

[54] **PHENOL COLOR COUPLERS**

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[51] Int. Cl..... **G03c 7/00**

[58] Field of Search..... **96/100, 56.6, 55,**  
**96/3**

[56] **References Cited**

**UNITED STATES PATENTS**

2,369,929	2/1945	Vittum et al.....	96/100
3,620,745	11/1971	Seymour.....	96/100

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[57] **ABSTRACT**

5-Aryl thiomethyl-2-amino phenols, 5-aryl sulfonyl-methyl-2-amino phenols and 5-aryl selenomethyl-2-amino phenols having utility as color photographic couplers in light sensitive silver halide emulsions or in photographic color developing compositions, as well as photographic elements having coated thereon silver halide emulsion layers containing such couplers are disclosed; also disclosed is a process for producing the couplers by reacting (1) a 2-amino phenol with (2) formaldehyde and (3) an arylthiol, an arylsulfinic acid or an arylselenol.

**36 Claims, No Drawings**

## PHENOL COLOR COUPLERS

The present invention relates to a new class of photographic phenolic couplers, silver halide emulsions and color developing compositions containing such couplers, photographic elements having such emulsions coated thereon, and methods for preparing such couplers.

By way of background, colored photographic images are obtained in the photographic art by coupling a silver image development by-product (i.e., oxidized aromatic primary amino developing agents) with a color-forming coupler compound. The subtractive process of color formation is ordinarily employed and the resulting cyan, magenta or yellow image dyes are complementary to the primary colors. Coupler compounds employed to produce cyan photographic dyes, for instance, are generally of the phenolic or  $\alpha$ naphtholic type. A majority of such couplers are known and described as "four-equivalent" couplers, and 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 only two exposed silver halide molecules during development to obtain one molecule of dye. Known "two-equivalent" couplers and methods for their utilization are disclosed, for instance, in U.S. Pat. Nos. 3,458,315 and 3,227,155 of Loria and Loria et al. respectively.

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

Successful couplers also must possess a number of important ancillary characteristics. It is desirable, for instance, to utilize non-diffusible couplers which require only minimal amounts of high-boiling non-removable coupler solvents and thereby obtain thinner and more durable photographic elements. It is also important that non-diffusible couplers of the above types be capable of precise incorporation into a silver halide emulsion with no adverse effects on 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, color components, etc.; such changes are capable of directly affecting the coating characteristics of the photographic emulsion. This fact is indicated, 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, coupler-induced changes in the physical properties of a 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.

U.S. Pat. No. 2,369,929 of Vittum, lists a class of acylamino phenols found useful in the color photographic art, and which have substituents in the No. 2 and No. 5 positions, one of said substituents being an alkyl group and the other an acylamino group. This patent, however, fails to suggest any modern functional advantage attributable to the presence of a No. 5-substituted arylthiomethyl, arylselenomethyl, or arylsulfonylmethyl radical.

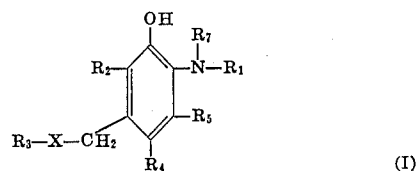
U.S. Pat. No. 2,322,376 of the Cleary et al relates to a class of phenol compounds having a floating substituent radical of the formula  $-(CH_2-S-R_1)$  in which  $R_1$  is defined as an alkyl, an aryl, a cycloalkyl, a cycloaryl or a naphthenyl radical. The indicated disclosure, however, fails to point out the surprising advantages of an arylthiomethyl group in the No. 5 position or indicate utilization for color photographic purposes.

It is an object of the present invention to obtain a new class of compounds suitable as cyan dye-forming couplers for color photographic purposes.

It is a further object of the present invention to provide new compounds which readily and efficiently react with oxidized color developer to produce stable indoaniline cyan dyes suitable for modern color photographic purposes and which are otherwise suitable for use in photographic emulsions, elements or in developer compositions.

It is a still further object of this invention to obtain a novel and efficient process for obtaining phenolic coupler compounds.

These and other objects of the invention are obtained by utilizing, as color photographic couplers, a class of phenolic cyan dye-forming color photographic couplers having an amino radical as the number 2 phenol or ring substituent group and an arylthiomethyl, an arylselenomethyl, or an arylsulfonylmethyl group as the number 5 phenolic ring substituent group. Compounds within the present invention are also conveniently described as 5-arylthiomethyl-2-amino phenols, 5-aryl-selenomethyl-2-amino phenols or 5-arylsulfonylmethyl-2-amino phenols having the general formula



wherein  $R_1$  is a hydrogen atom, an alkyl group inclusive of an alkyl group of 1-22 carbon atoms (e.g. methyl, dodecyl, docosyl), an aryl group such as a phenyl group or a naphthyl group (e.g. phenyl, chlorophenyl, pentafluorophenyl), an acyl group including a radical of the formula



in which R<sub>6</sub>' is an alkyl group of one to 20 carbon atoms, including substituted alkyl group such as aryloxyalkyl group (e.g. methyl, isopropyl and eicosyl), an alkylamino group of one to 20 carbon atoms (e.g. propylamino and octadecylamino), an arylamino group inclusive of a phenylamino group or a naphthylamino group (e.g. phenylamino or chlorophenylamino), a phenyl group, or a naphthyl group (e.g. phenyl, chlorophenyl and chloro-methylphenyl); R<sub>2</sub> and R<sub>5</sub> are each a hydrogen atom, a halo group such as chloro, or bromo, an aryl group such as a phenyl group or a naphthyl group exemplified by phenyl, methylphenyl and dichlorophenyl, also each can be an alkyl group or an alkoxy group wherein the alkyl moieties contain one to 15 carbon atoms and preferably one to four carbon atoms; R<sub>3</sub> is an aryl group, including a phenyl group or a naphthyl group, and exemplified by phenyl, a halo-phenyl group such as a chlorophenyl or dichlorophenyl, a methylphenyl or a chloromethylphenyl group;

R<sub>4</sub> is a hydrogen atom, or a coupling off group including a halo radical, such as chloro or fluoro, a thi-

ocyano, also an aryloxy group such as a phenoxy group, an alkoxy group having one to 20 carbon atoms such as methoxy, isopropoxy, dodecyloxy, pentadecyloxy, eicosyloxy and including a cycloalkoxy of four to eight carbon atoms;

R<sub>7</sub> is a hydrogen atom or an alkyl group such as alkyl of one to 20 carbon atoms exemplified by methyl, octyl and eicosyl; and X is defined as the bivalent group of the formulae —S—,

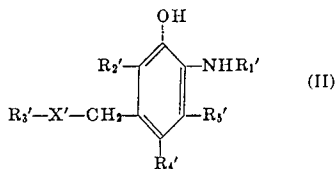


or —Se—.

The term "coupling off" group with respect to R<sub>4</sub> refers to a group that is cleaved off the number 4 or coupling position of the phenolic ring of the subject couplers on reaction with oxidized color developing agents such as aromatic primary amines including p-phenylenediamines and the like.

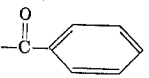

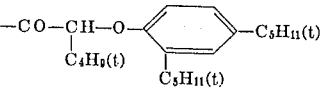


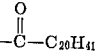
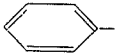
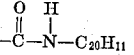
Compounds within the scope of the present invention are exemplified, for instance, in Table I, below, with reference to formula (II)

TABLE I

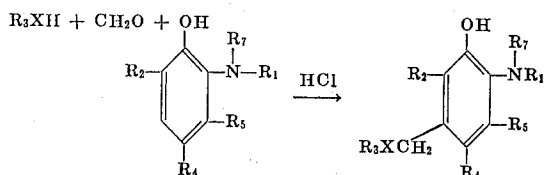


Compound number	R <sub>1</sub> '	R <sub>2</sub> '	X'	R <sub>3</sub> '	R <sub>4</sub> '	R <sub>5</sub> '
1		H	—Se—		H	H
2	Same as above	H			H	H
3	do	H			Cl	H
4	do	Cl	—S—		Cl	H
5	do	H	—S—	Same as above	Cl	H
6	do	Cl	—S—	do	Cl	H
7	H	H	—S—	do	Cl	H
8	H	H	—S—	do	H	H
9	H	C <sub>4</sub> H <sub>9</sub>	—S—	do	H	H
10	H	CH <sub>3</sub> —	—Se—	do	H	C <sub>4</sub> H <sub>9</sub> —
11	H	CH <sub>3</sub> —O—		do	H	C <sub>4</sub> H <sub>9</sub> —O—
12	H	C <sub>4</sub> H <sub>9</sub> —O—	—S—	do	F	H
13	H	C <sub>15</sub> H <sub>31</sub> —	—S—	do	F	CH <sub>3</sub> —O—
14	—H—HCl	Cl—	—S—	do	Cl—	H
15	Same as above	H			Cl—	H
16	H	H	—Se—	Same as above	H	H
17	H	H			H	H
18	H	H	—S—		F	H
19		C <sub>12</sub> H <sub>25</sub> —	—Se—		CH <sub>3</sub> —O—	H

TABLE I—Continued

Compound number	R <sub>1</sub> '	R <sub>2</sub> '	X'	R <sub>3</sub> '	R <sub>4</sub> '	R <sub>5</sub> '
20		H	—S—	Same as above		H
21		H	—S—	do	—S—CN	H
22		H	—S—	do	H	H
23	Same as above		—Se—	do	H	H
24		H	—S—		H	H
25		H	—S—	Same as above	H	H

