g), 1-bromodecane (152.7g), potassium carbonate (83.0g) and acetone (800ml) was heated under reflux for 40 hours. The mixture was passed through a steam-heated filter and the filtrate was evaporated under reduced pressure. The residue was recrystallized from petroleum-ether (b.p. 40-60 °C) to give 91.0g of product (75%).

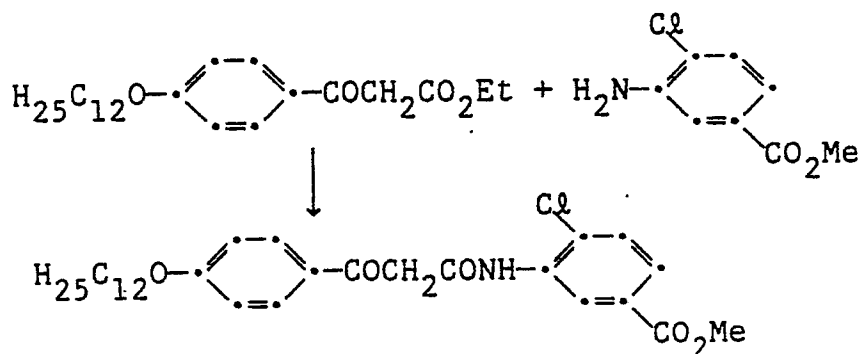
2) Ethyl 4-dodecyloxybenzoylacetate



A stirred mixture of sodium hydride (25.5g, 60% mineral oil dispersion), diethyl carbonate (115.0g) and toluene (300ml) was heated to 70 °C. 4-Dodecyloxyacetophenone (74.4g) in toluene (150ml) was added

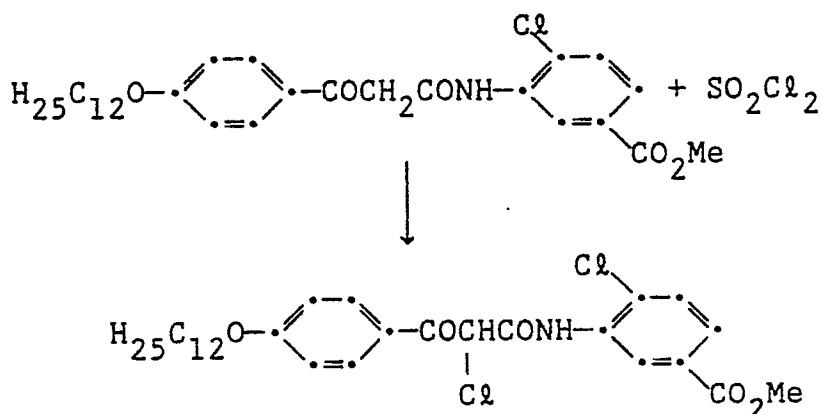
over 20 minutes. The stirred mixture was heated at 80 °C for 2 hours, then it was cooled and carefully acidified with glacial acetic acid. The mixture was diluted with water, then it was extracted with ethyl acetate (300ml). The extract was dried over magnesium sulphate and evaporated under reduced pressure. Xylene was added to the residue and the resulting solution was again concentrated under reduced pressure to remove traces of diethyl carbonate. The residue (101.4g) was used in the next stage without further purification.

3) Methyl 4-chloro-3-[2-(4-dodecyloxybenzoyl)acetamido]benzoate.



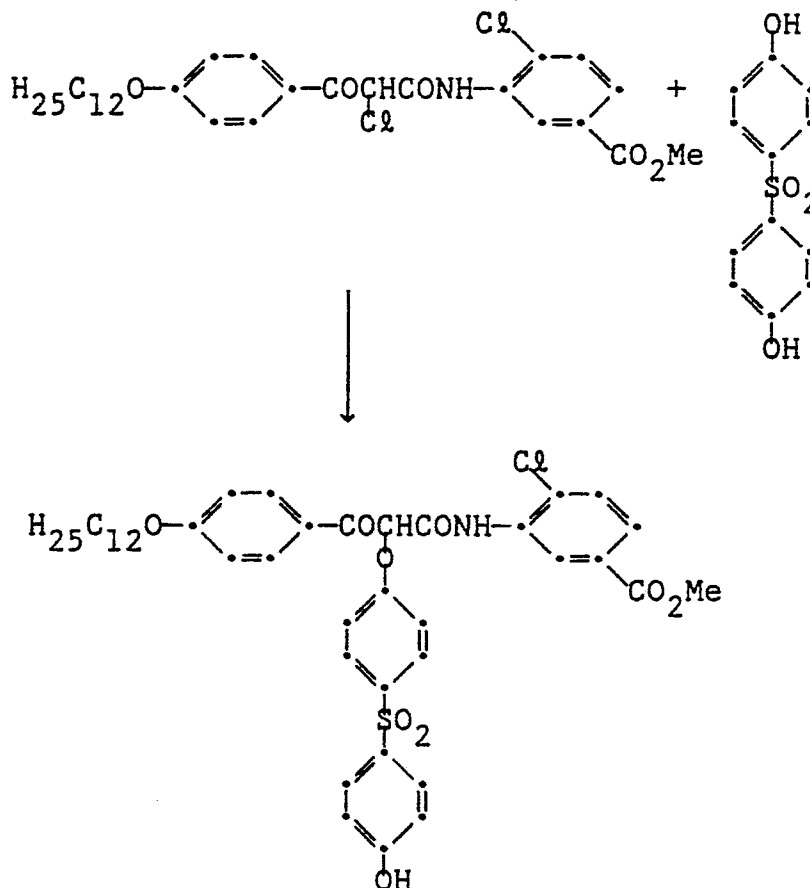
A stirred mixture of ethyl 4-dodecyloxybenzoate (45.6g, crude), methyl 3-amino-4-chlorobenzoate (20.0g) and xylene (400ml) was slowly distilled over 3 hours collecting about 200ml of distillate. The solution was allowed to cool and the resulting precipitate was filtered off. The product was recrystallized from acetonitrile to afford a flaky, white solid (33.9g, 60.8%).

4) Methyl 4-chloro-3-[2-chloro-2-(4-dodecyloxybenzoyl)acetamido]benzoate



Sulphuryl chloride (9.5g) was added over 30 minutes to a solution of the above solid (33.0g) in dichloromethane (300ml). The solution was stirred at ambient temperature for a further 1 hour before being concentrated under reduced pressure. The residue crystallized when slurried with acetonitrile. The resulting solid was recrystallized from acetonitrile to give 32.0g (91%) of pure product.

5) Methyl 4-chloro-3-[2-(4-dodecyloxybenzoyl)-2-(4-((4-hydroxyphenylsulphonyl))phenoxy)acetamido]benzoate



Nitrogen gas was passed through a solution of methyl 4-chloro-3-[2-chloro-2-(4-dodecyloxybenzoyl)acetamido]benzoate (22g) and sulphonyldiphenol (40g) in DMF (300ml) for 30 minutes before adding triethylamine (12.12g) dropwise with stirring. The temperature was raised to 45-50 °C and maintained for 2 hours. The reaction mixture was poured into stirred 5% hydrochloric acid (300ml) and the mixture was then stirred for 1 hour. The aqueous phase was decanted and the residual gum dissolved in ethyl acetate (300ml). The organic solution was washed successively with sodium carbonate solution (300ml) and water (300ml), then it was dried over magnesium sulphate and concentrated to dryness. The resulting gum was purified by elution through a silica gel column using mixtures of ethyl acetate and petroleum-ether (b.p. 60-80 °C) as the eluting solvent. The appropriate fractions were combined and concentrated under reduced pressure, and the resulting solid was recrystallized from ethyl acetate/petroleum ether to afford the required product as a white powder (14g, 46%).

HPLC analysis 99%, m.p. 153-8 °C

Elemental analysis:

$C_{24}H_{45}ClNO_3S$

req: C,64.3; H,6.2; Cl,4.9; N,1.8; S,4.3%:

found C 64.4; H 6.0; Cl 4.7; N 1.8; 4.2%.

The dye-forming couplers of this invention can be used in the ways and for the purposes that dye-forming couplers have been previously used in the photographic art.

Typically, the couplers are associated with a silver halide emulsion layer coated on a support to form a photographic element. As used herein, the term "associated with" signifies that the coupler is incorporated in the silver halide emulsion layer or in a layer adjacent thereto where, during processing, it is capable of reacting with silver halide development products.

The photographic elements can be single colour elements or multicolor elements. In a multicolour element, the yellow dye-forming couplers of this invention would usually be associated with a blue-sensitive emulsion, although they could be associated with an emulsion sensitized to a different region of the spectrum, or with a panchromatically sensitized, orthochromatically sensitized or unsensitized emulsion.

5 Multicolor elements contain dye image-forming units sensitive to each of the three primary regions of the spectrum. Each unit can be comprised of a single emulsion layer or of multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art.

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

15 In the following discussion of suitable materials for use in the emulsions and elements of this invention, reference will be made to Research Disclosure, December 1978, Item 17643, published by Industrial Opportunities Ltd., The Old Harbourmaster's, 8 North Street, Emsworth, Hants PO10 7DD, U.K. This publication will be identified hereafter as "Research Disclosure".

20 The silver halide emulsion employed in the 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.

25 In addition to the couplers of this invention, the elements of the invention can include additional couplers as described in Research Disclosure Section VII, paragraphs D, E, F and G and the publications cited therein. The couplers of this invention and any additional couplers can be incorporated in the elements and emulsions as described in Research Disclosures of Section VII, paragraph C and the publications cited therein.

30 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), antistain 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
35 modifiers (see Research Disclosure Section XXI).

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

40 Photographic elements 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 colour developing agent to reduce developable silver halide and oxidize the colour developing agent. Oxidized colour developing agent in turn reacts with the coupler to yield a dye.

45 Preferred colour developing agents are p-phenylene diamines. Especially preferred are 4-amino-3-methyl-N,N-diethylaniline hydrochloride, 4-amino-3-methyl-N-ethyl-N- β -(methanesulphonamido)-ethylaniline sulphate hydrate, 4-amino-3-methyl-N-ethyl-N- β -hydroxyethylaniline sulphate, 4-amino-3- β -(methanesulphonamido)ethyl-N,N-diethylaniline hydrochloride and 4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluene sulphonate.

50 With negative-working silver halide emulsions this processing step leads to a negative image. To obtain a positive (or reversal) image, this step can be preceded by development with a non-chromogenic developing agent to develop exposed silver halide, but not form dye, and then uniform fogging of the element to render unexposed silver halide developable. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

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

Photographic Testing

The methods of photographic testing used in the Examples below are carried out as follows.

5

(i) Preparation of Experimental Photographic Coatings

Each coupler of the invention was dissolved in half its weight of di-n-butyl phthalate, with one and a half times its weight of cyclohexanone as auxiliary solvent and dispersed in gelatin. The auxiliary solvent was
10 removed from the dispersion by continuous washing for 6 hours at 4 °C and pH 6.0.

Experimental photographic coatings were prepared by coating a cellulose acetate film support with a photosensitive layer comprising a dispersion of the novel coupler as formulated above coated at a laydown of 1.93 mmol/m², a silver bromoiodide emulsion at 0.81 Ag/m² and gelatin at 2.42 g/m². An overcoat containing gelatin at 0.89 g/m² was applied to the photosensitive layer. Bis-vinylsulphonylmethane at 1.75%
15 by weight of the total gelatin in the pack was also incorporated into the photosensitive layer. The dried experimental coating was then slit and chopped into 35mm x 12 inch test strips.

Couplers of the invention have also been dispersed with ethyl acetate as auxiliary solvent (subsequently removed by evaporation under reduced pressure) and also in the complete absence of main coupler solvent (NS dispersions) and photographic coatings were prepared as above.
20

(ii) Coupler Stability and Crystallinity Measurement

The crystallinity of each coupler dispersion prepared for testing was investigated by spreading a few
25 drops of dispersion on a microscope slide, placing a glass coverslip on top and viewing under a magnification of 1250x using Differential Interference Contrast to enhance the image.

In-film crystallinity of the coupler was assessed largely by visual inspection and deterioration in sensitometry.

In-film stability of the coupler was measured by incubating unexposed test strips for 24 hours at 21 °C and 50% relative humidity followed by 1 week dry incubation at 49 °C. The strips were then exposed and
30 processed as below and sensitometry compared with that of fresh test strips of the same coupler.

(iii) Sensitometric Testing

35

The 35mm test strips were exposed through a 0-4.0 neutral density (ND) step-wedge (0.2 ND step increments) test object and Daylight V, Wratten 35 and 38A and 0.3 ND filters. The strips were processed through a deep-tank sink line at 37.8 °C using the following standard process:

40	Colour Developer	2.5 minutes
	Bleach (Fell/EDTA)	4 minutes
	Wash	2 minutes
	Fix	4 minutes
	Wash	2 minutes

in which the solutions are those described in the C41 process described in the British Journal of
45 Photography Annual 1977 pages 204-5 in which the colour developing agent was 4-amino-3-methyl-N-ethyl-N-2-hydroxyethylaniline sulphate. The processed strips were then dried to give stepped yellow dye images.

In addition to the above standard conditions test strips were developed in a competing process with the addition of 5.0 g/l citrazinic acid (CZA) to the colour developer solution and adjustment of the pH to 10.0 with sodium carbonate.

50 For each test strip step-wedge densities were measured using a Macbeth TD504/Hewlett Packard 85 automatic transmission densitometer. Measurements were made of minimum density (D_{min}), maximum density (D_{max}), contrast (γ), and photographic speed (PS). The ratio of contrast in the CZA competing process to contrast in the standard process ($\gamma_{CZA}/\gamma_{STD}$) is quoted as an indication of in-film reactivity of the coupler.

55 Silver analysis (X-Ray Fluorescence) of the yellow dye step-wedges produced from a standard process in which the bleach step was omitted enabled silver development curves to be plotted. From these and the D/log E curves were generated Dye Density Yield Curves for each individual coupler.

(iv) Spectrophotometric Testing

35mm Test strips were exposed as above through a 0-0.3 ND step-wedge (0.1 incremental steps) test object and Daylight V, Wratten 35 and 38A filters and the correct ND filters to give an optical density of about 1.0. The strips were processed using the standard conditions described above and samples cut from the yellow dye image step with density closest to 1.0. Visible absorption spectra (normalized to 1.0 density) were obtained using a Pye Unicam SP8-100 Spectrophotometer. Dye hues are expressed in terms of the wavelength corresponding to the maximum absorption peak (λ max) and the half-bandwidth (HBW) calculated from the spectrophotometric curves.

Extinction coefficients of the yellow dyes were obtained from ethyl acetate solutions of the preformed dyes using a Varian DMS 90/Apple II automated uv/visible spectrophotometer.

(v) Dye Stability Testing

Yellow dye sample patches of density circa 1.0 were prepared as for spectrophotometric testing and their absorption spectra measured as above.

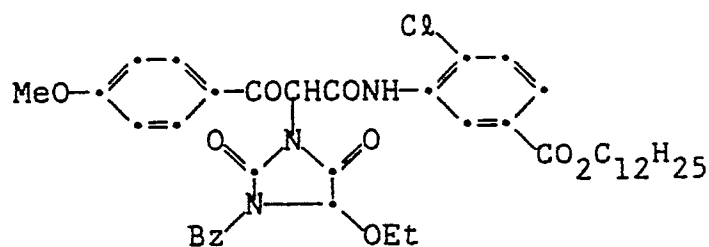
For the dark keeping experiment the yellow dye samples were incubated in a dark oven for periods of 1, 3 and 6 weeks at a constant 60°C and 70% relative humidity. The spectrophotometric curves of the samples were then remeasured and the degree of fade quoted as the fractional decrease in density at the absorption maximum (ΔD) relative to the initial density prior to fading.

Example 1

The dark/wet fade data for Couplers (1) to (11) are as follows and are compared with comparative compound (12), a commercially used benzoylacetanilide which bears a hydantoin coupling-off group.

Compound	Dark/wet fade (6 weeks)
(1)	0.04
(2)	0
(3)	0.06
(4)	0.04
(5)	-0.05
(6)	0
(7)	0
(8)	-0.03
(9)	0.01
(10)	0.04
(11)	0.07
(12) (Comparison)	-0.16

The structure of Coupler 12 is:



Et herein means ethyl and Bz means benzyl.

It can be seen that dye images formed from all of couplers (1)-(11) of this invention have superior dark/wet stability compared with that of prior art coupler (12).

5 Example 2

Table 1, containing examples of the invention (4) and (7), illustrates the superior Dmax and contrast consistently attained in dye images from couplers of the invention relative to a current commercial pivaloylacetylacetonide coupler (13).

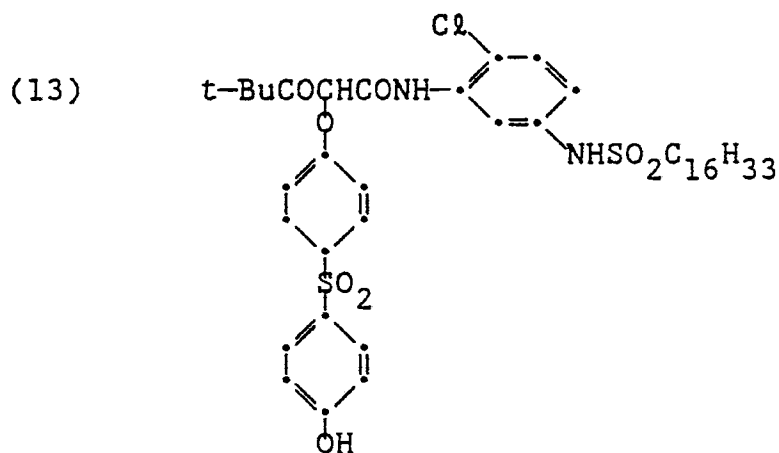
10 The dark/wet fade data for this set illustrates the superiority of the couplers of the invention (4) and (7) containing a phenolic leaving group over a current commercial benzoylacetylacetonide (12) which bears a heterocyclic leaving group.

The contrast ratios of this set illustrate the superior activity exhibited by the present benzoylacetylacetonides relative to the commercial pivaloylacetylacetonide (13).

15 Table 1

Compound	Dmax	Contrast	Contrast Ratio	D/W Fade 6 weeks
(4)	2.52	2.04	0.69	+0.04
(4) + CZA	2.01	1.41		
(7)	2.41	1.76	0.69	0.00
(7) + CZA	1.92	1.21		
(12)	2.37	1.75	0.70	-0.16
(12) + CZA	1.83	1.22		
(13)	2.04	1.36	0.60	+0.06
(13) + CZA	1.31	0.82		
Footnotes				
1) CZA denotes citrazinic acid. 2) A positive value for dye fade denotes an increase in dye density.				

While dyes formed from couplers (4) and (7) have good fade and contrast ratio, that from coupler (12) shows acceptable Dmax, contrast and reactivity but poor dark/wet fade and the dye from coupler (13) shows acceptable dark/wet fade but low Dmax and contrast.



Example 3

The effect of substituent Z in the general structure being a group or atom other than hydrogen in achieving excellent dark/wet fade data for a dye formed from coupler (6) compared against data for the dye from an analogous coupler (14) in which substituent Z is a hydrogen atom is illustrated in Table 2 below.

Table 2

	X	Y	Z	Dark/wet Fade (6 weeks)
(6)	OC ₁₂ H ₂₅	Cl	CO ₂ Me	0.00
(14)	OC ₁₂ H ₂₅	Cl	H	-0.23

Example 4

In Table 3 the excellent dark/wet fade characteristics exhibited by couplers of the invention (2), (6) and (11) are compared against analogous couplers (12), (15) and (16), respectively, which all bear the same heterocyclic coupling-off group (see structure (12)) instead of the preferred phenolic leaving group borne by couplers of the invention.

Table 3

	X	Y	Z	Dark/wet Fade (6 weeks)
(2)	OMe	Cl	CO ₂ C ₁₂ H ₂₅	0.00
(12)	OMe	Cl	CO ₂ C ₁₂ H ₂₅	-0.16
(9)	OC ₁₂ H ₂₅	Cl	CO ₂ Me	0.00
(15)	OC ₁₂ H ₂₅	Cl	CO ₂ Me	-0.21
(11)	OMe	Cl	SO ₂ NHC ₁₆ H ₃₃	0.07
(16)	OMe	Cl	SO ₂ NHC ₁₆ H ₃₃	-0.22

The superior dark/wet fade properties of dye images formed from the couplers of the invention are clearly demonstrated.

Example 5

Couplers of the invention where Y = Cl e.g. (2) form dyes having acceptable hue characteristics whereas the analogue (17) where Y = OMe does not (Table 4).

Table 4

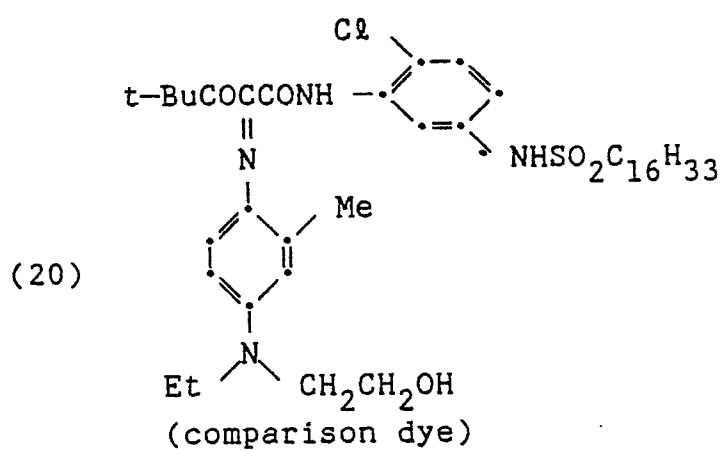
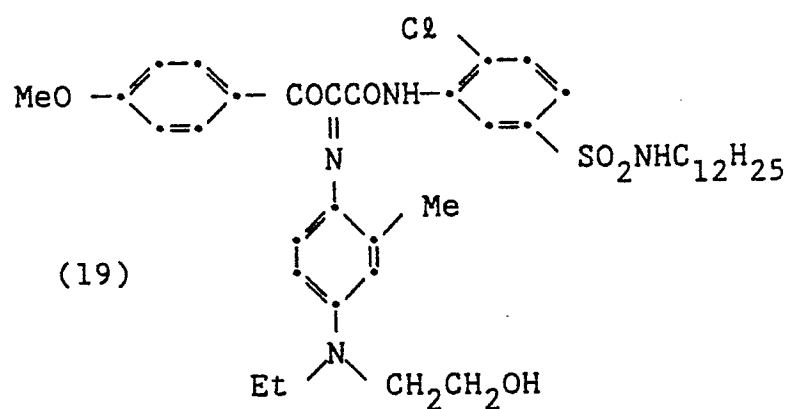
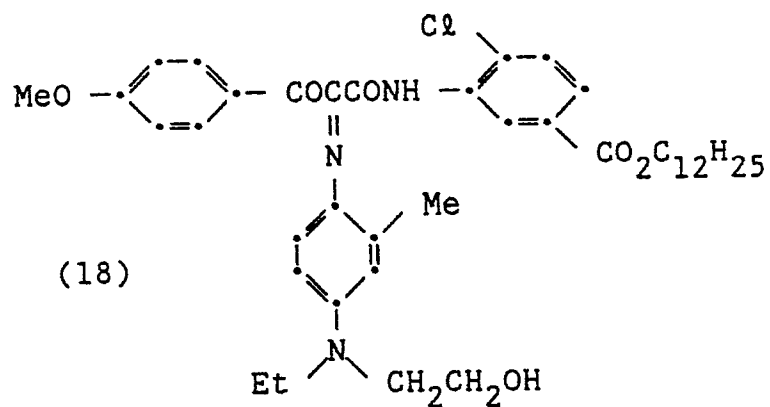
	X	Y	Z	λ_{max}
(2)	OMe	Cl	CO ₂ C ₁₂ H ₂₅	449.5
(17)	OMe	OMe	CO ₂ C ₁₂ H ₂₅	444.0

The extinction coefficients (measured in ethyl acetate solution) of the dyes (18) and (19) derived from benzoylacetanilide couplers of the invention have been shown to be significantly greater than the extinction coefficient of the dye (20) derived from a commercial pivaloylacetanilide coupler (Table 5).

Table 5

Dye	Extinction Coefficient (EtOAc soln.) ($\text{l mol}^{-1}\text{cm}^{-1}$)
(18)	2.01×10^4
(19)	2.30×10^4
(20)	1.73×10^4

The dyes have the following structures:



The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

5

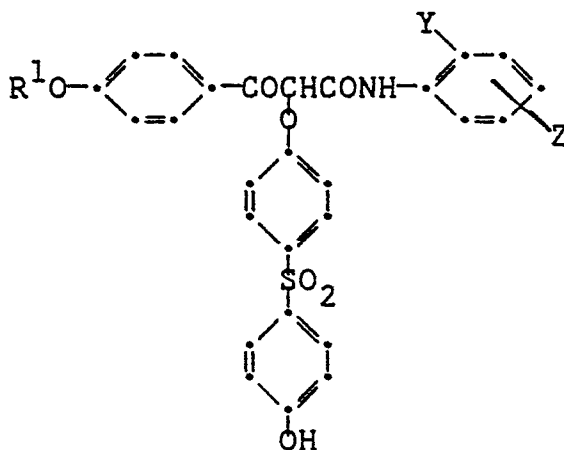
Claims

1. A colour photographic silver halide element comprising a support bearing at least one photographic silver halide emulsion layer and a non-diffusible yellow dye-forming para-R-oxybenzoylacetanilide coupler that has a combination of (a) a para-hydroxyphenylsulphonylphenoxy coupling-off group in the coupling-position, (b) a chloro or trifluoromethyl group in the ortho position on the anilide moiety, and (c) a group on the anilide moiety that is selected from (i) a sulphamoyl group, (ii) an aliphatic hydrocarbon group that is bonded to the anilide moiety directly or through a linking group that is a carbamoyl (-CONH-), oxycarbonyl (-CO-O-), carbonyloxy (-O-CO-), sulphonate (-O-SO₂-), sulphamoyl (-SO₂NH-), phosphate (-O-PO₂-) or alkylene, (iii) chlorine, and (iv) trifluoromethyl; wherein the coupler contains at least one ballast group on at least one of the anilide and para-R-oxybenzoyl moieties; and, wherein R is an unsubstituted or substituted cyclic or non-cyclic aliphatic hydrocarbon group.

15

2. A colour photographic silver halide element as in Claim 1 wherein the non-diffusible yellow dye-forming coupler is represented by the formula:

20



25

30

35

wherein

R¹ is an unsubstituted or substituted cyclic or non-cyclic aliphatic hydrocarbon group;

Y is chloro or trifluoromethyl;

40

Z is halogen, trifluoromethyl, -L-R² or -SO₂NR³R⁴ wherein

R² is an unsubstituted or substituted aliphatic hydrocarbon group,

R³ and R⁴ are individually hydrogen, an unsubstituted or substituted aliphatic hydrocarbon group or together represent the atoms completing a heterocyclic ring;

45

L is a direct bond or a carbamoyl (-CONH-), oxycarbonyl (-CO-O-), carbonyloxy (-O-CO-), sulphonate (-O-SO₂-), sulphamoyl (-SO₂NH-), phosphate (-O-PO₂-), or alkylene group;

at least one of R¹ and Z comprises a ballast group.

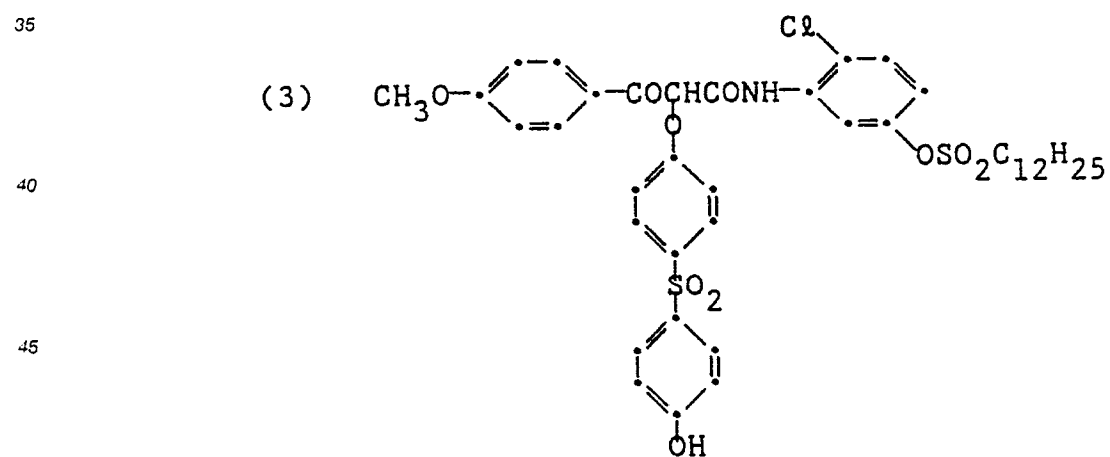
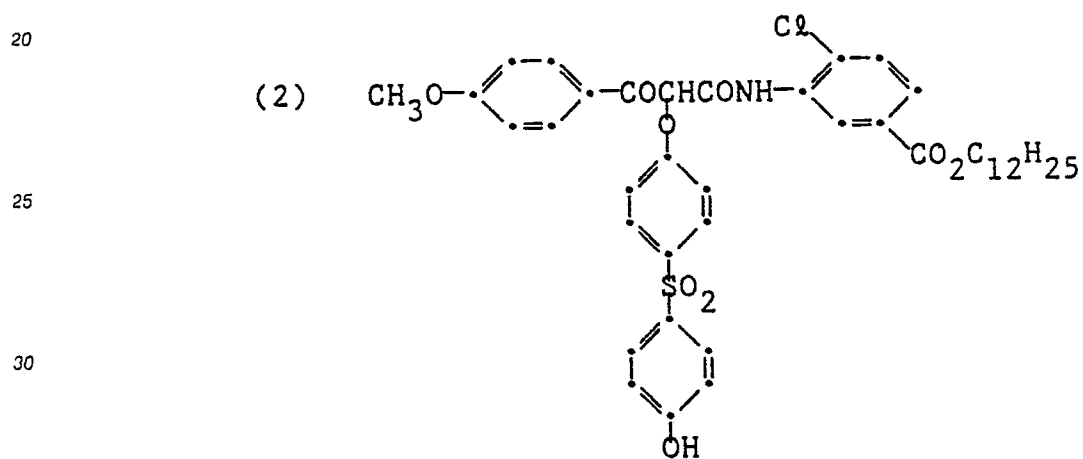
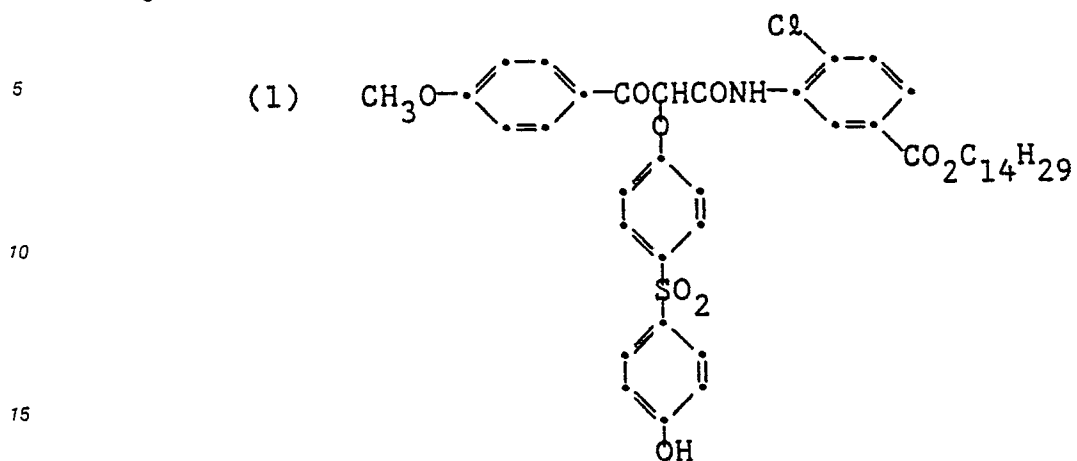
3. A colour photographic silver halide element as in Claim 2 wherein Z comprises a ballast group and R¹ is alkyl comprising 1 to 4 carbon atoms.

50

4. A colour photographic silver halide element as in Claim 2 wherein R¹ comprises a ballast group.

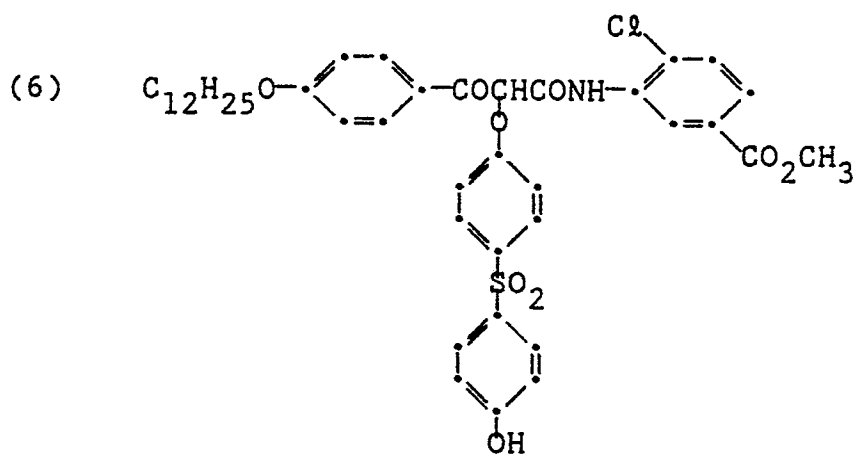
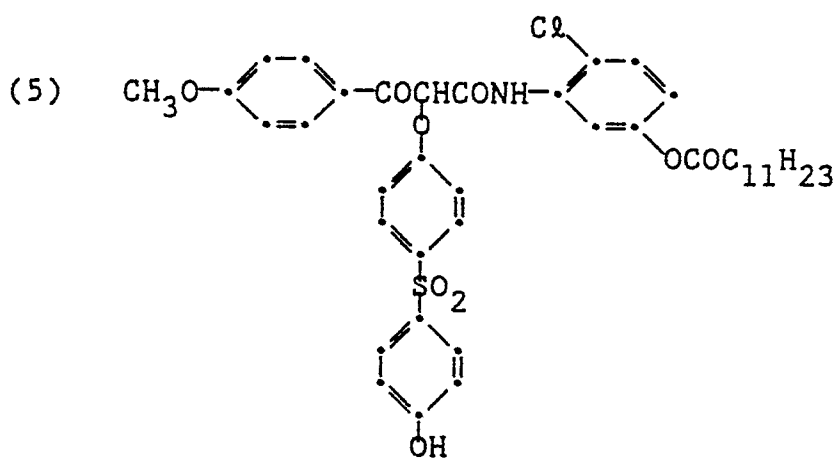
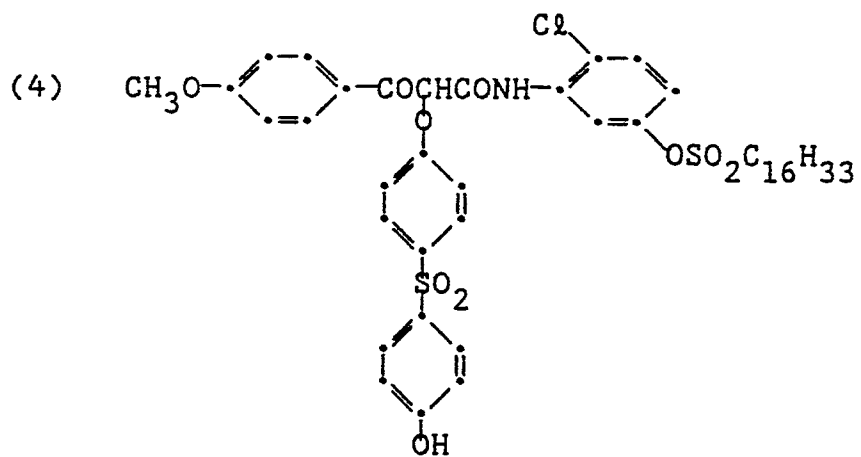
55

5. A colour photographic silver halide element as in Claim 1 wherein the coupler has one of the following structural formulae:



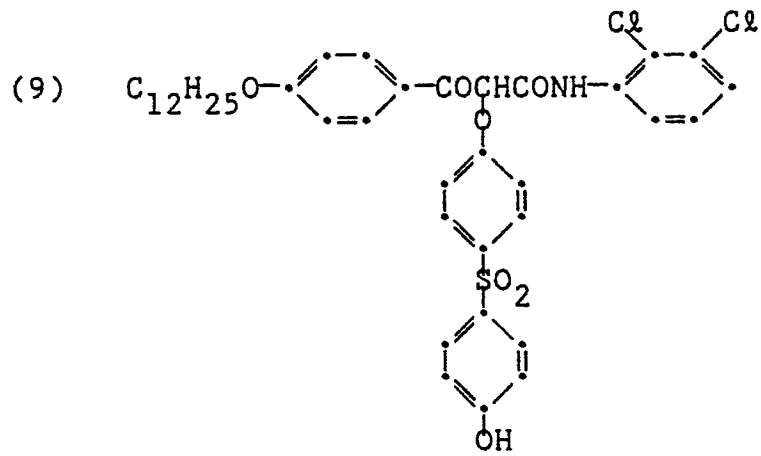
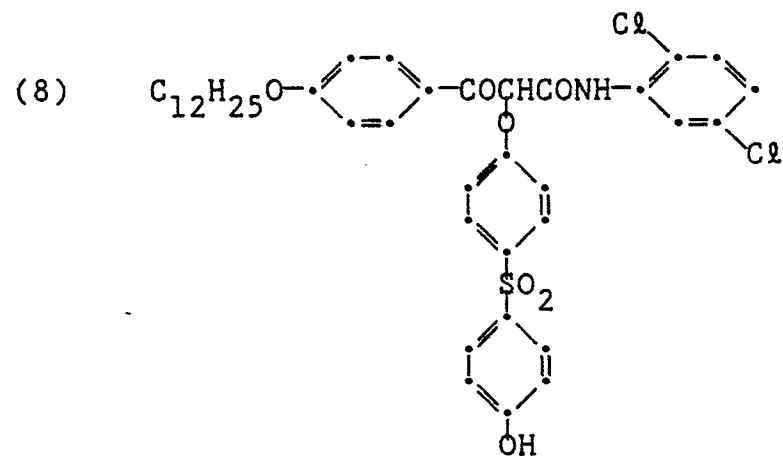
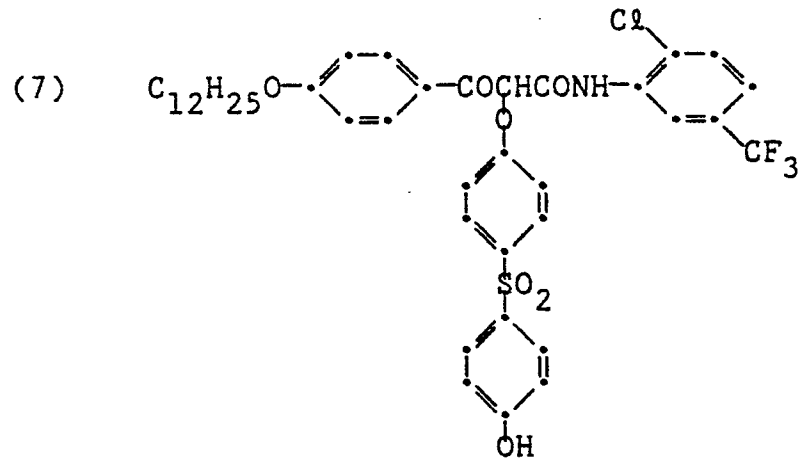
50

55



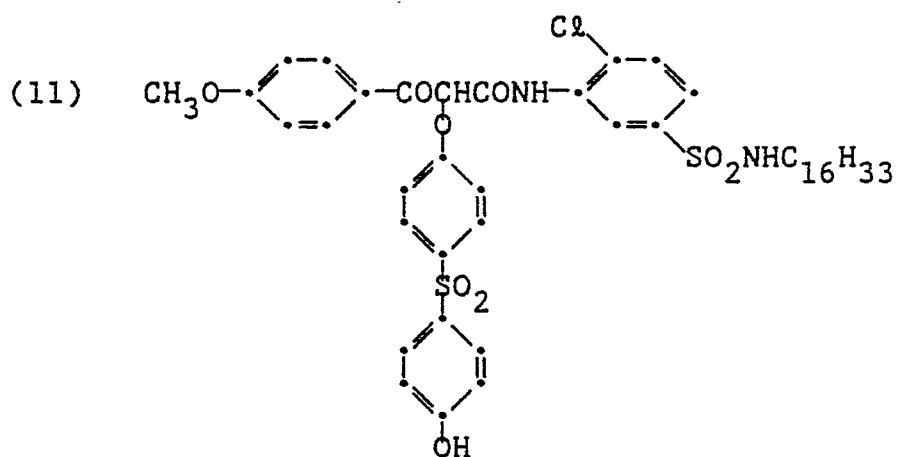
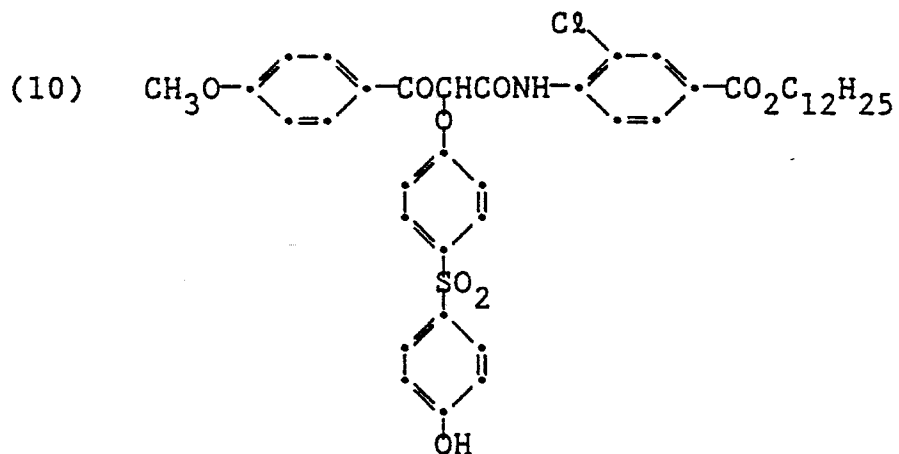
50

55



50

55



6. A colour photographic silver halide element as in any of Claims 1 to 5 comprising a support bearing at least one red-sensitive silver halide emulsion layer having associated therewith a cyan dye-forming material, at least one green-sensitive silver halide emulsion layer having associated therewith a magenta dye-forming material, and at least one blue-sensitive silver halide emulsion layer having associated therewith said non-diffusible yellow dye-forming coupler.

7. A process of forming a dye image in an exposed colour photographic silver halide element as defined in any of Claims 1 to 6 comprising developing the colour photographic silver halide element in a colour photographic developer.

8. A yellow dye-forming benzoylacetylacetanilide photographic colour coupler as defined in any of claims 1-5.

45

50

55

FIGURE 1
DYE DENSITY YIELD CURVES

