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1-HYDROXY-2-NAPHTHAMIDE COLORED COUPLERS

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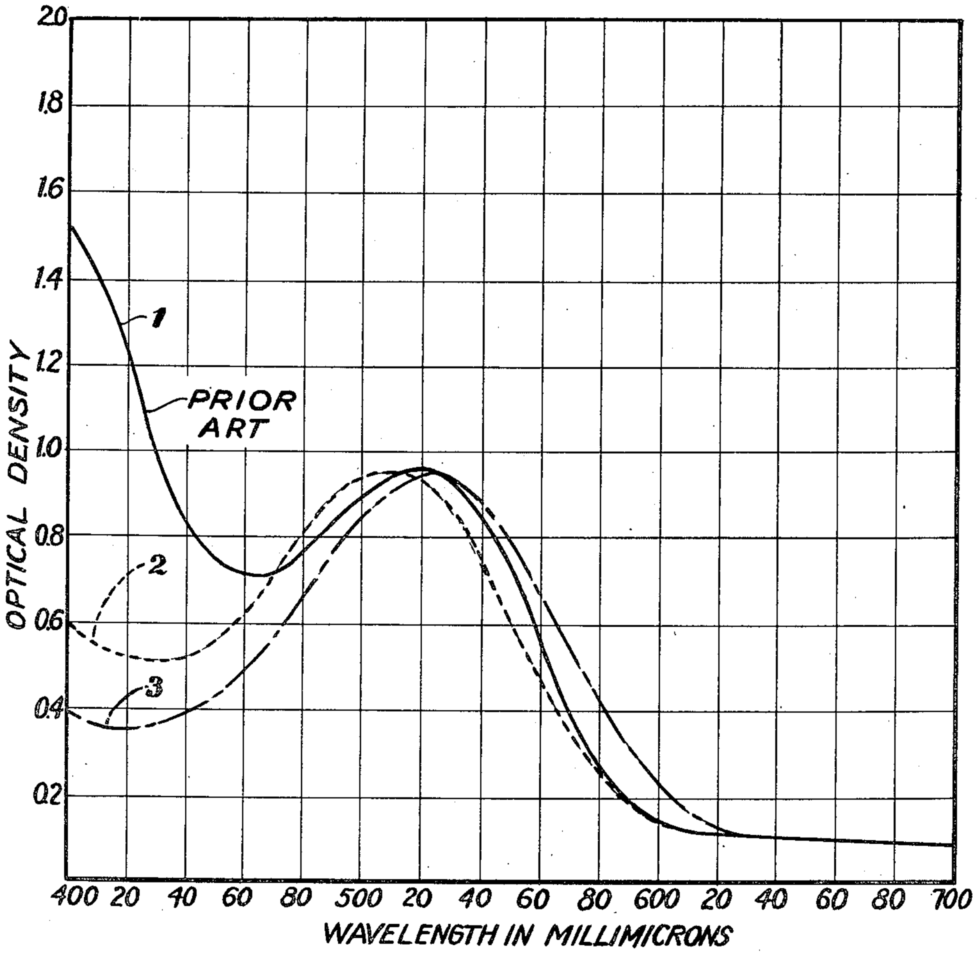

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1-HYDROXY-2-NAPHTHAMIDE COLORED COUPLERS

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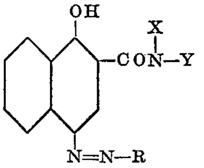
13 Claims. (Cl. 95—6)

This invention relates to color photography and particularly to color couplers for use in photographic processes.

Color-forming compounds which react with the development product of aromatic amino developing agents to form colored images upon photographic development are well known. Generally, these color-forming compounds of couplers are colorless or substantially colorless. This lack of color is usually desirable where the coupler is to be incorporated in the emulsion layer and the unused coupler remains after formation of the colored image. When the coupler is used in the developing solution, it may be colored without detriment to the final image and certain colored couplers have been used in this way.

In U. S. Patent 2,521,908 granted September 12, 1950, are described 1-hydroxy-2-naphthamide colored coupler compounds having the formula:



in which X is hydrogen or alkyl, Y is a mononuclear aryl radical, or an aralkyl radical and R is a mononuclear aryl radical.

These couplers are in themselves more or less strongly colored and during the coupling reaction, the arylazo group R—N=N—, which imparts the color to the coupler is destroyed or split off with the result that the original color of the coupler is destroyed and a new dye is formed upon coupling. Thus on developing an emulsion layer containing one of these colored couplers, the coupler color is destroyed and a new color is formed by the coupling reaction at those points where development occurs. There is formed in this way a dye image of one color combined with a photographically reversed dye image composed of unreacted coupler.

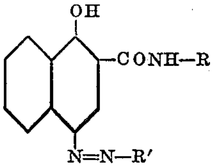
In these coupler compounds the position para to the phenolic hydroxyl group of the coupler, which is the reactive position of the coupler, is substituted with an azo group and this group is split off or removed by the oxidized developer when the azo-substituted coupler is treated with the oxidized developer either in aqueous solution or in the photographic emulsion layer. Thus the coupler may be converted to a differently colored compound and the azo group readily removed from it by means of reaction with the oxidized developing agent.

The coupler compounds of the patent are designed, as are the coupler compounds of our invention, to be incorporated into an emulsion layer and generally are used in one of the emulsion layers of a multilayer coating in order to secure masking effects described in the Hanson U. S. Patent No. 2,449,966 granted September 21, 1948. The Hanson process involves a color correction method in which a color coupler is incorporated in the photographic emulsion layer prior to exposure and upon development is converted to a colored image where the layer is exposed. The coupler remaining in the unexposed portions of the layer retains its original color and by suitable choice of the color of the final dye image a masking or correction effect can be obtained.

The coupler compounds of the patent are for the most part yellow to red in color and their absorption of blue light is therefore higher than their absorption of green light. Accordingly, while such compounds are very useful for the purposes mentioned, they are for certain uses not the most ideal. That is, when used for color correction purposes, the colored coupler compounds used for forming cyan dye images should absorb in the blue and green regions of the spectrum in approximately the same amount as the cyan dye itself absorbs in the blue and green regions. However, it is frequently desirable to use a colored coupler for the cyan dye image having higher green light absorption than blue light absorption, that is, a coupler compound which is magenta in color.

We have now discovered quite unexpectedly and as yet it is unexplained, that if the 1-hydroxy-4-arylazo-2-naphthanilide colored couplers are substituted in an ortho position on the anilide nucleus, the absorption is shifted in the desired direction, the colored couplers having greater green than blue light absorption and, of course, being more nearly magenta in color, as desired.

The novel coupler compounds contemplated by our invention therefore have the general formula:



wherein R represents a mononuclear aryl radical substituted in a position ortho to the amido group with either halogen, alkoxy or mononuclear aryloxy radicals and in which R′ represents a mononuclear aryl radical. Numerous examples illustrating R and R′ are provided in the description hereafter. While it appears likely that R′ may be a group other than a mononuclear aryl group, for example, a heterocyclic group, the invention has not as yet been extended in that direction. Similarly, it is likely that ortho substituents of R other than those indicated may be found to be useful.

The objects of the invention are, therefore, to provide the mentioned colored coupler compounds having improved light-absorption characteristics and to provide photographic emulsions containing the coupler compounds.

These objects are occomplished by providing the coupler compounds, examples of which are provided in the following description, as well as photographic emulsions containing the coupler compounds.

The accompanying drawings illustrate by means of graphical representation the mentioned improvement in light-absorption characteristics of the coupler compounds of the invention.

Colored coupler compounds illustrating our invention are derived from the following four parent colorless couplers:

1-hydroxy-2′,5′-dibutoxy-2-naphthanilide, I. — This compound was prepared by the condensation of phenyl 1-hydroxy-2-naphthoate with aminohydroquinone dibutyl ether at 150–200° C. The product, recrystallized from ligroin, melted at 93–94°. *Analysis.*—Calculated for $C_{25}H_{29}NO_4$: C, 73.7; H, 7.1. Found: C, 740.0; H, 7.1.

1-hydroxy-4-sec-amyl-2′-chloro-2-naphthanilide, II.—Prepared as above from 4-sec-amyl-2-chloroaniline and recrystallized from petroleum ether, II melted at 97–

98.5°. *Analysis.*—Calculated for $C_{22}H_{22}ClNA_2$; N, 9.6. Found: N, 9.4.

The substituted aniline used in this condensation was prepared by chlorination of 4-sec-amylacetanilide, M. P. 118–120°. The 4-sec-amyl-2-chloroacetanilide, an oil, was hydrolyzed to 4-sec-amyl-2-chloroaniline. *Analysis.*—Calculated: Cl, 17.9; Found, 17.9. M. P. of hydrochloride, 165–167°.

1 - hydroxy-5'-carboxy-2'-(2,4-di-tert-amylphenoxy)-2-naphthanilide, III, M. P. 259–261°.—This coupler was prepared as above, i. e., by the condensation of phenyl 1-hydroxy-2-naphthoate with 3-amino-4-(2,4-di-tert-amylphenoxy)benzoic acid, M. P. 179–181°. The latter was prepared by catalytic reduction of the corresponding nitro compound.

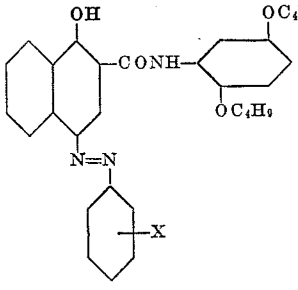
1 - hydroxy - 2'-(2,4-di-tert-amylphenoxy)-5'-[3,5-di-(carbomethoxy) - phenylcarbamyl]-2-naphthanilide, IV, M. P. 230–232°.—IV was prepared as above but from 2-(2,4-di-tert-amylphenoxy) - 5 - (3,5-dicarbomethoxy)-aniline, M. P. 210–212°, which was obtained by reduction of the corresponding nitro compound, 4-(2,4-diamylphenoxy) - 3-nitro-2',5'-dicarbomethoxybenzanilide, M. P. 112–114°. This was synthesized by condensing 4-(2,4-di-tert-amylphenoxy)-4-nitrobenzoyl chloride with dimethyl 5-aminoisophthalate.

The colored couplers themselves were prepared from the parent colorless couplers I, II, III and IV as follows:

The parent coupler was dissolved in 10 to 100 parts of pyridine. The suitable aqueous diazonium solution was added to the coupler-pyridine solution at 0° C. After the coupling reaction was complete, the azo dye was precipitated from the coupling solution by addition of water. The dye was collected, washed and recrystallized from a suitable organic solvent such as acetic acid, alcohol or ligroin.

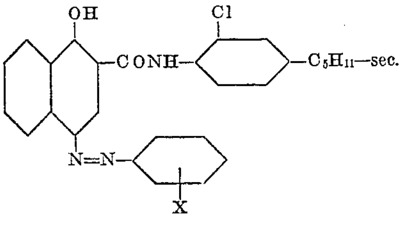
Thus the following tables illustrate the couplers prepared from the parent colorless couplers I, II, III and IV; that is, in the first table "H" under the heading "Substituent X" indicates that the coupler was prepared by coupling diazotized aniline with parent coupler I. Similarly, the "4-NHCOCH3" substituent refers to the coupling of diazotized amino acetanilide with I, etc.

Examples of colored couplers derived from I



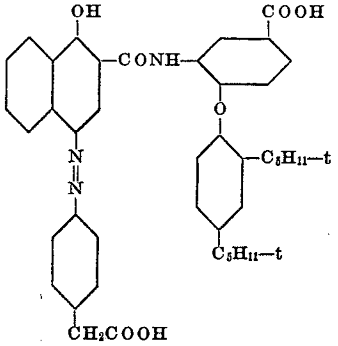
Substituent X	Name of Compound	λ_{max} of Azo Dye	M. P.	Analysis	
				Calcd.	Found
H	1-Hydroxy-2',5'-dibutoxy-4-phenylazo-2-naphthanilide.	504	143–143.5	N 8.2	8.4
4-NHCOCH3	1-Hydroxy-4-(4-acetamidophenylazo)-2',5'-dibutoxy-2-naphthanilide.	----------	.HOAc Solvate 223–224	N 8.9	8.6
4-CH2COOH	1-Hydroxy-4-[4-(carboxymethyl)-phenylazo]-2',5'-dibutoxy-2-naphthanilide.	----------	227–229	N 7.4	6.9
4-CN	1-Hydroxy-4-(4-cyanophenylazo)-2',5'-dibutoxy-2-naphthanilide.	500	165–166	N 10.4	10.7
2-CH3, 4-N(C2H5)2	1-Hydroxy-2',5'-dibutoxy-4-(4-diethylamino-2-methylphenylazo)-2-naphthanilide.	460	128–130	N 9.4	9.3
4-NO2	1-Hydroxy-2',5'-dibutoxy-4-(4-nitrophenylazo)-2-naphthanilide.	510	228–230	N 10.1	10.3
4-OCH3	1-Hydroxy-2',5'-dibutoxy-4-(4-methoxyphenylazo)-2-maphthanilide.	520	130–131	N 7.8	7.6
4-CH2SO3H	1-Hydroxy-2',5'-dibutoxy-4-[4-(sulfomethyl)phenylazo]-2-naphthanilide.	----------	241	N 6.9	6.1
2-OCH3	1-Hydroxy-2',5'-dibutoxy-4-(2-methoxyphenylazo)-2-naphthanilide.	----------	183–185	N 7.8	7.4
4-NO2, 2-OCH3	1-Hydroxy-2',5'-dibutoxy-4-(2-methoxy-4-nitrophenylazo)-2-naphthanilide.	----------	205–207	N 9.5	9.9
2,5-di-Cl	1-Hydroxy-2',5'-dibutoxy-4-(2,5-dichlorophenylazo)-2-naphthanilide.	----------	142–144	Cl 12.2	12.4
2,4,6-tri-Cl	1-Hydroxy-2',5'-dibutoxy-4-(2,4,6-trichlorophenylazo)-2-naphthanilide.	----------	128–135	Cl 17.2	17.3
2,5-di-OC4H9	1-Hydroxy-2',5'-dibutoxy-4-(2,5-dibutoxyphenylazo)-2-naphthanilide.	508	148–149	C 71.5 H 7.5 N 6.4	71.5 7.8 6.5
4-CH3	1-Hydroxy-2',5'-dibutoxy-4-(p-tolylazo)-2-naphthanilide.	400–514	139–141	C 73.1 H 6.7 N 8.0	72.9 6.8 8.1
4-C5H11-t	1-Hydroxy-4-(4-tertamylphenylazo)-2',5'-dibutoxy-2-naphthanilide.	400–514	145–147	C 74.3 H 7.4 N 7.2	74.4 7.4 7.5
2,5-di-OC2H5	1-Hydroxy-2',5'-dibutoxy-4-(2,5-diethoxyphenylazo)-2-naphthanilide.	522	200–202	C 70.2 H 6.9 N 7.0	69.7 7.2 7.6
4-N(C2H5)2	1-Hydroxy-2',5'-dibutoxy-4-(4-diethylaminophenylazo)-2-naphthanilide.	460	149–151	C 72.2 H 7.2 N 9.6	72.1 7.4 9.8

Examples of colored couplers derived from II



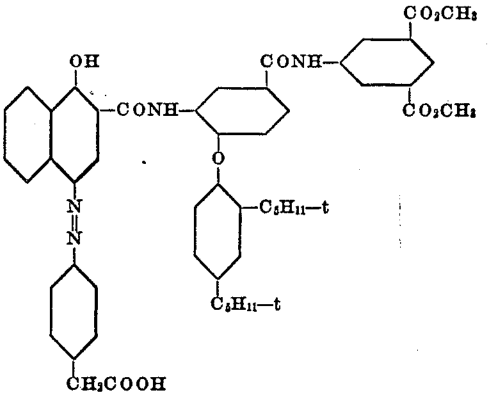
Substituent X	Name of Compound	λmax of Azo Dye	M. P.	Calcd.	Found
H	1-Hydroxy-4′-sec-amyl-2′-chloro-4-phenylazo-2-naphthanilide.	540	108–109	N 8.9	8.7
2-OCH_3, 4-NO_2	1-Hydroxy-4′-sec-amyl-2′-chloro-4-(2-methoxy-4-nitrophenylazo)-2-naphthanilide.	----------	220–223	N 10.2	10.5
2,5-di-OC_4H_9	1-Hydroxy-4′-sec-amyl-2′-chloro-4-(2,5-dibutoxyphenylazo)-2-naphthanilide.	506	194	C 70.0 H 6.8 Cl 5.8 N 6.8	70.4 7.1 5.6 7.0
2-OCH_3	1-Hydroxy-4′-sec-amyl-2′-chloro-4-(2-methoxyphenylazo)-2-naphthanilide.	518	178–180	C 69.4 H 5.6 Cl 7.1 N 8.4	69.6 5.5 7.5 8.9
4-CN	1-Hydroxy-4′-sec-amyl-2′-chloro-4-(4-cyanophenylazo)-2-naphthanilide.	500	220–222	N 11.3	11.4

Examples of colored couplers derived from III



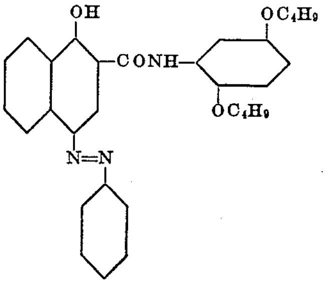
Substituent	Name of Compound	λmax of Azo Dye	M. P.	Calcd.	Found
4-CH_2COOH	1-Hydroxy-5′-carboxy-4-[4-(carboxymethyl) phenylazo]-2′-(2,4-di-tert-amylphenoxy)-2-naphthanilide.	524	205–210	N 6.0	5.6

Examples of colored couplers derived from IV

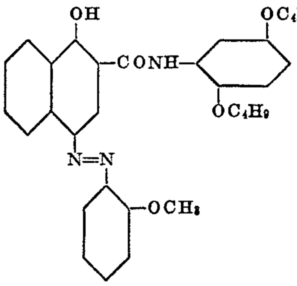


Substituent	Name of Compound	λmax of Azo Dye	M. P.	Calcd.	Found
4-CH_2COOH	1-Hydroxy-4-[(p-carboxymethyl) phenylazo]-2′-(2,4-di-tert-amylphenoxy)-5′-[3,5-di(carbomethoxy) phenylcarbamyl]-2-naphthanilide.	524	260–265	N 6.3	6.0

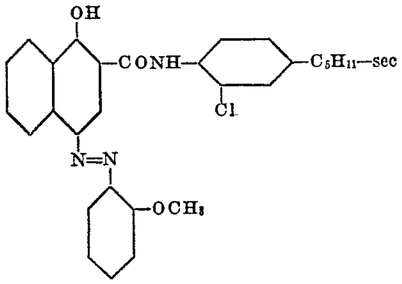
Preferred colored couplers provided above include the two immediately above prepared from intermediates III and IV, and the following:



1-hydroxy-2′,5′-dibutoxy-4-phenylazo-2-naphthanilide



1-hydroxy-2′,5′-dibutoxy-4-(2-methoxyphenylazo)-2-naphthanilide



1-hydroxy-4'-sec-amyl-2'-chloro-4-(2-methoxyphenylazo)-2-naphthanilide

The mentioned improvement residing in the coupler compounds of the invention relating to increased green light absorption compared to the coupler compounds of U. S. Patent 2,521,908, is illustrated in the drawings wherein are plotted the optical densities at various wavelengths of three colored couplers. Curve **1** shows the spectral absorption of compound No. 1 1-hydroxy-4-phenylazo-4'-(p-tert-butylphenoxy)-2-naphthanilide of U. S. Patent 2,521,908, from which it is evident that the coupler has higher blue than green light absorption. Curves **2** and **3** illustrate the spectral absorption characteristics of two typical couplers of the invention, respectively, 1-hydroxy-2'-5'-dibutoxy-4-phenylazo-2-naphthanilide and 1-hydroxy-4'-sec-amyl-2'-chloro-4-phenylazo-2-naphthanilide, from which it is apparent that the green light absorption of the two latter compounds predominates.

The coupler compounds of the invention are incorporated into hydrophilic colloid silver halide emulsion layers by means of coupler solvents as described in Martinez U. S. Patent 2,269,158 granted January 6, 1942, Mannes et al. U. S. Patent 2,304,940 granted December 15, 1942, and Jelley et al. U. S. Patent 2,322,027 granted June 15, 1943. For example, in making an emulsion above 0.5 gram of colored coupler can be dissolved in a coupler solvent such as 2 cc. of tricresyl phosphate by heating at elevated temperature. This dispersion of coupler is then mixed with a suitable quantity of gelatin solution such as 25 cc. preferably by passing the mixture through a colloid mill. Following this, the dispersion of coupler in gelatin solution is added to a gelatino silver halide emulsion in the desired quantity. The emulsion is then coated on to a suitable support such as transparent film base. When the emulsion is exposed and developed in a standard color process, the result is to obtain a cyan dye image in the exposed areas of the coating and a background of magenta colored coupler in the unexposed areas serving as a color-correcting image.

Various photographic developing agents can be employed with the couplers of my invention. The primary aromatic amino developing agents are generally suitable including the phenylenediamines and aminophenols. The alkyl phenylenediamines may be substituted in the amino group as well as in the ring. Suitable compounds are diethylparaphenylenediamine, monomethyl paraphenylenediamine, dimethyl paraphenylenediamine and para-aminophenol. These compounds are usually employed in the salt form, such as the hydrochloride or the sulfate which are more stable than the free amines. All of these compounds have a primary amino group which enables the oxidation product of the developer to couple with the color-forming compounds to form dye images.

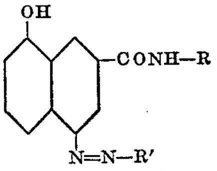
The following developing solution is suitable for developing gelatino silver halide layers containing colored couplers according to my invention:

2-amino-5-diethylamino toluene HCl	grams	2
Sodium sulfite	do	2
Sodium carbonate	do	20
Potassium bromide	do	2
Water to	liter	1

It will be understood that the examples and modifications set forth herein are illustrative only and that my invention is to be taken as limited only by the scope of the appended claims.

What we claim is:

1. A silver halide emulsion layer containing a coupler compound having the formula



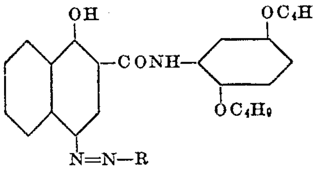
wherein R represents a mononuclear aryl ardical substituted in a position ortho to the amido group with a member of the group consisting of halogen, alkoxy and mononuclear aryloxy radicals, and R' represents a mononuclear aryl radical.

2. A silver halide emulsion layer containing a coupler compound having the formula of claim 1 wherein R represents a mononuclear o-alkoxy aryl radical and R' represents a mononuclear aryl radical.

3. A silver halide emulsion layer containing a coupler compound having the formula of claim 1 wherein R represents a mononuclear o-chloro aryl radical and R' represents a mononuclear aryl radical.

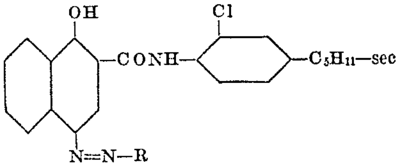
4. A silver halide emulsion layer containing a coupler compound having the formula of claim 1 wherein R represents a mononuclear o-aryloxy aryl radical and R' represents a mononuclear aryl radical.

5. A silver halide emulsion layer containing a coupler compound having the formula



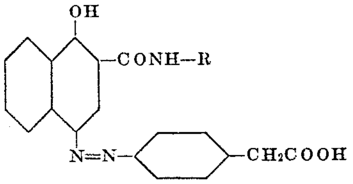
wherein R represents a mononuclear aryl radical.

6. A silver halide emulsion layer containing a coupler compound having the formula



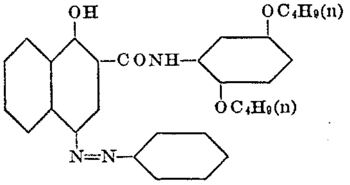
wherein R represents a mononuclear aryl radical.

7. A silver halide emulsion layer containing the coupler compound having the formula

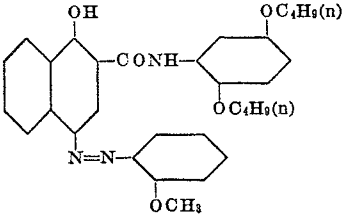


wherein R represents a mononuclear 2'-(2,4-di-tert-amylphenoxy)-aryl radical.

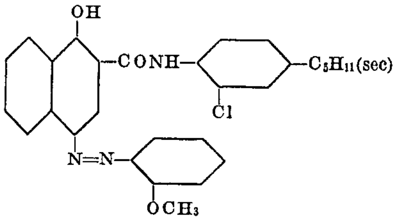
8. A silver halide emulsion layer containing a coupler compound having the formula



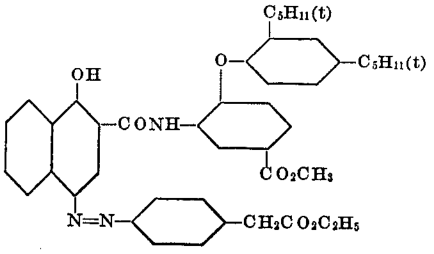
9. A silver halide emulsion layer containing a coupler compound having the formula



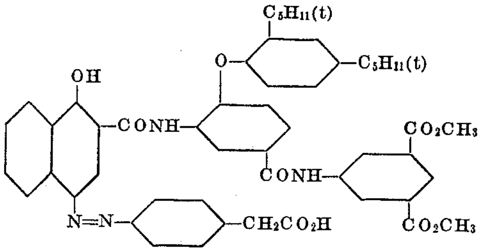
10. A silver halide emulsion layer containing a coupler compound having the formula



11. A silver halide emulsion layer containing a coupler compound having the formula



12. A silver halide emulsion layer containing a coupler compound having the formula



13. The mehod of developing a colored image in a silver halide emulsion layer which comprises incorporating in said layer a coupler compound selected from those having formulas set forth in claim 1, exposing the layer and developing it with a primary aromatic amino developing agent, thereby splitting off the —N═N—R′ group in the compound and coupling the compound at the point of splitting with the oxidation product of said developing agent to form a dye image.

References Cited in the file of this patent

UNITED STATES PATENTS

2,521,908	Glass et al.	Sept. 12, 1950