Compounds of the above-described type are conveniently prepared through the use of a condensation reaction involving (1) an aromatic thiol, selenol or sulfinic acid, (2) formaldehyde and (3) a 2-aminophenol, preferably in the presence of a mineral acid. The condensation reaction is exemplified as follows:



wherein the substituent groups are defined as above. The reaction as described, is unique insofar as it involves a one-step process in which the reaction takes place specifically at a position para to the amine substituent group of the phenol reactant rather than para to the OH group. This is true even in the presence of other substituent groups on the phenol ring, even one or more alkoxy groups.

The purposes of carrying out the above reaction, it is found that suitable o-amino phenol reactants can be obtained, for instance, by nitration, and reduction of the resulting nitrophenols and by preferential methylation when utilizing secondary amine-substituted reactants.

Ballasted non-diffusible dye-forming couplers within the present invention can be conveniently incorporated into a photographic element, particularly into a photographic silver halide emulsion layer thereof by initially dissolving the coupler into a high-boiling and/or one or more low-boiling organic solvents. The resulting solution is then dispersed into a gelatin solution with the aid of an emulsifier, and this coupler dispersion set, noodled, washed, and then melted and dispersed into a light-sensitive silver halide gelatin dispersion and coated onto a film support. Suitable solvents and techniques for this purpose are disclosed, for instance, in U.S. Pat. Nos. 2,949,360, 2,801,171, 2,322,827 and 2,304,939. The resulting photographic emulsions are generally described in the art so summarized, for instance, in section XXII, page 110, lines 1–50 of Product Licensing Index, Vol. 92, Publication 9232 (December, 1971).

Corresponding non-ballasted or lightly substituted diffusible coupler compounds can be conveniently incorporated into a developer solution in accordance

with art-recognized techniques as summarized, for instance, on lines 50–65 of section XXII of the above-cited Product Licensing Index.

An effective amount for non-diffusible couplers of the above type can range from about 25–200 mg/ft<sup>2</sup> of coated material, a concentration of 30–50 mg/ft<sup>2</sup> being generally satisfactory. Insofar as diffusible type couplers are concerned, a concentration of about 1.5 gm/liter to 1.9 gm/liter of developer solution is found sufficient.

Generally speaking, photographic elements suitable for use in the present invention comprise:

1. a support layer such as described in section X of Product Licensing Index, Vol. 92, Publication 9232 (December, 1971). Included among the possible support layers are hydrophobic resin layers which have been electron bombarded as described, for instance, in British Patents Nos. 971,058, 1,060,526 and U.S. Pat. Nos. 2,864,755 and 2,864,756 to improve adhesion of hydrophilic colloid layers coated over them. Such resin layers or film may be either self-supporting or may be coated over another support layer. Specific supports having useful hydrophobic surfaces include polyethylene terephthalate films electron-bombarded to have a contact angle less than 45° (U.S. Patent 3,220,842), an electron-bombarded surface comprising a chromium halide (U.S. Patent 3,117,865), or electron-bombarded hardened gelatin coated papers (Belgian Patent No. 671,661), etc..

2. An antihalation layer attached to the support 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;

3. One or more, preferably three light-sensitive and differently sensitized silver halide emulsion layers coated onto the support; the layers conveniently comprise a red-sensitized layer conveniently containing at least one phenolic cyan dye-forming coupler of the present invention; a green-sensitized emulsion layer containing at least one 5-pyrazolone-magenta-dye-forming coupler (ref. 823–4, Volume 5, Kirk-Othmer, "Encyclopedia of Chemical Technology" (1964), also U.S. Pat. Nos. 2,600,788, 2,908,573, 2,895,826, 3,519,429, 3,227,554, 3,062,653, and 2,983,608); and a blue-sensitized layer containing an open-chain yellow dye-forming ketomethylene coupler (ref. pages 822–23, Volume 5, Kirk-Othmer, "Encyclopedia of Chemical Technology" (1964), also U.S. Pat. Nos.

2,875,057, 2,895,826, 2,908,573, 3,265,506, 3,384,657, 3,408,194 and 3,447,928); a Carey-Lea filter layer is preferably interposed between the blue- and green-sensitized layers.

Suitable light-sensitive silver halide emulsion and references describing their preparation and chemical sensitization thereof are summarized, for instance, on page 107 in section I and III of Product Licensing Index, Vol. 92, Publication 9232 (December, 1971), and include emulsions of silver chloride, silver bromide, silver chlorobromide, silver bromiodide, silver chlorobromiodide and silver chloriodide.

4. One or more gelatin spacer layers between the light-sensitive emulsion layers or the emulsion layers and Carey-Lea filter layer as above described; and

5. A protective water-premeable overcoat layer, such as gelatin, poly-N-vinyl lactam, gum arabic, hydrophilic copolymer of N-acrylamidoalkyl botain (ref. U.S. Pat. No. 2,833,650), cellulose ethers and esters, alkali soluble polyvinyl phthalate (ref. U.S. Pat. No. 2,798,004); also water-soluble polymers having varying degrees of solubility, such as polyvinyl alcohol (optimally with surfactant), polyvinyl pyrrolidone polyalkylene oxides, polyvinyl alcohol and its derivatives such as partial esters, ethers and acetals exemplified by hydrolyzed polyvinylacetate, polyvinyl acetaldehyde acetal, polyvinyl butyraldehyde acetal, polyvinyl sodium o-sulfobenzaldehyde acetal, polyvinyl disodium 2,4-disulfobenzaldehyde acetal; and water-soluble copolymers and interpolymers exemplified by copoly (methyl vinyl ether/maleic anhydride), copoly (acrylic acid/methacrylic acid ethyl ester-maleic anhydride) and copoly (maleic anhydride/acrylic acid/vinyl acetate). The overcoat may conveniently contain an 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 Patent 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'-d-hydroxy 4,4'-dimethoxybenzophenone, 4,4'-diazidostilbene-2,2'-disulfonic acid sodium salt, and sodium  $\alpha$ -phenylhydrazone).

In addition, photographic materials and elements utilizing the present cyan-dye-forming couplers can usefully contain brighteners, such as stilbenes, triazines etc. pectral sensitizing dyes supersensitizing addenda, and also absorbing and filter dyes as summarized, for instance, on page 109 in sections XIV, XV and XVI of Product Licensing Index Volume 92 (December, 1971).

The invention is further described, although not limited by the following examples:

#### Example 1 (Compound No. 7)

A solution consisting of 14.5 g (0.1 mole) of p-chlorobenzenethiol and 7.6 ml (0.1 mole) of formalin in 50 ml of ethanol is added to a solution of 14.3 g (0.1 mole) of 2-amino-4-chlorophenol and 8.6 ml (0.1 mole) of concentrated hydrochloric acid in 50 ml of ethanol with continuous stirring. The resulting mixture is then maintained at room temperature for 0.5 hr. with combined stirring, then heated to reflux on a steam bath for 3 hrs. After cooling, the mixture is neutralized with a solution of sodium acetate, and the resulting solid collected, washed with water, and recrystallized from acetonitrile. 24 Grams (80%) of product identified as 2-Amino-4-chloro-5-(p-chlorophenylthiomethyl) phenol is obtained (m.p. 163°-165°C.).

Anal. Calcd. for  $C_{13}H_{11}Cl_2NOS$ : C, 52.0; H, 3.7; Cl, 23.6; N, 4.7.

Found: C, 51.8; H, 3.7; Cl, 23.3; N, 4.8.

#### Example 2 (Compounds No. 8 and 14)

Similarly prepared were 2-amino-5-(p-chlorophenylthiomethyl) phenol and 2-amino-4,6-dichloro-5-(p-chlorophenylthiomethyl) phenol utilizing 2-amino phenol and 2-amino-4,6-dichloro-phenol reactants. The structures of these compounds were confirmed by elemental, infrared and nuclear magnetic resonance analyses and the respective melting points found to be 168°-169°C. and 215°-216°C..

#### Example 3 (Compound 15)

To a stirred suspension of 40 g (0.2 mole) of sodium benzene sulfinate and 15.5 ml (0.2 mole) of formalin in 200 ml of ethanol is added a solution of 28.6 g (0.2 mole) of 2-amino-4-chlorophenol and 34.4 ml (0.4 mole) concentrated hydrochloric acid in 200 ml of ethanol. The resulting reaction mixture is stirred at room temperature for 0.5 hr. and then refluxed for 2 hr. on a steam bath. After cooling, the solid sodium chloride was filtered off and the filtrate was distilled under reduced pressure to a quarter of its original volume. The hydrochloride salt is then precipitated out by the addition of diethyl ether. A yield of 47 g (71%) of white solid product identified as 2-amino-4-chloro-5-phenylsulfonyl-methyl phenol was obtained, (m.p. 205°-206°C.).

Anal. for  $C_{13}H_{12}ClNO_3S.HCl$ : C, 47.8; H, 3.9; N, 4.2.

Found: C, 47.9; H, 3.8; N, 4.2.

#### Example 4 (Compound 16)

To a stirred solution of 15.7 g (0.1 mole) of benzeneselenol and 7.6 ml (0.1 mole) of formalin in 50 ml of ethanol is added a solution of 10.9 g (0.1 mole) of o-aminophenol and 8.6 ml (0.1 mole) of concentrated hydrochloric acid in 100 ml of ethanol. After stirring at room temperature for 0.5 hr. the mixture is refluxed for 2 hr. then cooled in an ice-bath and neutralized with sodium carbonate solution. The resulting solid is collected, washed with water and dried. The product, when recrystallized from methanol, gave 16.6 grams (60%) of white platelets identified as 2-amino-5-phenylselenomethyl phenol (m.p. 158°-159°C.).

Anal. Calcd. for  $C_{13}H_{13}NOSe$ : C, 56.2; H, 4.7; Se, 28.4.

Found: C, 56.0; H, 5.0; Se, 28.3.

#### Example 5 (Compound No. 5)

To a stirred solution of 6 g (0.02 mole) of 2-amino-4-chloro-5-(p-chlorophenylthiomethyl) phenol in 200 ml of dioxane is added 5.2 g (0.04 mole) of quinoline and 7.3 g (0.02 mole) of 2- $\alpha$ -(2,4-di-tert. pentyl phenoxy) hexanoyl chloride. After stirring at room temperature for 2 hrs., the mixture is poured onto 500 ml of ice-water and 5 ml of concentrated hydrochloric acid and the resulting solid was collected, washed with water, and recrystallized from ethanol to give 8.8 g (70%) of white needles identified as 2-[ $\alpha$ -(2,4-di-tert. pentylphenoxy) hexanoylamido]-4-chloro-5-(p-chlorophenylthiomethyl)phenol (m.p. 177°-178°C.).

Calcd. for  $C_{35}H_{45}Cl_2NO_3S$ : C, 66.6; H, 7.3; N, 2.2.

Found: C, 66.6; H, 6.9; N, 2.5.

#### Example 6

(Compounds 1-4 and 6) having melting points at (154°-155°C.), (165°-166°C.), (181°-182°C.), (142°-09°C.) and (113°-114°C.) are similarly prepared in accordance with the process of Examples 1 and 5.

#### Example 7

Six test film strips identified as Coatings 1-6 and consisting of supported single-layer gelatinous silver bromiodide emulsion coatings containing, per square foot of coating, 176 mg silver, 450 mg gelatin, 39 mg of di-

n-butyl phthalate as coupler solvent, and 75 mg of compounds 1-6 of this invention respectively, are exposed through a graduated-density test object and conventionally color developed, washed, bleached, washed, fixed, washed and dried. The dyes produced in proportion to the reproduced image are then spectrophotometrically evaluated and the results tabulated in the Table II below:

TABLE II

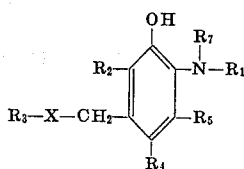
Coating No.	$\lambda_{\max}$ (nm)	$D_{\max}$ (max. density)
1	671	2.49
2	667	1.60
3	687	1.11
4	715	2.00
5	671	1.64
6	690	3.52

This invention has been described in detail with particular reference to a preferred embodiment thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A light sensitive photographic silver halide emulsion containing a ballasted non-diffusible phenolic cyan dye-forming coupler having an amino radical as the number 2 phenolic ring substituent group and an arylthiomethyl, an arylselenomethyl, or an arylsulfonylmethyl as the number 5 phenolic ring substituent group.

2. A light sensitive photographic silver halide emulsion containing a ballasted cyan dye-forming coupler having the formula



wherein

$R_1$  is a hydrogen atom, an-alkyl group, an aryl group, an acyl group or a carbamyl group;

$R_2$  and  $R_5$  each are a hydrogen atom, a halo group, an aryl group, an alkyl group or an alkoxy group;

$R_3$  is an aryl group;

$R_4$  is a hydrogen atom or a coupling-off group;

$R_7$  is a hydrogen atom or an alkyl group; and

$X$  is a bivalent group of the formulae  $-\text{S}-$ ,



or  $-\text{Se}-$ .

3. A light sensitive silver halide emulsion of claim 2 wherein

$X$  is  $-\text{S}-$ ;

$R_1$  is a phenoxyalkylcarbonyl group or a hydrogen atom;

$R_7$  is a hydrogen atom or an alkyl group of one-three carbon atoms;

$R_2$  and  $R_5$  are individually defined as a hydrogen atom or a chloro group;

$R_3$  is phenyl or a chlorophenyl group; and

$R_4$  is a hydrogen atom or a coupling off group.

4. A light sensitive silver halide emulsion of claim 2 wherein

$X$  is  $-\text{Se}-$ ;

$R_1$  is a phenoxyalkylcarbonyl group or a hydrogen atom;

$R_7$  is a hydrogen atom or an alkyl group of one to three carbon atoms;

5  $R_2$  and  $R_5$  are individually defined as a hydrogen atom or a chloro group;

$R_3$  is phenyl or a chlorophenyl group; and

$R_4$  is a hydrogen atoms or a coupling off group.

5. A light sensitive silver halide emulsion of claim 2 wherein

$X$  is



15  $R_1$  is a phenoxyalkylcarbonyl group or a hydrogen atom;

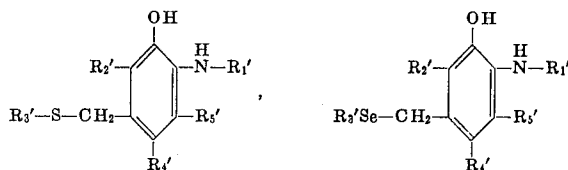
$R_7$  is a hydrogen atom or an alkyl group of one to three carbon atoms.

20  $R_2$  and  $R_5$  are individually defined as a hydrogen atom or a chloro group;

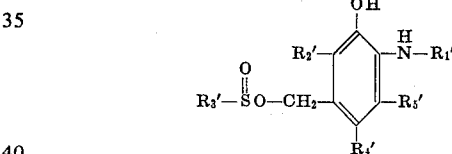
$R_3$  is phenyl or a chlorophenyl group; and

$R_4$  is a hydrogen atom or a coupling off group.

6. A light sensitive photographic silver halide emulsion containing a ballasted cyan dye-forming coupler having the formulae



or



wherein

$R_1'$  is a hydrogen atom, an alkyl group of one to 22 carbon atoms or a radical of the formula



in which

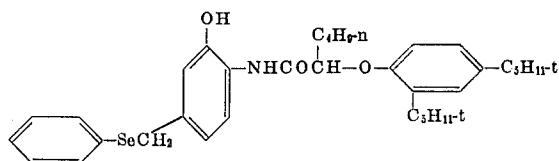
$R_6'$  is an alkyl group of one to 20 carbon atoms, an alkylamino group of one to 20 carbon atoms, a phenylamino group, a naphthylamino group, a phenyl group or a naphthyl group;

$R_2'$  and  $R_5'$  are each a hydrogen atom, a halo group, a phenyl group, a naphthyl group, an alkyl group, or an alkoxy group wherein the alkyl moieties thereof contain one to 15 carbon atoms;

$R_3'$  is a phenyl group or a naphthyl group; and

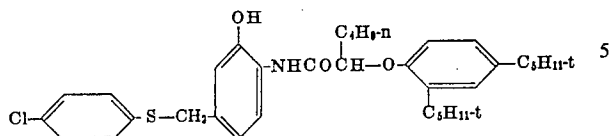
$R_4'$  is a hydrogen atom, a halo group, a thiocyanato group, a phenoxy group, or an alkoxy group of one to 20 carbon atoms.

7. A light sensitive silver halide emulsion containing a cyan dye-forming coupler of the formula

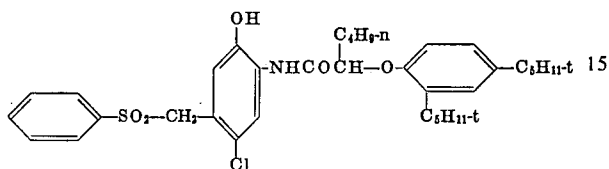


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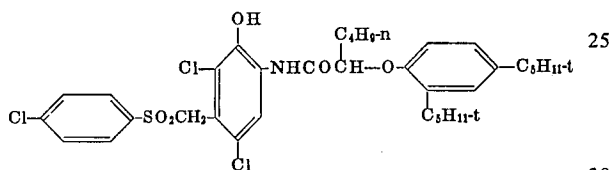
8. A light sensitive silver halide emulsion containing a cyan dye-forming coupler of the formula



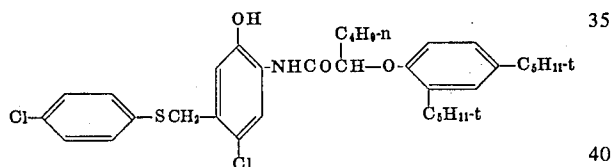
9. A light sensitive silver halide emulsion containing a cyan dye-forming coupler of the formula



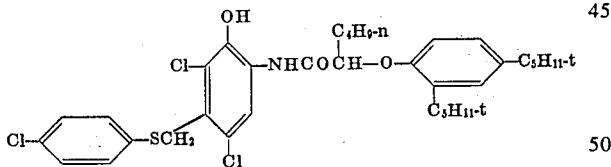
10. A light sensitive silver halide emulsion containing a cyan dye-forming coupler of the formula



11. A light sensitive silver halide emulsion containing a cyan dye-forming coupler of the formula

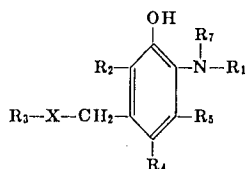


12. A light sensitive silver halide emulsion containing a cyan dye-forming coupler of the formula



13. A color photographic element comprising a support having at least one silver halide emulsion layer and containing a phenolic cyan dye-forming color photographic coupler having an amino radical as the number 2 phenolic ring substituent and an arylthiomethyl, an arylselenomethyl, or an arylsulfonylmethyl group as the number 5 phenolic ring substituent group.

14. A color photographic element comprising a support layer having at least one silver halide emulsion layer and containing a phenolic cyan dye-forming color photographic coupler of the formula



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wherein

R<sub>1</sub> is a hydrogen atom, an-alkyl group, an aryl group, an acyl group or a carbamyl group;  
R<sub>2</sub> and R<sub>3</sub> each are a hydrogen atom, a halo group, an aryl group, an alkyl group or an alkoxy group;  
R<sub>3</sub> is an aryl group;  
R<sub>4</sub> is a hydrogen atom or a coupling-off group;  
R<sub>7</sub> is a hydrogen atom or an alkyl group; and  
X is a bivalent group of the formulae —S—



or —Se—.

15. A color photographic element of claim 14 wherein

X is —S—;

R<sub>1</sub> is a phenoxyalkylcarbonyl group or a hydrogen atom;

R<sub>7</sub> is a hydrogen atom or an alkyl group of one to three carbon atoms;

R<sub>2</sub> and R<sub>3</sub> are individually defined as a hydrogen atom or a chloro group;

R<sub>3</sub> is phenyl or a chlorophenyl group; and

R<sub>4</sub> is a hydrogen atom or a coupling off group.

16. A color photographic element of claim 14

wherein

X is —Se—;

R<sub>1</sub> is a phenoxyalkylcarbonyl group or a hydrogen atom;

R<sub>7</sub> is a hydrogen atom or an alkyl group of one to three carbon atoms;

R<sub>2</sub> and R<sub>3</sub> are individually defined as a hydrogen atom or a chloro group;

17. A color photographic element of claim 14

wherein

X is



R<sub>1</sub> is a phenoxyalkylcarbonyl group or a hydrogen atom;

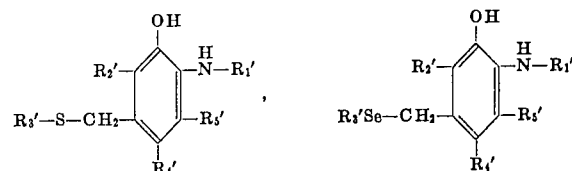
R<sub>7</sub> is a hydrogen atom or an alkyl group of one to three carbon atoms;

R<sub>2</sub> and R<sub>3</sub> are individually defined as a hydrogen atom or a chloro group;

R<sub>3</sub> is phenyl or a chlorophenyl group; and

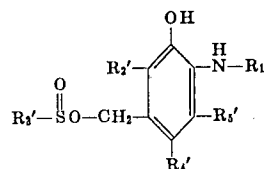
R<sub>4</sub> is a hydrogen atom or a coupling off group.

18. A color photographic element comprising a support layer having at least one silver halide emulsion layer and containing a phenolic cyan dye-forming color photographic coupler of the formulae



or

65



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wherein

R<sub>1</sub> is a hydrogen atom, an alkyl group of 1-22 carbon atoms or a radical of the formula



in which

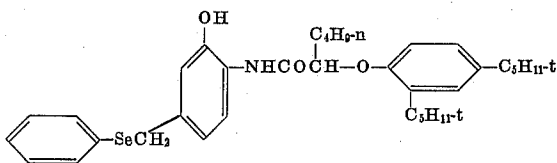
R<sub>6</sub> is an alkyl group of one to 20 carbon atoms, an alkylamino group of 1-20 carbon atoms, a phenylamino group, a naphthylamino group, a phenyl group or a naphthyl group;

R<sub>2</sub> and R<sub>3</sub> are each a hydrogen atom, a halo group, a phenyl group, a naphthyl group, an alkyl group, or an alkoxy group wherein the alkyl moieties thereof contain one to 15 carbon atoms;

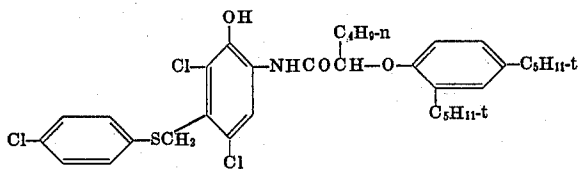
R<sub>3</sub> is a phenyl group or a naphthyl group; and

R<sub>4</sub> is a hydrogen atom, a halo group, a thiocyanato group, a phenoxy group, or an alkoxy group of one to 20 carbon atoms.

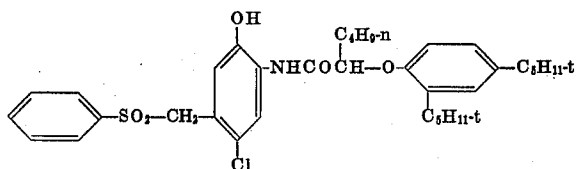
19. A color photographic element comprising a support having at least one silver halide emulsion layer containing a cyan dye-forming coupler of the formula



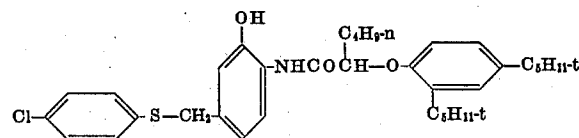
20. A color photographic element comprising a support having at least one silver halide emulsion layer containing a cyan dye-forming coupler of the formula



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

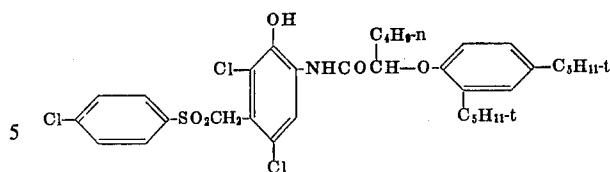


22. A color photographic element comprising a support having at least one silver emulsion layer containing a cyan dye-forming coupler of the formula

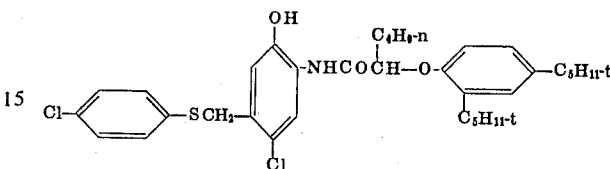


23. A color photographic element comprising a support having at least one silver halide emulsion layer containing a cyan dye-forming coupler of the formula

14

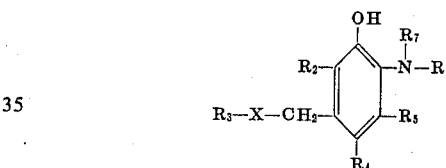


24. A color photographic element comprising a support having at least one silver halide emulsion layer containing a cyan dye-forming coupler of the formula



25. A color photographic developer composition comprising a photographic color developing agent and a diffusible phenolic cyan dye-forming coupler having an amino radical as the number 2 phenolic ring substituent group and an arylthiomethyl, an arylselenomethyl, or an arylsulfonylmethyl group as the number 5 phenolic ring substituent group.

26. A color photographic developer composition comprising a photographic color developing agent and a diffusible phenolic cyan dye-forming coupler of the formula



wherein

R<sub>1</sub> is a hydrogen atom, an alkyl group, an aryl group, an acyl group or a carbamyl group;

R<sub>2</sub> and R<sub>5</sub> each are a hydrogen atom, a halo group, an aryl group, an alkyl group or an alkoxy group;

R<sub>3</sub> is an aryl group;

R<sub>4</sub> is a hydrogen atom or a coupling-off group;

R<sub>7</sub> is a hydrogen atom or an alkyl group; and

X is a bivalent group of the formulae —S—,



or —Se—.

27. A developer composition of claim 26 wherein X' is —S—;

R<sub>1</sub> is a hydrogen atom;

R<sub>7</sub> is a hydrogen atom or an alkyl group of one to three carbon atoms; R<sub>2</sub> and R<sub>5</sub> are individually defined as a hydrogen atom or a chloro group;

60 R<sub>3</sub> is phenyl or a chlorophenyl group and

R<sub>4</sub> is a hydrogen atom, a chloro group, a thiocyanato group, a phenoxy group or an alkoxy group having one to 12 carbon atoms.

28. A developer composition of claim 26 wherein X is —Se—;

R<sub>1</sub> is a hydrogen atom;

R<sub>7</sub> is a hydrogen atom or an alkyl group of one to three carbon atoms.





UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,779,763 Dated December 18, 1973  
Inventor(s) Philip T. S. Lau

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

Column 4, line 46 (Compound No. 9) under the heading "R<sub>5</sub>" ", "H" should read ---Cl---;

Column 8, line 64, "09°C.)" should read -- 143°C.) -- .

Column 9, line 58, "phenoxyalckylcarbonyl" should read ---phenoxyalkylcarbonyl---.

Signed and sealed this 20th day of August 1974.

(SEAL)  
Attest:

McCOY M. GIBSON, JR.  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents