

[54] **SILVER HALIDE EMULSION CONTAINING
ACYLAMIDOPHENOL PHOTOGRAPHIC
COUPLERS**

[75] Inventors: **Philip T. Lau; Ilmari F. Salminen;
Leo E. Beavers**, all of Rochester,
N.Y.

[73] Assignee: **Eastman Kodak Company**,
Rochester, N.Y.

[22] Filed: **Oct. 1, 1973**

[21] Appl. No.: **402,566**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 213,812, Dec. 29,
1971, abandoned.

[52] U.S. Cl. **96/55; 96/74; 96/100**

[51] Int. Cl. **G03c 7/00; G03c 1/40**

[58] Field of Search..... **96/100, 74, 55**

[56] **References Cited**

UNITED STATES PATENTS

2,197,311 4/1940 Merckx et al..... 96/100

2,330,291	9/1943	Kirby	96/100
2,357,394	9/1944	Frohlich et al.	96/100
3,519,429	7/1970	Lestina	96/100
3,758,308	9/1973	Beavers et al.	96/100
3,779,763	12/1973	Lau.....	96/100

Primary Examiner—J. Travis Brown
Attorney, Agent, or Firm—J. T. Lewis

[57] **ABSTRACT**

Cyan dye-forming phenolic or α -naphtholic coupler compounds having a p-hydroxy-alkylphenoxy-alkylcarbonamido substituent in a non-coupling ring position thereon; a silver halide emulsion containing at least one of such coupler; a color photographic element comprising a support and at least one silver halide emulsion containing the above coupler applied thereto; and a method for preparing a cyan photographic dye by reacting one of the above defined couplers with oxidized color developing agent.

41 Claims, No Drawings

SILVER HALIDE EMULSION CONTAINING ACYLAMIDOPHENOL PHOTOGRAPHIC COUPLERS

This application is a continuation-in-part of copending U.S. patent application Ser. No. 213,812, filed Dec. 29, 1971 and now abandoned.

This invention relates to a novel group of phenolic and α -naphtholic coupler compounds. More specifically, the present invention relates to a group of new color photographic couplers which are usefully incorporated into a photographic element or emulsion layer thereof to obtain cyan dye images having increased D max values.

Colored images are customarily obtained in the photographic art by coupling the development product (i.e., oxidized aromatic primary amino developing agents) with a color-forming or coupling compound in para position. The subtractive process of color formation is ordinarily employed in multicolor photoelements and the resulting image dyes are usually cyan, magenta or yellow dyes which are formed in silver halide layers sensitive to complementary light.

A majority of such color photographic couplers are known and described as four-equivalent couplers, which are characterized in requiring the development of four light-exposed silver halide molecules in order to ultimately produce one molecule of dye. Also widely used, are so-called two equivalent couplers in which a non-chromophoric coupling-off group is substituted in coupling position. Couplers of this type are functionally characterized by requiring the development of two exposed silver halide molecules during development to obtain one molecule of dye. Known two-equivalent couplers have coupling-off groups such as halo, alkoxy, acyloxy, aryloxy, arylthio, cyclooxy or thiocyanogroups substituted in p-position in the case of phenolic or α -naphtholic couplers. Additional couplers of this type are demonstrated, for instance, in U.S. Pat. Nos. 3,458,315 and 3,227,155.

Suitability of an organic compound as a color photographic coupler, however, depends upon more than general reactivity. Consideration is also given to the color balance, contrast, grain size and general sharpness of the dye images obtained. A coupler should be stable and produce stable photographic dyes having precise spectral absorption characteristics when reacted with oxidized developer.

Successful color photographic couplers also possess a number of important ancillary characteristics. It is de-

emulsion viscosity, adhesion characteristics, or the unity of an emulsion layer during modern high-speed multilayer application onto a film backing.

Undesirable changes may also be caused by additives such as wetting agents and color components, and these changes can directly affect the coating characteristics of a photographic emulsion. This problem is suggested, for instance, on page 250 of the text by Zelikman and Levi, entitled "Making and Coating Photographic Emulsions;" The Focal Press (1964).

Including antihalation and gelatin interlayers, up to eight or more separate layers may be applied to a film base to obtain a modern color photographic element (ref. Kirk-Othmer, Vol. 5, pages 812-845, Encyclopedia of Chemical Technology (1950). For this reason any induced changes in the physical properties of an emulsion coating may well be as important as coupler reactivity with oxidized developer.

The above-listed characteristics are not necessarily complete and are often incompatible since the color photographic technology of recent years is complex and functionally interrelated. In fact, some coupler characteristics considered advantageous in earlier photographic art may now even be considered undesirable.

For the above reasons, it is necessary and desirable to discover new coupler compounds.

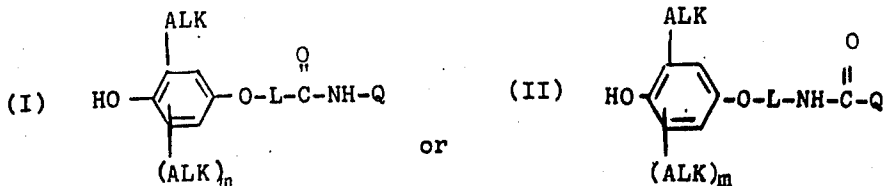
It is an object of this invention to obtain a new class of cyan dye-forming couplers inclusive of the 2- and 4-equivalent type suitable for modern color photographic purposes.

It is a further object of this invention to provide new coupler compounds which will readily and efficiently react with oxidized color developer to obtain cyan dye images having substantially improved Dmax values.

It is a still further object of this invention to obtain novel photographic elements and photographic emulsions utilizing couplers of this invention for color photographic purposes.

These and other objects of the invention are obtained by utilizing a phenolic or α -naphtholic cyan dye-forming coupler compound having a p-hydroxy-m-alkylphenoxy-alkylcarbonamido substituent group substituted on a ring position of the phenolic or α -naphtholic nucleus of the coupler. The alkylcarbonamido moiety in the above substituent group is replaced with an alkylcarbonyl moiety when the substituent group is attached to an α -naphthol coupler ring in the No. 2 position.

Particularly useful couplers of the invention have the formulae



sirable, for instance, for a non-diffusible coupler to be soluble in minimal amounts of high-boiling coupler solvent in order to obtain thinner and more durable photographic elements. It is also important that non-diffusible couplers be capable of precise incorporation into a silver halide emulsion with no adverse effects on

wherein

m is 0-3;

L is a divalent alkylene group, such as an alkylene group having 1-20 carbon atoms, including a branched chain alkylene group;

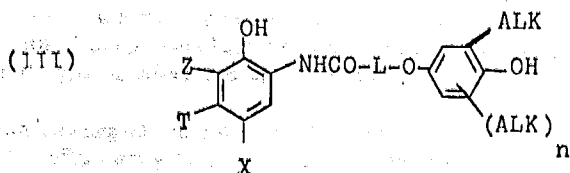
ALK is an alkyl group of 1-15 carbon atoms, particu-

larly an alkyl group of 1-8 carbon atoms, such group including a branched alkyl such as a secondary or tertiary alkyl group of 4-8 carbon atoms, and exemplified by methyl, isopropyl, tert. butyl and pentadecyl;

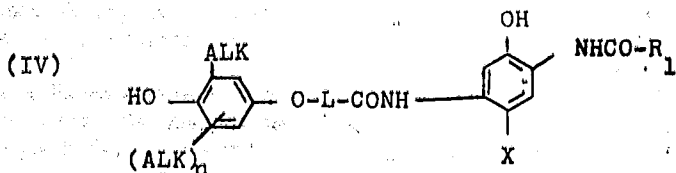
Q is a phenolic- or α naphtholic-cyan dye-forming coupler moiety having 1-3 of the above-described p-hydroxy-arylphenoxy-alkylcarbonamido or p-hydroxy-dialkylphenoxy-alkylcarbonamido substituent groups attached on a ring position of the phenolic or α -naphtholic nucleus of the coupler, the alkylcarbonamido moiety of the substituent group being replaced as above with an alkylcarbonyl moiety when the substituent group is attached to an α -naphtholic coupler in the No. 2 ring position.

Suitable dye-forming coupler moieties of the above-defined types (i.e. Q) are exemplified, for instance in the U.S. Pat. Nos. 2,275,292; 2,367,531; 2,423,730; 2,474,293; 2,706,684; 2,725,292; 2,772,161; 2,772,162; 2,895,826; 2,908,573; 2,920,961; 2,976,146; 3,002,836; 3,034,892; 3,227,550; 3,227,554; 3,265,506; 3,311,476; 3,419,390; 3,458,315 and 3,476,563.

Illustrative compounds within the scope of the present invention are more specifically described in formulae



and



wherein

L is defined as above, and is preferably a branched divalent alkylene group of 10-20 carbon atoms; ALK represents an alkyl group as defined above; n is 0-1;

X is defined as (1) hydrogen; (2) a halo group such as fluoro or chloro; (3) an aryloxy group such as a phenoxy group; (4) a thioaryl group such as a phenylthio or a naphthylthio group; (5) an alkoxy group of 1-20 carbon atoms inclusive of cycloalkoxy of 4-8 carbon atoms exemplified by methoxy, isopropoxy, octyloxy, eicosyloxy, and cyclohexyloxy groups; (6) a thioalkyl group of 1-20 carbon atoms inclusive of cycloalkylthio; (7) an acyloxy group of the formula



wherein R_2 is an alkyl group of 1-20 carbons or an aryl group such as a phenyl or a naphthyl group inclusive of halo-, alkoxy- or alkyl-substituted aryl groups; (8) a thiocyanate group; or (9) a heterocyclic radical having a 5-6 membered heterocyclic nucleus with at least one nitrogen, oxygen, or sulfur atom, the heterocyclic nucleus being attached to the ring by a bridging -O- or -S- group.

T is (1) a halo group, such as a chloro or fluoro group; (2) an alkyl group inclusive of an alkyl group of 1-20 carbon atoms such as methyl, isopropyl and eicosyl; or (3) an alkoxy group inclusive of an alkoxy group of 1-20 carbon atoms such as methoxy, isopropoxy, or eicosyloxy.

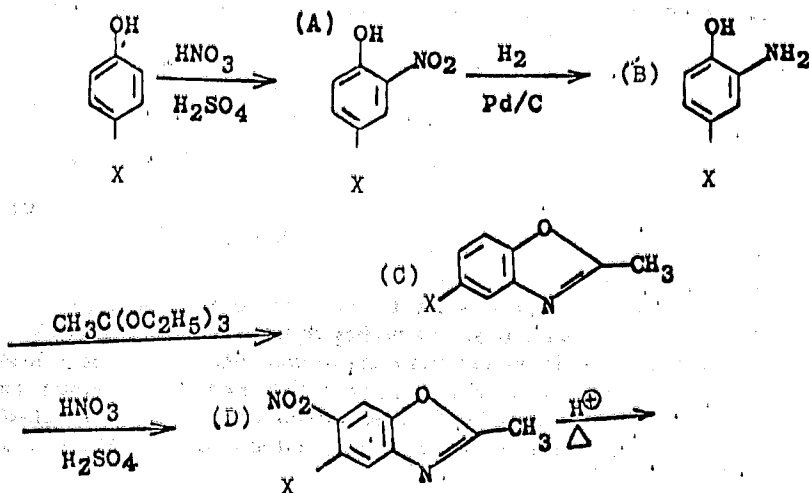
Z is individually defined as in T.

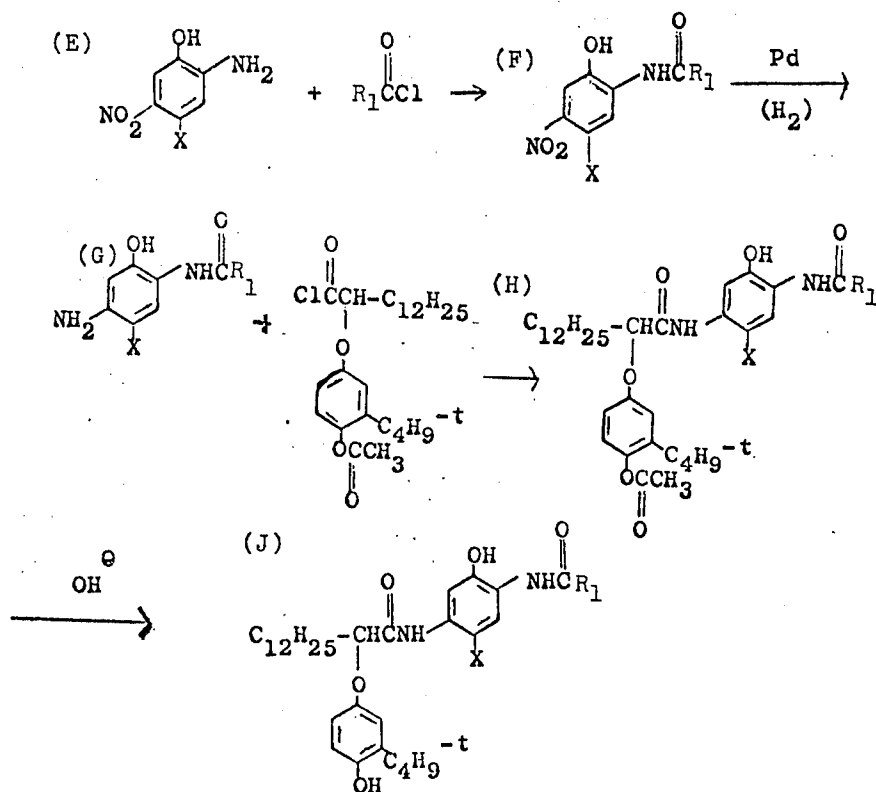
R_1 is (1) an aryl group such as a phenyl or a naphthyl group exemplified by a fluorophenyl such as p-fluorophenyl or pentafluorophenyl, as an alkylphenyl such as p-methylphenyl or trifluoromethylphenyl; or (2) -NH- R_3 wherein R_3 is hydrogen, an alkyl group of 1-20 carbon atoms, or an aryl group such as a phenyl or a naphthyl group.

Coupler compounds of the invention can be pre-

45

pared, for example, from the corresponding p-substituted phenol by nitration and hydrogenation to obtain an o-amino m-nitro precursor which is then reacted with an acid chloride. A suitable reaction mechanism is described as follows:





30

wherein X and R_1 are defined as above.

Where the o-substituent radical of the coupler moiety in formula IV is a ureido group such as a phenyl ureido, steps (A) through (E) may be followed by reac-

tion with an aryl isocyanate to obtain a corresponding o-ureido substituted intermediate.

Compounds within the scope of the present invention are exemplified, for instance, in Tables I, IA, and II below with reference to formulae V and III.

40

(V)

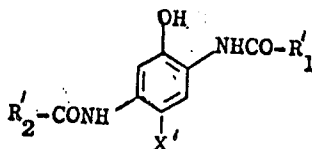


TABLE I

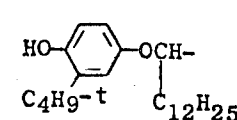
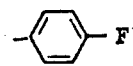
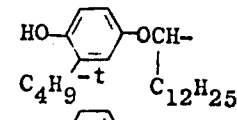
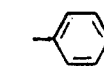
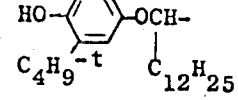
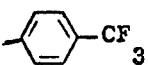
Coupler No.	R_2'	R_1'	X'
1			H
2			H
3			H

TABLE I - Continued

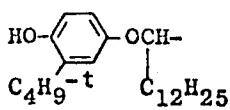
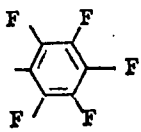
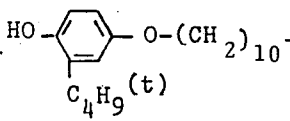
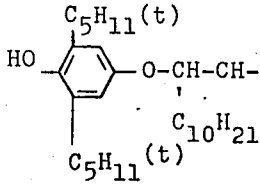
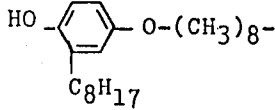
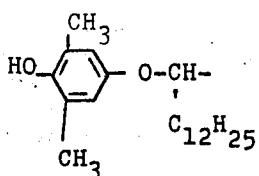
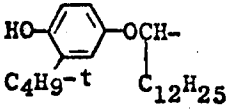
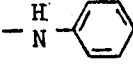
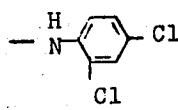
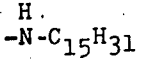
Coupler No.	R ₂ '	R ₁ '	X'
4			F
5		"	F
6		"	F
7		"	H
8		"	Cl
9			H
10	"	"	F
11	"	"	Cl
12	"		H
13	"	"	F
14	"	"	Cl
15	"		H

TABLE I - Continued

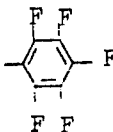
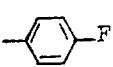
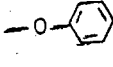
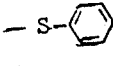
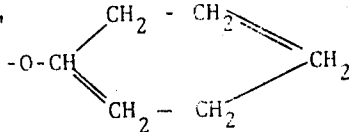
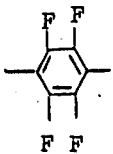
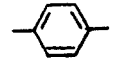
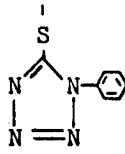

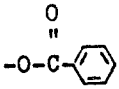
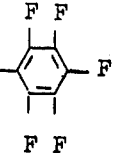
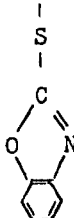
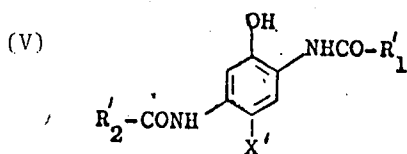
Coupler No.	R' ₂	R' ₁	X'
16	"		-O-C ₈ H ₁₅
17	"		
18	"	"	
19	"	"	
20	"		-S-CN
21	"		
22	"	"	-NH-SO ₂ - 
23	"	"	-NH-SO ₂ -CH ₃
24	"	"	
25	"		

Table I—Continued

Coupler No.	R ₂ '	R ₁ '	X'
26	"	"	

Table IA



Coupler No.	R ₂ '	R ₁ '	X'	m.p.
27			H	70-75°C
28	"		H	145-146°C
29	"		Cl	
30	"		H	128-130°C
31	"	"	F	163-164°C
32	"	"	Cl	165-167°C
33	" -NH-		H	75-85°C
34	" -NH-		F	81-83°C
35	" -NH-		H	121-123°C
36	" -NH-		H	104-106°C
37	" -NH-		-Cl	146-148°C
38	" -NH-		-Cl	103-106°C
39	" -NH-		H	70-80°C

(III)

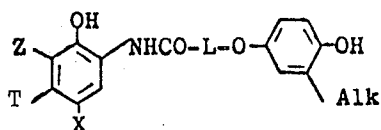

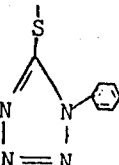


TABLE II

Coupler No.	X	T	Z	L	ALK
1	Cl-	CH ₃ -	Cl-	-CH- C ₁₂ H ₂₅	(t)C ₄ H ₉ -
2	"	C ₈ H ₁₇ -O-	Cl-	"	"
3	"	Cl-	CH ₃ -O-	"	"
4	"	CH ₃ (CH ₂) ₆ CH ₂ -	Cl-	(CH ₂) ₁₅	"
5	"	C ₁₈ H ₅₁ -	CH ₃ -	-CH- C ₁₂ H ₂₅	"
6	"	C ₁₈ H ₃₇ -	(t)C ₅ H ₁₁ -	"	"
7	-O-CH ₃	-O-C ₂ H ₅	Cl-	-CH- C ₁₂ H ₂₅	(t)C ₅ H ₁₁
8	-O- 	C ₄ H ₉ -	"	"	"
9		C ₄ H ₉ -O	CH ₃ -O-	-CH-CH ₂ -CH ₃ - C ₁₁ H ₂₃	
10	H	CH ₃ O	Cl-	"	(t)C ₄ H ₉

60

The ballasted non-diffusible type cyan couplers of the present invention are usefully incorporated into light-sensitive photographic silver halide emulsion layers and applied onto an emulsion support or film base in a single- or multi-layer color photographic material by known methods (example: the solvent and Fisher fat-tail methods) as described, for instance, in Mannes

et al. in U.S. Pat. No. 2,304,939-40 and Jelley et al. in U.S. Pat. No. 2,322,027, in which high-boiling organic solvents are used to dissolve the coupler. Further useful procedures are described, for instance, in Vittum et al. U.S. Pat. No. 2,801,170; Fierke et al. U.S. Pat. No. 2,801,171 (July 1957); and Julian U.S. Pat. No. 2,479,360 (August 1960), whereby low-boiling or

water-soluble organic solvents are used with or in place of a high-boiling solvent. In the case of multi-layer photographic materials or elements, the non-diffusible coupler compounds are generally incorporated into the red-sensitive silver halide emulsion layer and preferably utilize minimal amounts of high-boiling solvents.

Generally speaking, a useful coupler concentration will vary from about 25–200 mg/ft² of coated material, a range of 30–50 mg/ft² being generally satisfactory for use in photographic paper, with overlapping and higher concentrations found useful in color photographic films.

A variety of color coupler-containing photographic materials and elements are obtainable utilizing the above family of cyan dye-producing couplers. Generally speaking, however, such photographic materials and elements will comprise the following main components:

(A) A support layer such as cellulose nitrate film, cellulose acetate film, polyvinylacetal film, polystyrene film, poly (ethylene terephthalate) film, polyethylene film, polypropylene film and related films of resinous materials as well as paper, polyethylene coated paper, glass, and others.

(B) An antihalation layer such as a dye-containing gelatin, starch, etc., as described, for instance, in Glafkides "Photographic Chemistry," Volume 1, pages 470–471, Arrowsmith Ltd. 1958;

(C) One or more, preferably three light-sensitive and differently-sensitized color coupler-containing silver halide emulsion layers coated onto the support, optionally with one or more gelatin spacer layers between. The support is conveniently coated in succession with a red-sensitive layer containing one or more of the above-defined class of cyan-dye-producing coupler, a green-sensitive layer and a blue-sensitive layer, either with or without a Carey-Lea filter layer between the blue- and green-sensitive layers. The three differently color-sensitized layers can also be arranged in any other order over one another that is desirable, with the exception that a Carey-Lea filter layer cannot be placed over a blue-sensitive layer.

The light-sensitive silver halide emulsions can include coarse, regular, or fine grain silver halide crystals or mixtures thereof such as silver chloride, silver bromide, silver bromiodide, silver chlorobromide, silver chloriodide, silver chlorobromiodide and mixtures thereof; such emulsions are described, for instance, in "The Photographic Journal," Volume LXXIX, May 1939, pages 330–338; "Journal of Photographic Science," Volume 12, No. 5, Sept/Oct 1964, pages 242–251, and also in U.S. Pat. Nos. 2,184,013; 2,456,953; 2,541,472; 2,563,785; 3,367,778 and 3,501,307. Such silver halide emulsions typically are gelatin emulsions although other hydrophilic colloids can be used in accordance with usual practice.

(D) One or more gelatin or hydrophilic spacer layers between the light-sensitive emulsion layers or the emulsion layers and Carey-Lea filter layer as above described; and

(E) A protective water-permeable overcoat layer, such as gelatin or other hydrophilic colloids. The overcoat may conveniently contain aldehyde scavenger such as described, for instance, in U.S. Pat. Nos. 3,236,652; 3,287,135; 3,220,839; 2,403,927; and British Pat. No. 623,448, and other ingredients such as buffering agents (e.g., an acidic or basic material); and

ultra-violet light absorbers such as 2,2'-di-hydroxy 4,4'-dimethoxybenzophenone, 4,4'-dimethoxybenzophenone; 4,4'-diazidostilbene-2,2'-disulfonic acid sodium salt, and sodium-(α -phenylhydrazone).

In addition, photographic materials and elements utilizing the present cyan-dye-forming couplers can usefully contain brighteners such as stilbenes, triazines, oxazoles and coumarins as described, for instance, in German Pat. Nos. 972,067; 115,024; and in U.S. Pat. No. 2,933,390; they may also contain spectral sensitizing dyes to impart additional sensitivity to light-sensitive silver halide emulsion layers.

This invention is further described, although not limited, by the following examples. Examples V–VII include couplers not of the invention for purposes of comparison.

EXAMPLE I

-Acylamido-acylamido-5-aminophenol

A solution of 0.1 mole of 2-amino-5-nitrophenol and 0.2 mole of quinoline in 300 ml of dioxane is admixed with a solution of 0.1 mole of acid chloride in 50 ml of dioxane. The resulting reaction mixture is stirred at room temperature for 1 hour, then poured into 1 liter of ice water containing 10–15 ml of concentrated hydrochloric acid. The solid product then is collected, washed with water and recrystallized from aqueous ethanol solvent. .05 Mole 2-acylamido-5-nitrophenol intermediate product is dissolved into 200 ml of dioxane containing a teaspoonful of palladium-on-charcoal. This mixture is then placed in a Parr bottle and reduced under hydrogen (40 psi) at 40°C. After about 30 min. the reaction mixture is filtered; a solution of the 2-acylamido-5-amino product (ref. pg. 6 intermediate G) can be used directly for preparation of desired couplers.

EXAMPLE II

Coupler 2 of Table I

200 ml of a dioxane containing 11.4 g (0.05 mole) of 2-benzamido-5-aminophenol prepared by the general procedure described above on page 6 and in Example I is admixed with 13 g (0.1 mole) of quinoline and 22.7 g (0.05 mole) of (3-tert-butyl-4-acetoxyphenoxy) tetradecanoyl chloride. The mixture is stirred at room temperature for 2 hours, then poured onto 500 ml of ice-water containing 10–15 ml of concentrated HCl. The resulting resinous solid is then collected, triturated with petroleum ether and recrystallized from cyclohexane; (m.p. 119°–120°C). The above acetoxy intermediate is then dissolved in 200 ml of ethanol and treated with 50 ml of 2 percent alcoholic potassium hydroxide. After stirring for 0.5 hour, the mixture is pured onto 500 ml of ice-water and then acidified with concentrated hydrochloric acid. The resulting viscous oil is separated out, and triturated with petroleum ether until it solidifies. Upon recrystallization from CHCl₃-petroleum ether there is obtained a product identified as coupler No. 2 (m.p. 133°–135°C).

EXAMPLE III

Couplers 1, 3 and 4 of Table I

Couplers 1, 3 and 4 are prepared as in Example II from the corresponding 2-(4-fluoro-benzamido)-5-aminophenol, 2-(4-trifluoromethylbenzamido)-5-aminophenol, and 2-pentafluorobenzamido-4-fluoro-5-

aminophenol respectively. The couplers have melting points of 84°-86°, 147°-149°, and 118°-119°C.

EXAMPLE IV

Coupler 1 of Table II

To a solution of 5.8 g (0.03 mole) of 2-amino-4,6-dichloro-5-methyl phenol in 500 ml of acetic acid is added with stirring 2.5 g of sodium acetate and 13.6 g (0.03 mole) of (3-tert-butyl-4-acetoxyphenoxy) tetradecanoyl chloride. The mixture is stirred for 1 hour, poured onto 1 liter of ice-water, and the resulting gummy solid collected and dissolved in diethyl ether. After drying over Na₂SO₄ the diethyl ether solvent is removed under reduced pressure and triturated with petroleum ether until it solidifies. The solid obtained is then dissolved in 300ml of ethanol and treated with 50ml of 2 percent alcoholic potassium hydroxide. After stirring under a blanket of nitrogen for 0.5 hour, the mixture is drowned in ice-water and strongly acidified with HCl. The resulting gelatinous solid is collected,

trituated with petroleum ether, and recrystallized from acetonitrile to obtain 8.5 g of product having a m.p. of 81°-82°C.

EXAMPLE V

Related Couplers For Comparison, See Table III

Using the general reaction mechanism suggested on page 6 and demonstrated in Example II and otherwise disclosed in U.S. Pat. Nos. 2,322,027 and 2,801,171, five 2,5-disubstituted phenolic compounds are prepared from phenol, *p*-fluorophenol or *o*,*p*-dichloro-*m*-methyl phenol to obtain coupler products structurally distinguishable from the above-described compounds within the present invention. The couplers obtained are identified as I-VII and found to have melting points at 166°-167°C., 155°-156°C., 184°-185°C., 133°-134°C., 194°-195°C., 112°-113°C., and 122°-123°C.. These compounds are structurally identified, below with respect to formula V and Table III.

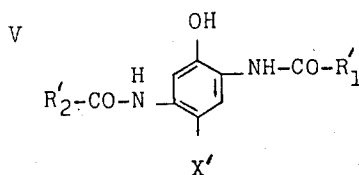
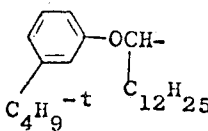
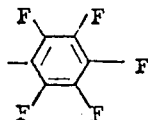


TABLE III

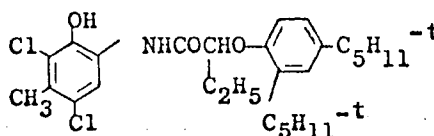
Compound No.	R' ₂	R' ₁	X'
I			H
II			H
III			H
IV			F
V			F

TABLE III—Continued

Compound No.	R ₂ '	R ₁ '	X'
VI			F

and as

VII



EXAMPLE VI

Twenty-four photographic test film strips respectively as 1A, 1B . . . 5B, 1A, 1B . . . VIIB, are prepared by coating a transparent cellulose acetate support with light-sensitive gelatinous silver bromo-iodide emulsion coating to obtain 136 mg silver/ft², 450 mg gelatin/ft², and 78 mg/ft² of one of coupler 1-5 and I-VII, and A and B strips containing equal molar amounts of the same coupler dissolved into 39 mg/ft² of di-n-butyl phthalate with B-ethoxy ethyl acetate as auxiliary solvent, then dispersed into an aqueous gelatin solution, etc., in the manner described, for instance, in Example 1 of U.S. Pat. No. 2,949,360. The ratio of coupler solvent to coupler for this purpose is 1:½. The coated strips are sensitometrically exposed through a graduated-density test object and processed in the usual manner at 20°C., one duplicate being treated with Color Developing Solutions A and B, as hereinafter described. The strips are then stop-fixed, washed, silver bleached, washed, fixed, washed, stabilized and dried in the usual manner, thereafter tested as explained below, and evaluated to determine their maximum image dye density, and light and heat fading characteristics. The results set forth in Table IV.

Color Developing Solution A

H ₂ O	800	ml
Sodium hexameta phosphate	0.5	g
Na ₂ SO ₃	2.0	g
4-Amino-3-methyl-N,N-diethyl aniline hydrochloride	2.0	g
Na ₂ CO ₃ · H ₂ O	20.0	g
50% NaBr Solution	3.46	ml
H ₂ O to	1	liter
(pH 10.86)		

Color Developing Solution B

H ₂ O	800	ml
Benzyl alcohol	4.0	ml
Sodium hexameta phosphate	0.5	g
Na ₂ SO ₃	2.0	g
40% NaOH solution	0.4	ml

-Continued

Color Developing Solution B

4-Amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)-ethylaniline sesquisulfate hydrate	5.0	g
50% NaBr solution	1.72	ml
H ₂ O to	1	liter
(pH 10.75)		

Light Fading Tests

The extent to which the image dyes fade under the influence of light is determined by subjecting processed coatings to a simulated 21-day north skylight exposure (SANS) and determining the resulting decrease in dye density in an area having an initial dye density of approximately 1.2. The resulting "Light Fade" is recorded as density units.

The extent to which unreacted coupler causes unwanted stain under the influence of light is determined by exposing processed coatings to SANS, as above described, and recording the resulting increase in density to blue light (420 nm) in a D min area of the coating. This increase is termed "PrintOut" (PO) and is recorded in terms of percent density increase.

Heat Fading Tests

The extent to which the image dyes fade under the influence of heat and humidity is determined by subjecting coatings to a temperature of 60°C at a relative humidity of 70 percent for 1 week. The resulting decrease in image dye density is termed "Heat Fade" (H.F.) and is measured in terms of decrease in dye density in density units.

The effect of heat on unreacted coupler is determined by subjecting coatings to the above heat and humidity conditions, and determining the increase in density (i.e. yellowing) in a D min area (420 nm) of the coating, and recording this in terms of per cent density increase.

TABLE IV

Coupler No.	Dev.	D_{max}	λ_{max}	LF	% Po	HF	% Yell.	Coupler M.P. °C.
1	A	3.68	665	0.07	0	0	8	84-86
	B	3.19	651	0.07	1	+0.03	9	
2	A	2.85	662	0.08	1	0	3	133-135
	B	3.00	649	0.09	2	0	4	
3	A	3.13	662	0.09	1	+0.02	5	147-149
	B	2.96	649	0.06	1	+0.04	6	
4	A	3.91	667	0.04	2	+0.02	7	118-119
	B	3.52	649	0.05	3	+0.02	7	
5	A	3.63	672	0.05	0	+0.15	4	81-82
	B	3.48	651	0.06	1	+0.10	7	
I	A	2.74	663	0.14	1	+0.03	6	166-167
	B	2.32	653	0.18	2	+0.03	6	
II	A	2.50	668	0.13	1	+0.01	1	155-156
	B	2.00	657	0.12	0	0	1	
III	A	2.81	662	0.07	1	0	3	184-185
	B	2.30	652	0.12	0	0	4	
IV	A	3.20	654	0.08	0	+0.03	5	133-134
	B	2.90	664	0.07	0	+0.02	5	
V	A	3.40	669	0.09	2	+0.02	7	194-195
	B	3.22	654	0.08	3	+0.02	8	
VI	A	3.80	661	0.10	2	+0.03	7	112-113
	B	3.15	646	0.07	2	+0.03	7	
VII	A	3.45	664	0.03	0.5	+0.06	5	122-123
	B	3.27	655	0.03	0.5	+0.04	7	

25

Based on the above data, it is apparent that a substantially higher D_{max} value is obtained when using the coupler compounds of the present invention (Arabic number) with analogous compounds outside of the present invention (Roman numerals) without substantial disadvantage with respect to other important coupler characteristics.

EXAMPLE VII

The experiment described in Example VI is repeated with the exception that the coupler used is initially dissolved in the low-boiling removable auxiliary solvents without using the retained higher boiling coupler solvent (i.e., the di-n-butyl phthalate).

After exposure, development and testing as in Example VI, the results are evaluated and reported in Table V.

Couplers 1-4 of the invention have D_{max} cyan dye image values which are photographically satisfactory and possess the additional advantages associated with systems having no retained high boiling coupler solvent (i.e. increased durability and better image resolution).

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

We claim:

1. A photographic silver halide emulsion containing as color photographic coupler a phenolic cyan dye-forming coupler compound having a p-hydroxy-m-alkylphenoxyalkylcarbonamido group substituted on a non-coupling ring position of the phenolic nucleus of the coupler.

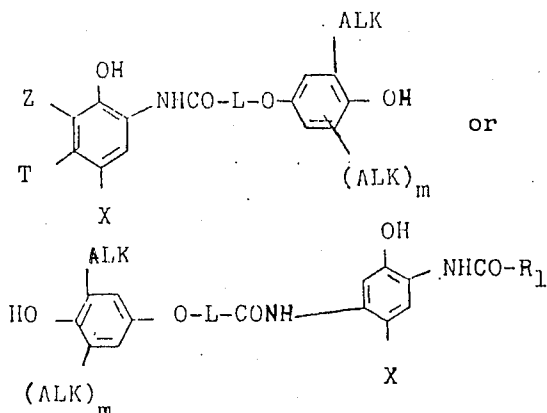
50

TABLE V

Coupler No.	Dev.	λ_{max}	LF	% PO	HF	% Yell.	Coupler M.P. °C.	
1	A	2.36	673	0.34	1	0	7	84-86
	B	2.65	655	0.30	0	+0.02	9	
2	A	2.17	673	0.44	1	0	2	133-135
	B	2.46	653	0.35	2	0	3	
3	A	1.54	659	0.35	0	0	4	147-149
	B	2.04	655	0.31	1	+0.03	7	
4	A	1.82	680	0.17	4	+0.06	10	118-119
	B	2.03	657	0.12	7	+0.05	10	
I	A	.98	665	0.25	3	+0.05	6	166-167
	B	1.49	651	0.30	4	+0.06	7	
II	A	.56						155-156
	B	.85						
III	A	.98	659	0.12	0	+0.06	3	184-185
	B	1.06	650	0.15	0	+0.02	2	
VII	A	1.48	668	0.22	5	+0.07	7	194-195
	B	1.92	651	0.25	7	+0.01	8	

23

2. A photographic silver halide emulsion containing at least one color photographic coupler having the formula



wherein

m is 0-3;

L is a divalent alkylene group;

ALK is an alkyl group of 1-15 carbon atoms;

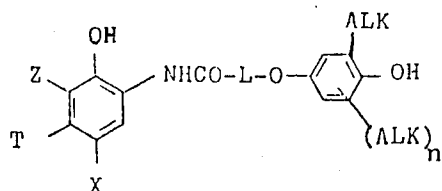
X is (1) hydrogen, (2) a halo group, (3) an aryloxy group, (4) a thioaryl group, (5) an alkoxy group, (6) a thioalkyl group, (7) a thiocyno group, (8) a heterocyclic radical having a 5-6 membered heterocyclic nucleus with at least one nitrogen, oxygen, or sulfur atom, said heterocyclic nucleus being attached to the ring by a bridging $-O-$ or $-S-$ group, or (9) an acyloxy group of the formula R_1-CO-O wherein R_2 is an alkyl group of 1-29 carbon atoms or an aryl group;

T is (1) a halo group, (2) an alkyl group or (3) an alkoxy group;

Z is individually defined as in T; and

R_1 is (1) an aryl group of (2) $-NH-R_3$, in which R_3 is hydrogen, an alkyl group of 1-20 carbon atoms or an aryl group.

3. A photographic silver halide emulsion containing a color photographic coupler having the formula



wherein

n is 0-1

L is a divalent alkylene group of 10-20 carbon atoms;

ALK is an alkyl group of 1-8 carbon atoms;

X is (1) hydrogen, (2) a halo group, (3) an alkoxy group, (4) an arylthio group, (5) a thiocyno group, (6) a heterocyclic radical having a 5-6 membered heterocyclic nucleus with at least one nitrogen, oxygen, or sulfur atom, said heterocyclic nucleus being attached to the ring by a bridging $-O-$ or $-S-$ group or (7) an acyloxy group of the formula R_2-CO-O wherein R_2 is an alkyl group of 1-20 carbon atoms or an aryl group;

T is (1) a halo group, (2) an alkyl group or (3) an alkoxy group; and

24

Z is individually defined as in T.

4. A photographic silver halide emulsion of claim 2 wherein

L is a divalent branched alkylene group of 10-20 carbon atoms;

X is hydrogen or a halo group;

T is an alkoxy group of 1-20 carbon atoms; and

Z is individually defined as an alkyl group, an alkoxy group or a halo group.

5. A photographic silver halide emulsion of claim 2 wherein

L is a divalent branched alkylene group of 10-20 carbon atoms;

X is a hydrogen or a halo group;

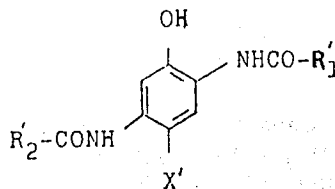
T is an alkyl group, an alkoxy group or a halo group; and

Z is an alkoxy group of 1-20 carbon atoms.

6. A photographic silver halide emulsion of claim 2 wherein

ALK is a tertiary alkyl group of 4-8 carbon atoms.

7. A photographic silver halide emulsion containing a color photographic coupler having the formula



wherein

X' is hydrogen, fluoro, chloro, alkoxy of 1-8 carbon atoms, phenoxy, thiophenyl, cyclohexyloxy, thiocyno, 1-phenyl-5-tetrazolethio, phenylsulfonamido, lower alkyl sulfonamido, phenylcarboxy, or benzoxazolethio;

R_1 is phenyl, p-fluorophenyl, trifluoromethyl phenyl, pentafluorophenyl, a phenylamino, a dichloro phenylamino, or an alkylamino having 1-15 carbon atoms; and

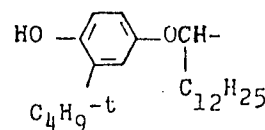
R_2 is a p-hydroxy-alkylphenoxy-alkyl, or a p-hydroxy-dialkylphenoxy alkyl group.

8. A photographic silver halide emulsion of claim 7 wherein

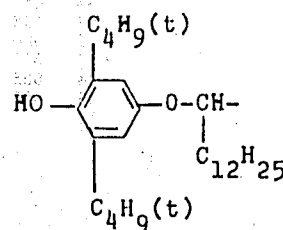
R_1 is phenyl, p-fluorophenyl, pentafluorophenyl, trifluoromethylphenyl, phenyl amino, or alkylamino of 1-15 carbon atoms;

X' is hydrogen, fluoro, or chloro; and

R_2 is a substituent of the formulae

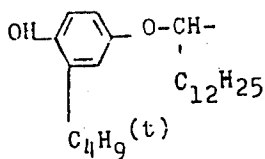


or

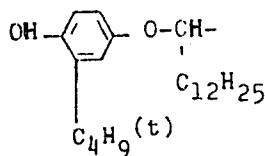


25

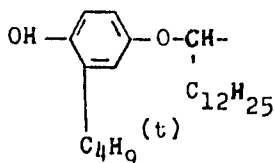
9. A photographic silver halide emulsion of claim 7 wherein
 R'₁ is p-fluorophenyl; and
 R'₂ is



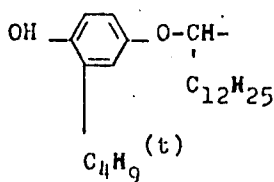
10. A photographic silver halide emulsion of claim 7 wherein
 R'₁ is phenyl; and
 R'₂ is



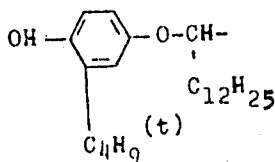
11. A photographic silver halide emulsion of claim 7 wherein
 R'₁ is p-trifluoromethyl phenyl; and
 R'₂ is



12. A photographic silver halide emulsion of claim 7 wherein
 X' is a halo group;
 R'₁ is pentafluoro phenyl; and
 R'₂ is

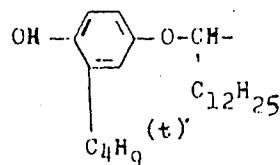


13. A photographic silver halide emulsion of claim 7 wherein
 X' is hydrogen
 R'₁ is phenylamino; and
 R'₂ is



14. A photographic silver halide emulsion of claim 7 wherein
 X' is hydrogen;
 R'₁ is 2,4-dichlorophenylamino; and
 R'₂ is

26

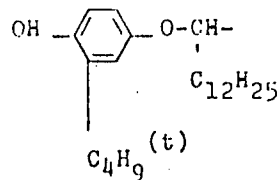


5

15. A photographic silver halide emulsion of claim 7 wherein
 X' is fluoro;
 R'₁ is phenylamino; and
 R'₂ is

10

15

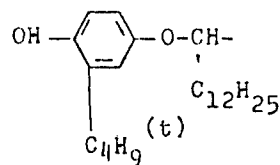


20

16. A photographic silver halide emulsion of claim 7 wherein
 X' is chloro;
 R'₁ is phenylamino; and
 R'₂ is

25

30



17. A silver halide emulsion containing 4,6-dichloro-5-methyl-2[α(p-hydroxy-m-tert. butylphenoxy)-tridecylcarbonamido]phenol.

18. A silver halide emulsion containing 4-fluoro-5[α-(p-hydroxy-m-tert. butylphenoxy)tridecylcarbonamido]-2-(pentafluorophenyl carbonamido)-phenol.

40

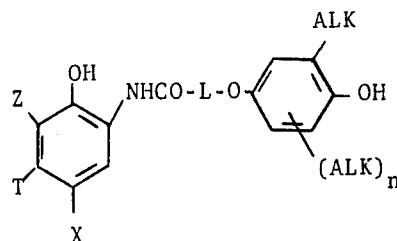
19. A color photographic element comprising a photographic silver halide emulsion layer containing as a cyan dye-forming coupler a phenolic cyan dye-forming coupler compound having a p-hydroxy-alkylphenoxy-alkylcarbonamido group, or a p-hydroxy-dialkylphenoxy-alkylcarbonamido substituent group substituted on a non-coupling ring position of the phenolic nucleus of the coupler.

45

20. A color photographic element comprising a support and at least one photographic silver halide emulsion applied thereto containing a cyan dye-forming coupler of the formula

50

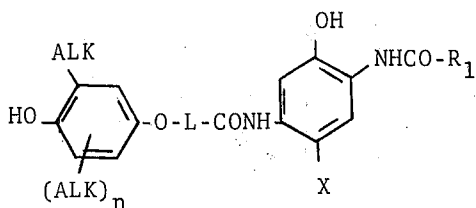
55



60

65

27



wherein

n is 0-1;

L is a divalent alkylene group;

ALK is an alkyl group of 1-15 carbon atoms;

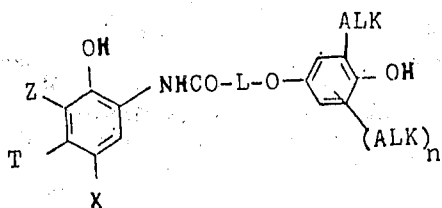
X is (1) hydrogen, (2) a halo group, (3) an aryloxy group, (4) a thioaryl group, (5) an alkoxy group, (6) a thioalkyl group, (7) a thiocyno group, (8) a heterocyclic radical having a 5-6 membered heterocyclic nucleus with at least one nitrogen, oxygen, or sulfur atom, said heterocyclic nucleus being attached to the ring by a bridging $-O-$ or $-S-$ group, or (9) an acyloxy group of the formula R_2-CO-O wherein R_2 is an alkyl group of 1-20 carbon atoms or an aryl group;

T is (1) a halo group, (2) an alkyl group or (3) an alkoxy group;

Z is individually defined as in T ; and

R_1 is (1) an aryl group or (2) $-NH-R_3$, in which R_3 is hydrogen, an alkyl group of 1-20 carbon atoms or an aryl group.

21. A color photographic element comprising a support and at least one photographic silver halide emulsion applied thereto containing a cyan dye-forming coupler of the formula



wherein

n is 0-1

L is a divalent alkylene group of 10-20 carbon atoms;

ALK is an alkyl group of 1-8 carbon atoms;

X is (1) hydrogen, (2) a halo group, (3) an alkoxy group, (4) an arylthio group, (5) a thiocyno group, (6) a heterocyclic radical having a 5-6 membered heterocyclic nucleus with at least one nitrogen, oxygen, or sulfur atom, said heterocyclic nucleus being attached to the ring by a bridging

28

$-O-$ or $-S-$ group or (7) an acyloxy group of the formula R_2-CO-O wherein R_2 is an alkyl group of 1-20 carbon atoms or an aryl group;

T is (1) a halo group, (2) an alkyl group or (3) an alkoxy group; and

Z is individually defined as in T .

22. A color photographic element of claim 20 wherein

L is a divalent branched alkylene group of 10-20 carbon atoms;

X is hydrogen or a halo group;

T is an alkoxy group of 1-20 carbon atoms; and

Z is individually defined as an alkyl group, an alkoxy group, or a halo group.

23. A color photographic element of claim 20 wherein

L is a divalent branched alkylene group of 10-20 carbon atoms;

X is a hydrogen or a halo group;

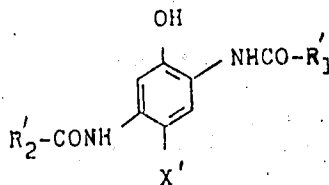
T is an alkyl group, an alkoxy group or a halo group; and

Z is an alkoxy group of 1-20 carbon atoms.

24. A color photographic element of claim 20 wherein

ALK is a tertiary alkyl group of 4-8 carbon atoms.

25. A color photographic element comprising a support and at least one photographic silver halide emulsion applied thereto containing a cyan dye-forming coupler of the formulae



wherein

X' is hydrogen, fluoro, chloro, alkoxy of 1-8 carbon atoms, phenoxy, thiophenyl cyclohexyloxy, thiocyno, 1-phenyl-5-tetrazolethio, phenylsulfonamido, lower alkyl sulfonamido, phenylcarboxy, or benzoxazolethio;

R_1' is phenyl, p-fluorophenyl, trifluoromethyl phenyl, pentafluorophenyl, a phenylamino, a dichloro phenylamino, or an alkylamino having 1-15 carbon atoms; and

R_2' is a p-hydroxy-alkylphenoxy-alkyl, or a p-hydroxy-dialkylphenoxyalkyl group.

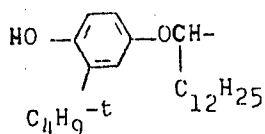
26. A color photographic element of claim 25 wherein

R_1' is phenyl, p-fluorophenyl, pentafluorophenyl, trifluoromethylphenyl, phenyl amino, or alkylamino of 1-15 carbon atoms;

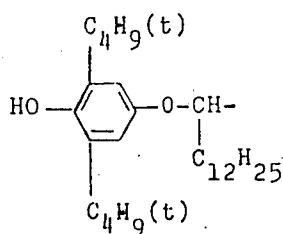
X' is hydrogen, fluoro, or chloro; and

R_2' is a substituent of the formulae

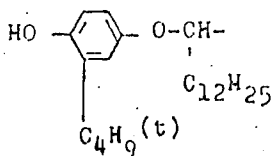
29



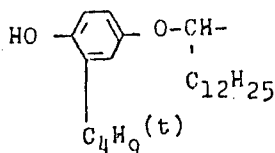
or



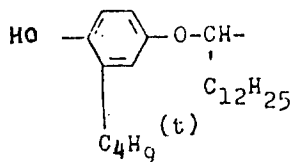
27. A color photographic element of claim 25 wherein
 R'₁ is p-fluorophenyl; and
 R'₂ is



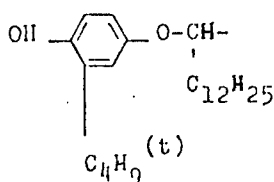
28. A color photographic element of claim 25 wherein
 R'₁ is phenyl; and
 R'₂ is



29. A color photographic element of claim 25 wherein
 R'₁ is p-trifluoromethyl phenyl; and
 R'₂ is



30. A color photographic element of claim 25 wherein
 X' is a halo group;
 R'₁ is pentafluoro phenyl; and
 R'₂ is

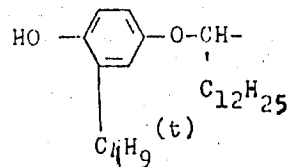


31. A color photographic element of claim 25 wherein

30

X' is hydrogen
 R'₁ is phenylamino; and
 R'₂ is

5

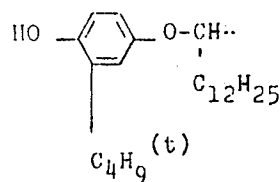


10

32. A color photographic element of claim 25 wherein
 X' is hydrogen
 R'₁ is 2,4-dichlorophenylamino; and
 R'₂ is

15

20

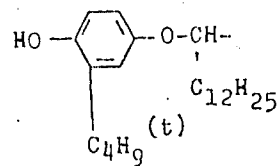


25

33. A color photographic element of claim 25 wherein
 X' is fluoro;
 R'₂ is phenylamino; and
 R'₂ is

30

35

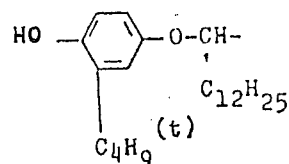


40

34. A color photographic element of claim 25 wherein
 X' is chloro;
 R'₁ is phenylamino; and
 R'₂ is

45

50



35. A color photographic element comprising a photographic silver halide emulsion layer containing 4,6-dichloro-5-methyl-2[α-(p-hydroxy-m-tert. butylphenoxy) tridecylcarbonamido] phenol as a cyan dye-forming coupler.

36. A color photographic element comprising a support, at least one photographic silver halide emulsion and 4-fluoro-5[α-(p-hydroxy-m-tert. butylphenoxy) tridecylcarbonamido]-2-(pentafluorophenyl carbonamido)-phenol as a cyan dye-forming coupler.

37. A color photographic element comprising a photographic silver halide emulsion layer containing 5-[α-(p-hydroxy-m-(t)-butylphenoxy-tridecylcarbonamido)-2-(p-trifluoromethyl phenyl-carbonamido)]phenol.

31

32

38. A color photographic element comprising a photographic silver halide emulsion layer containing 5-[α -(p-hydroxy-m-(t)-butylphenoxy)-tridecylcarbonamido]-2-(phenyl) phenol.

39. A color photographic element comprising a photographic silver halide emulsion layer containing 5-[α -(p-hydroxy-m-(t)-butylphenoxy)-tridecylcarbonamido]-2-(p-fluoromethyl phenyl)-phenol.

40. A method for preparing a cyan photographic dye comprising contacting a phenolic coupler compound having a p-hydroxyphenoxy-m-alkyl carbonamido substituent in a non-coupling ring position with oxidized color developing agent during development of an imagewise exposed silver halide emulsion containing said coupler.

41. A photographic silver halide emulsion as in claim

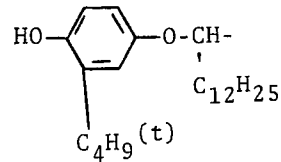
8

wherein

X is chloro,

5 R₁ is p-chlorophenyl, and

R₂ is



20

25

30

35

40

45

50

55

60

65

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,880,661

DATED : April 29, 1975

INVENTOR(S) : Philip T. Lau, Ilmari F. Salminen and Leo E.
Beavers

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 8, "alylphenoxy" should read ---alkyl-
phenoxy---

Column 16, line 19, delete the second occurrence of
"acylamido" and insert --- 2- --- before the first occurrence of
"acylamido";

Column 23, line 33, (claim 2) " R_1 " should read --- R_2 ---, and
same line, "1-29" should read --- 1-20 ---;

Column 27, line 17, (claim 20) "hydroge" should read
---hydrogen---

Column 30, line 30, (claim 33) " R'_2 " should read --- R'_1 ---

Signed and Sealed this

twenty-fourth Day of February 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks