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MAGENTA-COLORED CYAN-FORMING COUPLERS

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12 Claims. (Cl. 96—55)

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

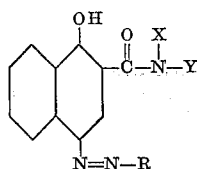
Color-forming compounds which react during photographic development with the development product of aromatic amino developing agents to form colored images are well known. Generally, these color-forming compounds are colorless or substantially colorless. This lack of color is usually desirable when the coupler is to be incorporated in the emulsion layer and the unused coupler remains after formation of the colored image.

Couplers which are in themselves more or less strongly colored and which contain a chromophore group which is split off or destroyed during and by means of the coupling reaction with the result that the original color of the coupler is destroyed and a new dye is formed upon coupling are disclosed in Glass, Vittum and Weissberger U.S. Patents 2,453,661, November 9, 1948; 2,455,169, November 30, 1948; 2,455,170, November 30, 1948; 2,521,908, September 12, 1950; and Graham U.S. 2,706,684, April 19, 1955.

Upon development of 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, consisting of the new dye and the residual colored coupler. The theory of color correction requires that the sum of the absorption of the residual colored coupler and the undesired absorption of the image dye should be nearly constant.

In order to correct for color deficiencies of the cyan dye produced upon color development, it is desirable to have magenta-colored couplers with high green-absorption relative to the blue-absorption and no red-absorption. This is especially true where overcorrection is desired. This requirement is not always fulfilled by colored couplers of prior art.

In U.S. Patent 2,521,908, 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. All the compounds described in this patent are yellow to orange-red in color, rather than the desired magenta color.

In U.S. Patent 2,706,684 are described 1-hydroxy-2-naphthanilide colored coupler compounds having the above formula in which X is hydrogen, Y is a mononuclear aryl radical substituted in a position ortho to the amido group with either halogen, alkoxy or mononuclear aryloxy radicals and R is a mononuclear aryl radical. Most of these coupler compounds have the desired magenta color. However, since this color depends upon

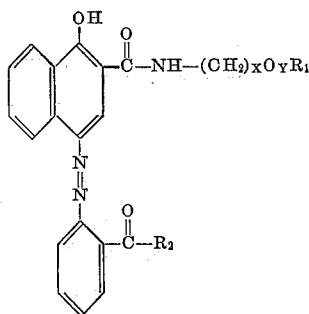
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the presence of a substituent in an ortho position on the anilide nucleus, the cyan dye produced during color development must also contain this nucleus. Although such compounds are useful, there are instances where this restriction of the type of cyan dye which can be produced would be objectionable. For instance, the dyes produced by color development of the colored couplers described in the above patent are greenish rather than cyan in color, since their absorption maxima are well in the infrared.

It is therefore an object of the present invention to provide magenta-colored cyan-forming couplers which will make it possible to correct for the color deficiencies in the cyan dye produced upon color development. A further object is to provide couplers which are not only magenta-colored but which are significantly less restricted than prior art compounds with respect to the types of cyan dyes which can be produced by means of photographic color development. A further object is to provide magenta-colored cyan-forming couplers which demonstrate unusually large bathochromic shifts that are unexpected in view of the small chemical differences from other couplers. A further object is to provide a magenta-colored cyan-forming coupler which will overcorrect for the deficiencies in the cyan dye produced upon color development. A still further object is to provide non-diffusing magenta-colored cyan-forming couplers which can be used in combination with uncolored cyan-forming couplers in photographic silver halide emulsions to correct for the color deficiencies in the cyan dye produced upon color development. Other objects will appear from the following description and claims.

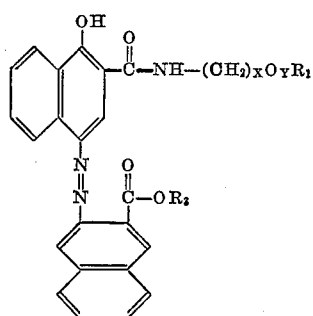
These and other objects are accomplished by means of this invention by using magenta-colored cyan-forming couplers which we have discovered. These new couplers all have a nucleus consisting of a 1-hydroxy naphthamide with an oxaralkyl, an alkyl, an aryl, or an aryloxyphenyl substituent on the amide group and an azo group substituent para to the hydroxyl. This common nucleus is connected either to a 1-phenyl-2-keto grouping or to a 2-naphthyl-3-carbalkoxy group. These couplers are not only magenta-colored but all have a max of at least 500 mμ and demonstrate unusually large bathochromic shifts from prior art couplers. These bathochromic shifts are unexpected in view of the small chemical differences between our couplers and the non-magenta-colored cyan-forming couplers known before. These couplers are not only magenta-colored but give much more freedom than prior art compounds because of the types of cyan dyes which can be produced from them during color development. Our couplers which have an alkyl, aryloxyalkyl, or alkyl substituted aryloxyalkyl radical attached to their amido group produce dyes upon color development that are truly cyan in color.

The preferred embodiments of this invention are magenta-colored cyan-forming coupler compounds selected from the group consisting of compounds with the general formulas:



and

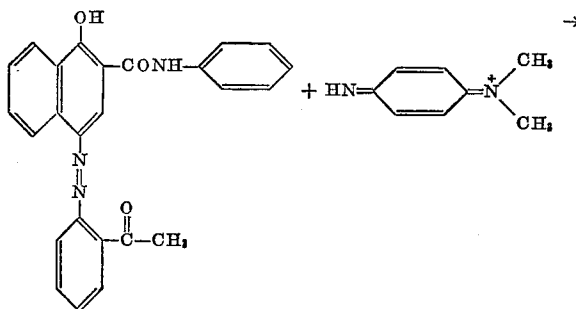
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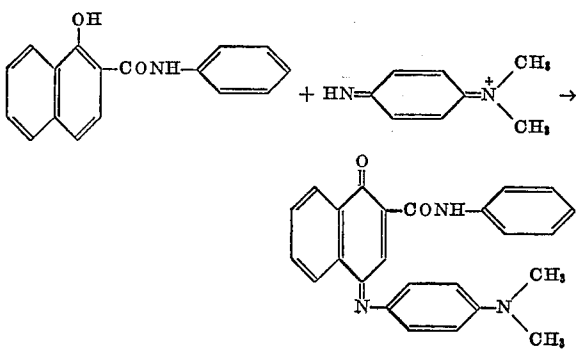
wherein X is an integer in the range of 0-4; Y is 0 or 1; R₁ is a member selected from the group consisting of phenyl radicals, alkyl radicals having from 6 to 15 carbon atoms, alkyl-substituted phenyl radicals and alkyl-substituted phenoxy phenyl radicals; R₂ is an alkyl group of 1-4 carbon atoms in either straight or branched chains; and R₃ is an alkyl group having 1 to 12 carbon atoms in either straight or branched chains.

The alkyl substituents on the phenyl and phenoxyphenyl radical of R₁ can be varied widely in size however they usually have from 1 to 15 carbon atoms.

The azo group attached to the active carbon which is para to the naphtholic hydroxyl 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 a light-sensitive photographic element. Thus, the coupler can be converted to a differently colored compound and the azo group readily removed from it by means of reaction with the oxidized developing agent. Although the exact mechanism of this reaction is not completely understood, the reaction appears to proceed as follows:



The compounds of this invention can be used in admixture with uncolored couplers which appear to react as follows:

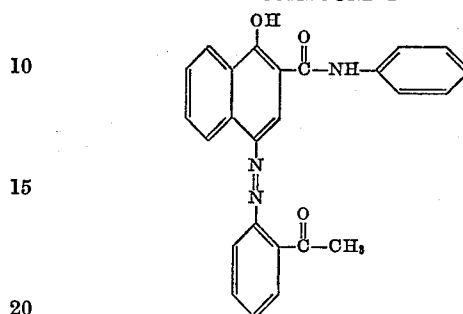


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to form the same dye as is formed from the colored coupler.

Typical compounds embodying the invention and which can be used according to our invention include the following which illustrate the invention but to which the invention is not limited:

COMPOUND I

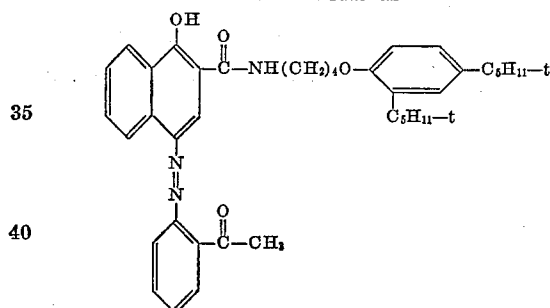


1-hydroxy-4-(2-acetyl phenylazo)-2-naphthamide

[Melting point—231-232° C.]

Composition	Calculated	Found
C	73.4	73.6
H	4.6	4.5
N	10.3	10.2

COMPOUND II

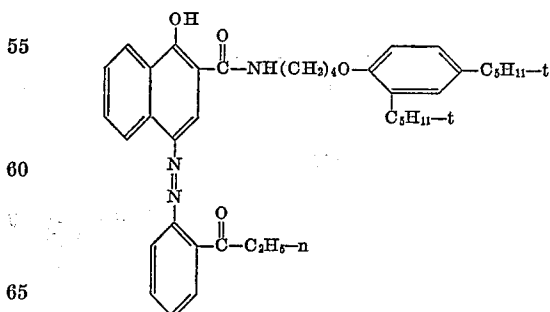


1-hydroxy-4-(2-acetyl phenylazo)-N-[5-(2,4-di-tert-amyloxy)butyl]-2-naphthamide

[Melting point—132-133° C.]

Composition	Calculated	Found
C	75.4	76.0
H	7.5	7.5
N	6.8	7.0

COMPOUND III

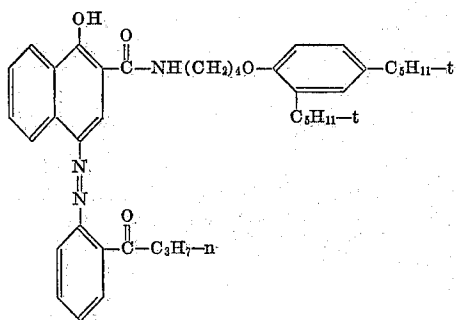


1-hydroxy-4-(2-propionyl phenylazo)-N-[5-(2,4-di-tert-amyloxy)butyl]-2-naphthamide

[Melting point—144-145° C.]

Composition	Calculated	Found
C	75.6	75.6
H	7.7	7.3
N	6.6	6.6

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COMPOUND IV

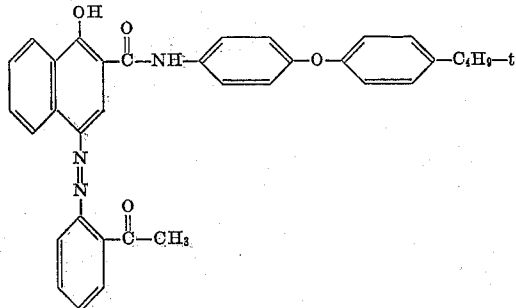


1-hydroxy-4-(2-butyryl phenylazo)-N-[δ-(2,4-di-tertiary-amyl phenoxy)butyl]-2-naphthamide

[Melting point—134–135° C.]

Composition	Calculated	Found
C.....	75.8	75.6
H.....	7.9	7.7
N.....	6.5	6.4

COMPOUND V

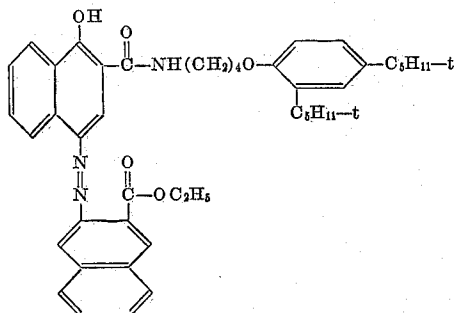


1-hydroxy-4-(2-acetyl phenylazo)-N-[4(p-tertiary-butyl phenoxy)phenyl]-2-naphthamide

[Melting point—233–239° C.]

Composition	Calculated	Found
C.....	75.4	75.7
H.....	5.6	5.5
N.....	7.5	7.6

COMPOUND VI

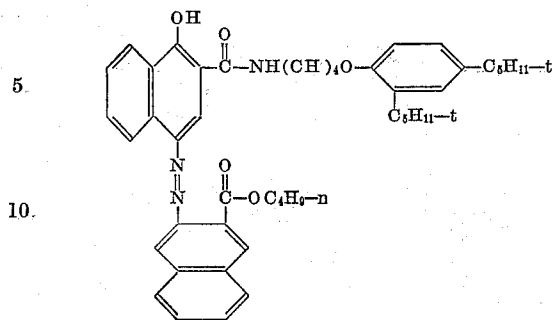


1-hydroxy-4-(3-carbomethoxy-2-naphthylazo)-N-[δ-(2,4-di-tertiary-amylphenoxy)butyl]-2-naphthamide

[Melting point—166–167° C.]

Composition	Calculated	Found
C.....	75.3	75.4
H.....	7.3	7.3
N.....	6.0	6.3

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COMPOUND VII

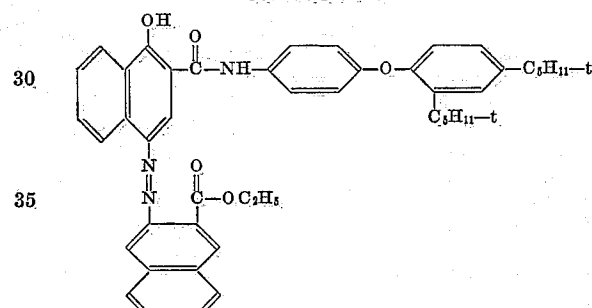


1-hydroxy-4-(3-carbobutoxy-2-naphthylazo)-N-[δ-(2,4-di-tertiary-amylphenoxy)butyl]-2-naphthamide

[Melting point—135–136.5° C.]

Composition	Calculated	Found
C.....	75.7	75.5
H.....	7.5	7.9
N.....	5.8	5.9

COMPOUND VIII

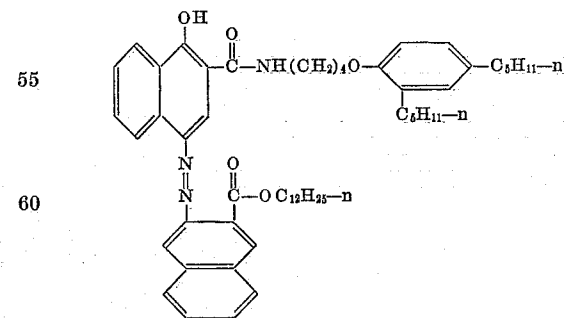


1-hydroxy-4-(3-carbomethoxy-2-naphthylazo)-N-[4-(2,4-di-tertiary-amylphenoxy)phenyl]-2-naphthamide

[Melting point—209–210° C.]

Composition	Calculated	Found
C.....	76.5	77.4
H.....	6.5	6.6
N.....	5.8	5.8

COMPOUND IX



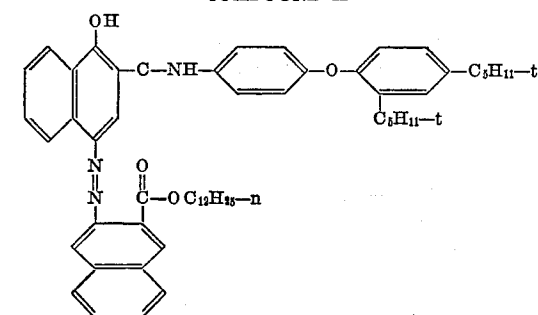
1-hydroxy-4-(3-carbododecoxy-2-naphthylazo)-N-[δ-(2,4-di-n-amylphenoxy)butyl]-2-naphthamide

[Melting point—92–95° C.]

Composition	Calculated	Found
C.....	76.9	76.7
H.....	8.5	8.
N.....	5.0	5.0

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COMPOUND X



1-hydroxy-4-(3-carbodecoxy-2-naphthylazo)-N-[4-(2,4-di-tertiary-amylphenoxy)phenyl]-2-naphthamide

[Melting point—117–119° C.]

Composition	Calculated	Found
C	78.1	78.
H	7.8	7.29
N	4.9	5.3

The objects of this invention can be accomplished with other colored coupler compounds as defined herein having a nucleus of 1-hydroxy-4-phenylazo-2-naphthamide with other aryl, alkyl, aryloxyalkyl or aryloxyphenyl radicals substituted on the amide and other keto groups substituted on the carbon at the 2-position of the phenylazo group, or with other colored couplers as defined herein having a nucleus consisting of 1-hydroxy-4-(2-naphthylazo)-2-naphthamide with other alkyl, aryl, aryloxyalkyl or aryloxyphenyl radicals substituted on the amide and other carbalkoxy or acyl groups substituted on the carbon in the 3rd position on the 2-naphthylazo group. All of these compounds have the common characteristic of being magenta-colored before development and forming a cyan dye upon development.

All of these compounds are further characterized by the unexpected bathochromic shift they demonstrate which makes them valuable for color correction in photographic silver halide emulsions.

The preferred colored coupler compounds of this invention have a $\lambda_{\max}$ of at least 500 $m\mu$. Typical $\lambda_{\max}$ values are shown in the following table.

TABLE I

Compound	$\lambda_{\max}$ Absorption Measurement Made on Film Coating in $m\mu$
I.	513
II.	508
III.	504
IV.	505
V.	515
VI.	519
VII.	522
VIII.	523
IX.	516
X.	518

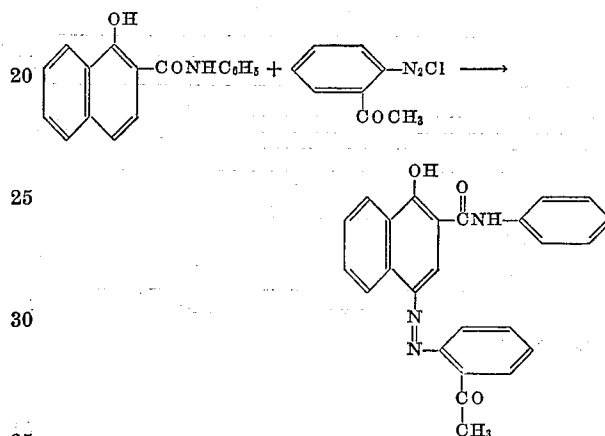
Our couplers show unusually and unexpectedly large bathochromic shifts from corresponding coupler compounds having a carbalkoxy group on the carbon in the two position on the phenylazo part of the nucleus and are, therefore, superior for correcting the color deficiencies of the cyan dye formed by color development. This is illustrated by the bathochromic shift of 13 $m\mu$ shown between the $\lambda_{\max}$ value for Compound IV and the corresponding carbalkoxy derivative 1-hydroxy-4-(2-carbopropoxy phenylazo) - N-[δ -2,4-di-tertiary - amylphenoxy]butyl]-2-naphthamide. This is further illustrated by the bathochromic shift of 32 $m\mu$ shown between the $\lambda_{\max}$ value for Compound VII and the coupler 1-hydroxy-4-(2-carbobutoxy phenylazo)-N-[δ -2,4-di-tertiary - amylphenoxy]-butyl]-2-naphthamide. The very large bathochro-

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mic shifts of 26 and 43 $m\mu$ respectively between our Compound IV and Compound 9 of U.S. Patent 2,521,908 and between our Compound VII and Compound 9 of U.S. Patent 2,521,908 are also evidenced by very marked differences in color. Our compounds are magenta-colored while Compound 9 of U.S. Patent 2,521,908 is orange-colored.

The compounds employed according to our invention may be prepared by any suitable method such as the reaction of the 1-hydroxy-2-naphthamide with the appropriate diazonium chloride compound. Equal molar quantities of the 1-hydroxy-2-naphthamide and aminehydrochloride are used. A 10% excess of NaNO_2 over the equal molar amount is used to prepare the diazonium chloride from the aminehydrochloride.

Compound I is prepared as follows:



The 1-hydroxy-2-naphthylamine (13.2 g., 0.05 mole) is dissolved in 200 ml. pyridine and the solution chilled in an ice bath. O-amino acetophenone hydrochloride (8.6 g., 0.05 mole) is dissolved in 50 ml. 10% hydrochloric acid and the solution chilled to 0° C. Sodium nitrite (3.9 g., 0.05 mole+10% excess) is dissolved in 5 ml. H_2O and added to the chilled acid solution. After 30 minutes, sulfamic acid is added to the diazonium solution to remove excess sodium nitrite and the diazonium solution is added to the chilled pyridine solution with stirring. After several hours the dye is collected, washed well with H_2O and dried. The dye is recrystallized from one liter glacial acetic acid. A yield of 13.5 g. was obtained by using this procedure.

Compound II is prepared by the following procedure. Commercial 2,4-tertiary-di-amylphenol and γ -chlorobutyronitrile are condensed in the presence of alkali. The resultant γ -2,4-tertiary-di-amylphenoxybutyronitrile is reduced to δ -2,4-tertiary-di-amylphenoxybutylamine and the amine condensed with an equivalent amount of 1-naphthol-2-carboxylic acid phenyl ester to give 1-hydroxy - N - [δ (2,4 - ditertiary-amylphenoxy) - n-butyl]-2-naphthamide. This naphthamide (38. g., 0.08 mole) is dissolved in 200 ml. pyridine and the solution chilled in an ice bath. O-amino-aceto phenone hydrochloride (13.7 g., 0.08 mole) is dissolved in 50 ml. of 10% hydrochloric acid, the solution is chilled to 0° C. and sodium nitrite (6.1 g., 0.088 mole) dissolved in 25 ml. H_2O is added. After 30 minutes the excess sodium nitrite is removed with sulfamic acid. The diazonium solution is slowly added to the pyridine solution and after several hours 1500 ml. H_2O is added. The dye is collected and washed well with H_2O . After drying, the dye is recrystallized from 1500 ml. of acetonitrile twice. A yield of 33. g. was obtained by using this procedure.

Compounds III, IV, and V are prepared in the same manner as Compound II using the couplers and diazonium salts listed in Table II. Compound V is purified by recrystallization from butanol in place of the acetonitrile used for Compound II.

TABLE II

Compound	Coupler	Diazonium Salt
III-----	1-hydroxy-N-[δ (2,4-di-tertiary- amylphenoxy)-butyl]-2- naphthamide.	O-propionyl benzene diazonium chloride
IV-----	do-----	O-butyl benzene diazonium chloride.
V-----	1-hydroxy-N-[4-(4-ter- tiary-butylphenoxy)-phenyl]- 2-naphthamide.	O-acetyl benzene diazonium chloride.

Compound VI is prepared by the following procedure. Ethyl-3-amino-2-naphthoate (28. g., 0.13 mole) dissolved in 100 ml. glacial acetic acid is added with stirring to a mixture of 100 ml. concentrated hydrochloric acid and 100 g. of ice. A solution of sodium nitrite (10. g., 0.13 mole +10% excess) in 25 ml. H₂O is added to the acid solution. After 30 minutes in an ice bath, sulfamic acid is added to remove excess sodium nitrite. This diazonium solution is added with stirring to an ice-chilled solution of the naphthamide dissolved in 500 ml. of pyridine. After standing several hours 500 ml. of H₂O is added and the dye is collected, washed well with H₂O and dried. The product, coupler Compound VI, is recrystallized from one liter of butanol. A yield of 79. g. was obtained by using this procedure.

Compounds VII and VIII are prepared in the same manner as Compound VI using the couplers and diazonium salts shown in Table III. N-propanol, and 1:1 dioxane: ethanol are the solvents used to recrystallize Compounds VII and VIII respectively in place of butanol.

TABLE III

Compound	Coupler	Diazonium Salt
VII-----	1-hydroxy-N-[δ (2,4-di-ter- tiary-amylphenoxy)-n- butyl]-2-naphthamide.	3-(n-butoxycarbonyl)- β -naphthalene dia- zonium chloride.
VIII-----	1-hydroxy-N-[4-(2,4-di- tertiary-amylphenoxy) phenyl]-2-naphthamide.	3-(ethoxycarbonyl)- β - naphthalene dia- zonium chloride.

Compound IX is prepared by the following procedure. The 3-carbolauroxy-2-naphthylamide (2.37 g., 0.0067 mole) is slurried in 20 ml. glacial acetic acid at room temperature and 20 ml. 10% hydrochloric acid added. Sodium nitrite (0.52 g., 0.0075 mole) dissolved in 5 ml. H₂O and a small amount of ice are added to the hydrochloride mixture. This mixture is stirred in an ice bath for 30 minutes after which the excess sodium nitrite is destroyed with sulfamic acid. The diazonium solution is added with stirring to an ice chilled solution of the naphthamide (3.16 g., 0.0067 mole) dissolved in 25 ml. of pyridine. Coupler Compound IX, the product, is collected after several hours and recrystallized from n-propanol. A yield of 3.6 g. was obtained.

Compound X is prepared in the same manner as Compound IX by reacting 1-hydroxy-N-[4-(2,4-di-tertiary-amylphenoxy)-phenyl]-2-naphthamide with 3-carbolauroxy-2-naphthylene diazonium chloride.

Our compounds can be incorporated either in a developer solution or in the emulsion layer of photographic material according to their intended use and diffusion characteristics. They can be used in any photographic silver halide emulsion where cyan-forming couplers are used. A preferred use is in an emulsion layer of either a single or a multilayer color photographic material in order to secure color correction by masking effects described in Hanson U.S. Patent 2,449,966. The Hanson process involves the color correction method in which a colored color-forming coupler is incorporated in the photographic emulsion layer prior to exposure and upon development is converted to a differently colored image where the layer was exposed. The coupler remaining in the unexposed portion of the layer retains its original color and by a suitable choice of the color of the original

coupler and the color of the final dye image, a masking or color correction effect can be obtained. The compounds of this invention provide colored couplers which are magenta-colored and still form the desired cyan image.

Our magenta-colored cyan-forming coupler compounds can be used alone or in conjunction with uncolored cyan-forming couplers to control the amount of correction or overcorrection produced by the masking process. The use of colored with uncolored couplers is described in Vittum et al. U.S. Patent 2,428,054, September 30, 1947. Usually when uncolored and colored couplers are used together for correction masking, a colored coupler is selected which forms an image of the same dye or a dye of the same hue as the image dye formed with the uncolored coupler upon coupling with the development product of a color developer such as a primary aromatic amino developing agent. The relative proportions of the colored and uncolored couplers used in the mixture can be readily determined from spectral absorption curves or from densitometric curves as illustrated by Vittum et al. In general when our colored couplers are used with uncolored couplers rather than being used alone, they will be used in an amount between 10% and 70% of the total amount of colored and uncolored couplers.

The differently sensitized superimposed emulsion layers of a multilayer color photographic material can be arranged in any order on conventional types of support. Gelatin interlayers can be coated between the photographic elements or emulsion layers used to record each of the three individual primary colors.

The following examples illustrate typical ways in which our couplers can be incorporated and used in color photographic material:

Example I

0.15 gram of 1-hydroxy-N-[δ (2,4-di-tertiary-amylphenoxy)butyl]-2-naphthamide and 0.19 gram of 1-hydroxy-4-(2-acetylphenyl)-N-1-[δ (2,4-di-tertiary-amylphenoxy)butyl]-2-naphthamide, coupler Compound II, were dissolved in 0.67 gram of tri-o-cresyl phosphate by heating to about 120° C. with stirring. This solution was intimately mixed with and dispersed in one containing 17.7 ml. of 10% gelatin and 2.0 ml. of 5% alkanol B. The dispersion was mixed at 40° C. with 12.5 ml. of a melted negative speed silver bromide emulsion, 1.5 ml. of 7.5% saponin was added and the mixture was coated on a cellulose acetate support. After drying, the coating was exposed under an image and developed for 10 minutes in a 2-amino-5-diethylaminotoluene developing composition of the following formula to form a silver and cyan dye image:

	g.
4-amino-N,N-diethyl-3-methylaniline hydrochloride	2
4-amino-N,N-diethyl-3-methylaniline hydrochloride	20
Sodium sulfite	2
Potassium bromide	2
Water to make 1 liter.	

The film was then treated in a conventional acid stop bath for five minutes, washed for five minutes. The silver image and residual silver halide were removed by (1) treating five minutes in a potassium ferricyanide-potassium bromide bleach, (2) washing for five minutes and (3) fixing for five minutes in a hypo fixing bath. The film was given a final wash for ten minutes. The result was a negative cyan dye image having maximum absorption at a wavelength of 694 m μ and in the unexposed areas a masking colored coupler image having a maximum absorption at a wavelength of 508 m μ .

Example II

A multilayer color film was made as follows using emulsion melts made in a manner similar to that described in the single layer example above:

(1) A gelatin dispersion of a yellow coupler, α -ben-

zoyl-4-[α -(2,4 - di - tertiary-amyphenoxy)acetamido]-2-methoxyacetanilide dissolved in di-n-butylphthalate, was added to a blue-sensitive gelatin silver halide emulsion and coated as the bottom layer,

(2) A gelatin interlayer,

(3) A gelatin dispersion of cyan coupler, 1-hydroxy-N-[δ -(2,4 - di-tertiary - amyphenoxy)butyl] - 2 - naphthamide and Compound II, 1-hydroxy-4-(2-acetylphenylazo)-N-[δ - (2,4 - di - tertiary - amyphenoxy)butyl] - 2 - naphthamide dissolved in tri-o-cresylphosphate, was added to a red-sensitive silver halide emulsion, and coated as the third layer,

(4) A gelatin interlayer was coated as the fourth layer,

(5) A gelatin dispersion of magenta coupler, 1-(p-tertiarybutylphenoxyphenyl)-3 - α - (p-tertiarybutylphenoxy)propionyl-amino-5-pyrazolone, and colored magenta coupler, 1 (p-tertiary-butylphenoxyphenyl)-3- α -(p-tertiarybutylphenoxy) - propionylamino - 4 - (p-methoxyphenylazo)-5-pyrazolone, dissolved in tri-o-cresylphosphate, was added to a green-sensitive silver halide emulsion and coated as the top sensitive layer. The film was exposed and processed in the same manner as the single layer material above to yield a color-corrected three color dye image.

Example III

0.35 gram of 1-hydroxy-4-(2-acetylphenylazo)-N-[δ -(2,4-ditertiary amyphenoxy)butyl] - 2 - naphthamide, coupler Compound II, was dissolved in 0.70 gram of tri-o-cresyl phosphate by heat to about 120° C. with stirring. This solution was intimately mixed with and dispersed in one containing 17.7 ml. of 10% gelatin and 2.0 ml. of 5% alkanol B. The dispersion was mixed at 40° C. with 12.5 ml. of melted negative speed silver bromide emulsion, 1.5 ml. of 7.5 saponin was added, and the mixture was coated on a cellulose acetate support. After drying, the coating was exposed under an image and developed for 10 minutes in the developer composition defined in Example I. The film was then treated in a conventional acid short stop bath for 5 minutes, and washed for 5 minutes. The silver image and residual silver halide were removed by the procedure described in Example I. The result was a negative cyan dye image having maximum absorption at a wavelength of 694 m μ and in the unexposed areas a masking colored coupler image having a maximum absorption at a wavelength of 508 m μ .

The color developing agents used for development of emulsion layers containing our couplers or for the development of emulsion layers in the presence of our couplers include the well-known primary aromatic amino silver halide developing agents such as the phenylenediamines including the alkyl phenylene diamines and alkyl toluene diamines. These developing agents are usually used in the salt form such as the hydrochloride or sulfate which is more stable than the amine. The p-amino-phenols and their substitution products may also be used where the amino group is unsubstituted. The N-alkyl sulfonamido alkyl-p-phenylenediamine agents of U.S. Patent 2,193,015 are also very useful. All of the developing agents have an unsubstituted amino group which enables the oxidation product of the developer to couple with the color-forming compounds that form a dye image.

The couplers of our invention are used in photographic emulsions of the developing out type.

The emulsions can be chemically sensitized by any of the accepted procedures. The emulsions can be digested with naturally active gelatin, or sulfur compounds can be added such as those described in Sheppard U.S. Patent 1,574,944; Sheppard and Punnett U.S. Patent 1,623,499; and Sheppard and Brigham U.S. Patent 2,410,689.

The emulsions can also be treated with salts of the noble metals such as ruthenium, rhodium, palladium,

iridium, and platinum. Representative compounds are ammonium chloropalladate, potassium chloroplatinate, and sodium chloropalladate, which are used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in Smith and Trivelli U.S. Patent 2,448,060, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245 and 2,566,263.

The emulsions can also be chemically sensitized with gold salts as described in Waller, Collins, and Dodd U.S. Patent 2,399,083 or stabilized with gold salts as described in Damschroder U.S. Patent 2,597,856 and Yutzy and Leermakers U.S. Patent 2,597,915. Suitable compounds are potassium chloroaurate, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

The emulsions can also be chemically sensitized with reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850), polyamines, such as diethylene triamine (Lowe and Jones U.S. Patent 2,518,698), polyamines, such as spermine (Lowe and Allen U.S. Patent 2,521,925), or bis(β -aminoethyl) sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926).

The emulsions can also be optically sensitized with cyanine and merocyanine dyes, such as those described in Brooker U.S. Patents 1,846,301; 1,846,302; and 1,942,854; White U.S. Patent 1,990,507; Brooker and White U.S. Patents 2,112,140; 2,165,338; 2,493,747; and 2,739,964; Brooker and Keyes U.S. Patent 2,493,748; Sprague U.S. Patents 2,503,776 and 2,519,001; Heseltine and Brooker U.S. Patent 2,666,761; Heseltine U.S. Patent 2,734,900; VanLare U.S. Patent 2,739,149; and Kodak Limited British Patent 450,958.

The emulsions can also be stabilized with the mercury compounds of Allen, Byers, and Murray U.S. Patent 2,728,663; Carroll and Murray U.S. Patent 2,728,664, and Leubner and Murray U.S. Patent 2,728,665; the triazoles of Heimbach and Kelly U.S. Patent 2,444,608; the azaindenes of Heimbach and Kelly U.S. Patents 2,444,605 and 2,444,606; Heimbach U.S. Patents 2,444,607 and 2,450,397; Heimbach and Clark U.S. Patent 2,444,609; Allen and Reynolds U.S. Patents 2,713,541 and 2,743,181; Carroll and Beach U.S. Patent 2,716,062; Allen and Beilfuss U.S. Patent 2,735,769; Reynolds and Sagal U.S. Patent 2,756,147; Allen and Sagura U.S. Patent 2,772,164, and those disclosed by Birr in the Z. wiss. Phot. 47 2 (1952); the quaternary benzothiazolium compounds of Brooker and Staud U.S. Patent 2,131,038; and the zinc and cadmium salts of Jones U.S. Patent 2,839,405.

The emulsions may also contain speed-increasing compounds of the quaternary ammonium type of Carroll U.S. Patent 2,271,623; Carroll and Allen U.S. Patent 2,288,226; and Carroll and Spence U.S. Patent 2,334,864; and the polyethylene glycol type of Carroll and Beach U.S. Patent 2,708,162.

The emulsions may contain a suitable gelatin plasticizer such as glycerin; a dihydroxy alkane such as 1,5-pentane diol as described in Milton et al. U.S. Serial No. 588,951, filed June 4, 1956 now U.S. Patent 2,960,404, issued November 15, 1960; an ester of an ethylene bis-glycolic acid such as ethylene bis(methyl glycolate) as described in Milton U.S. Serial No. 662,564, filed May 31, 1957 now U.S. Patent 2,904,434, issued September 15, 1959; bis-(ethoxy diethylene glycol) succinate as described in Gray U.S. Serial No. 604,333, filed August 16, 1956 now U.S. Patent 2,940,854, issued June 14, 1960 or a polymeric hydrosol as results from the emulsion polymerization of a mixture of an amide of an acid of the acrylic acid series, an acrylic acid ester and a styrene-type compound as described in Tong U.S. Serial No. 311,319, filed September 24, 1952 now U.S. Patent 2,852,386, issued September 16, 1958. The plasticizer may be added to the emulsion before or after the addition of a sensitizing dye, if used.

The emulsion may be hardened with any suitable hardener for gelatin such as formaldehyde; a halogen-substituted aliphatic acid such as mucobromic acid as described in U.S. Patent 2,080,019 of White; a compound having a plurality of acid anhydride groups such as 7,8-diphenylbicyclo(2,2,2) - 7 - octene - 2,3,5,6 - tetracarboxylic dianhydride, or a dicarboxylic or a disulfonic acid chloride such as terephthaloyl chloride or naphthalene-1, 5-disulfonyl chloride as described in U.S. Patents 2,725,294 and 2,725,295 of Allen and Carroll; a cyclic 1,2-diketone such as cyclopentane-1,2-dione as described in U.S. Patent 2,725,305 of Allen and Byers; a bisester of methanesulfonic acid such as 1,2-di-(methanesulfonyl)-ethane as described in U.S. Patent 2,726,162 of Allen and Laakso; 1,3-dihydroxymethylbenzimidazole-2-one as described in U.S. Patent 2,732,316 of July, Knott and Polak; a dialdehyde or a sodium bisulfite derivative thereof, the aldehyde groups of which are separated by 2-3 carbon atoms such as β -methyl glutaraldehyde bis-sodium bisulfite as described in U.S. application Serial No. 556,031 of Allen et al., filed December 29, 1955; a bis-aziridine carboxamide such as trimethylene bis(1-aziridine carboxamide) as described in Allen et al. U.S. Serial No. 599,891, filed July 25, 1956 now U.S. Patent 2,950,197, issued August 23, 1960; or 2,3-dihydroxy dioxane as described in Jeffreys U.S. Serial No. 624,968, filed November 29, 1956 now U.S. Patent 2,870,013, issued January 20, 1959.

The emulsions may have been supplied with a coating aid such as saponin; a lauryl or oleyl monoether of polyethylene glycol as described in U.S. Patent 2,831,766 of Knox and Davis; a salt of a sulfated and alkylated polyethylene glycol ether as described in U.S. Patent 2,719,087 of Knox and Davis; an acylated alkyl taurine such as the sodium salt of N-oleoyl-N-methyl taurine as described in U.S. Patent 2,739,891 of Knox, Twardokus, and Davis; the reaction product of a dianhydride of tetracarboxybutane with an alcohol or an aliphatic amine containing from 8 to 18 carbon atoms which is treated with a base, for example, the sodium salt of the monoester of tetracarboxybutane as described in Knox et al. U.S. Serial No. 485,812, filed February 2, 1955 now U.S. Patent 2,843,487, issued July 15, 1958; a water-soluble maleopimarate or a mixture of a water-soluble maleopimarate and a substituted glutamate salt as described in U.S. Patent 2,823,123 of Knox and Fowler; an alkali metal salt of a substituted amino acid such as disodium N-(carbo-p-tert. octylphenoxy)pentaoxy glutamate as described in Knox et al. U.S. Serial No. 600,679, filed July 30, 1956; or a sulfosuccinamate such as tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate or N-lauryl disodium sulfosuccinamate as described in Knox et al. U.S. Serial No. 691,125, filed October 21, 1957 now U.S. Patent 2,992,108, issued July 11, 1961.

The couplers which we have described may be used in various kinds of photographic emulsions. Various silver salts may be used as the sensitive salt such as silver bromide, silver iodide, silver chloride or mixed silver halides such as silver chlorobromide or silver bromoiodide. The couplers can be used in emulsions of the mixed-packet type, such as described in Godowsky U.S. Patent 2,698,794 or emulsions of the mixed-grain type, such as described in Carroll and Hanson U.S. Patent 2,592,243. These couplers can also be used in emulsions which form latent images predominantly on the surface of the silver halide crystal or in emulsions which form latent images predominantly inside the silver halide crystal, such as those described in Davey and Knott U.S. Patent 2,592,250.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions there may be employed as the dispersing agent for the silver halide in its preparation, gelatin or some other colloidal material such as colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound.

Some colloids which may be used as polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in U.S. Patent 2,286,215 of Lowe; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19-26% as described in U.S. Patent 2,328,808 of Lowe and Clark, a water-soluble ethanolamine cellulose acetate as described in U.S. Patent 2,322,085 of Yutzky; a polyacrylamide having a combined acrylamide content of 30-60% and a specific viscosity of 0.25-1.5 or an imidized polyacrylamide of like acrylamide content and viscosity as described in U.S. Patent 2,541,474 of Lowe, Minsk and Kenyon; zein as described in U.S. Patent 2,563,791 of Lowe; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in U.S. Patent 2,768,154 of Unruh and Smith, or containing cyanoacetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in U.S. Patent 2,808,331 of Unruh, Smith, and Priest; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in Illingsworth U.S. Serial No. 527,872, filed August 11, 1955, now U.S. Patent 2,852,382, issued September 16, 1958.

If desired, compatible mixtures of two or more of these colloids may be employed for dispersing the silver halide in its preparation.

The couplers of our invention can be incorporated in photographic silver halide emulsions with any of the well-known uncolored cyan-forming couplers such as the following:

- 1-hydroxy-2-naphthanilide
- 1-hydroxy-N-[δ -(2,4-ditertiary-amyphenoxy)butyl]-2-naphthamide
- 1-hydroxy-N-[4(p-tertiarybutyl phenoxy)phenyl]-2-naphthamide
- 1-hydroxy-N-[4-(2,4-ditertiary-amyphenoxy)phenyl]-2-naphthamide
- 1-hydroxy-2-naphthoic-N-methylanilide
- 1-hydroxy-2-(N-ethyl,N- α -naphthyl)-naphthamide
- 1-hydroxy-2-(N-isoamyl,N-phenyl)-naphthamide
- 1-hydroxy-2-(N-isobutyl,N-p-amyphenyl)-naphthamide
- 1-hydroxy-2-(N-amyphenyl,N- α -naphthyl)-naphthamide
- 2-hydroxy-4'-[α (p-tertiary butylphenoxy)-propionamido]-diphenyl
- 2-(β -naphthalenesulfonamino)-phenol
- 2-(4'-phenoxybenzoylamino)-phenol
- 2[α -(4'-tertiary butylphenoxy)-propionylamino]-phenol
- 2- α -(p-tertiary amyphenoxy)-n-butylamino-5-methylphenol
- 2-(p'-tertiary amyphenoxy-p-benzoyl)amino-4-chloro-5-methylphenol
- 2-phenylcarbonyl-5-stearamidophenol
- 2-carbophenoxy-5-ethoxyphenol

Our couplers can be incorporated in emulsions with any of the uncolored cyan-forming couplers described in such U.S. patents as the following:

Inventor	U.S. Patent	Date of Issue
Salminen et al.	2,313,586	March 9, 1943.
Porter et al.	2,346,080	April 4, 1944.
Vittum et al.	2,362,598	November 14, 1944.
Salminen et al.	2,367,531	January 16, 1945.
Vittum et al.	2,369,929	February 20, 1945.
Weissberger	2,474,293	June 28, 1949.
Do.	2,589,004	March 11, 1952.
Godowsky	2,698,794	January 4, 1955.
Cressman	2,698,795	Do.
Sprung	2,704,709	March 22, 1955.
Hanson	2,704,711	Do.
Parmeter	2,710,802	June 14, 1955.
Salminen	2,710,803	Do.
Salminen et al.	2,728,660	December 27, 1955.
Tong	2,772,163	November 27, 1956.

Photographic emulsions containing our couplers may be coated on transparent supports such as glass, cellulose esters, or on a non-transparent reflecting material such as paper or opaque cellulose ester.

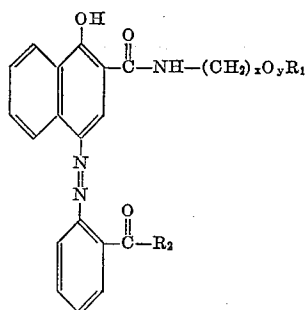
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The novel magenta-colored cyan-forming couplers of our invention described hereinabove, have λ_{MAX} of at least 500 m μ and show unusually large bathochromic shifts which make them valuable in color photography. These bathochromic shifts which are unexpected because of the relatively small chemical differences between our compounds and the non-magenta-colored cyan-forming compounds make the couplers of our invention particularly valuable for correcting the undesired green-light absorption of cyan dyes produced by color development. Our magenta-colored couplers produce upon color development, dyes that are cyan in color. This is a very significant advantage over prior art couplers which are limited as to usefulness by the greenish cyan colored dyes they produce upon color development. Our couplers can be used in any photographic emulsion where cyan couplers are used or can be used as we have described. Although our couplers can be used alone in a photographic silver halide emulsion, they are usually used in admixture with uncolored cyan-forming couplers to obtain the color correction for which they are particularly valuable. Our magenta-colored couplers are most useful in color photography, however they can also be used to dye any other materials which are dyed with azo dyes.

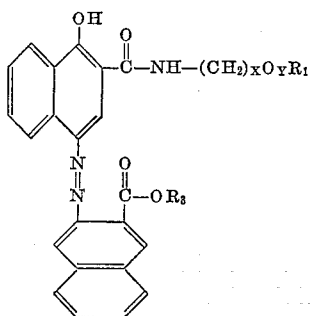
The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A photographic silver halide emulsion containing a magenta-colored cyan-forming coupler compound selected from the group consisting of compounds of the formula:



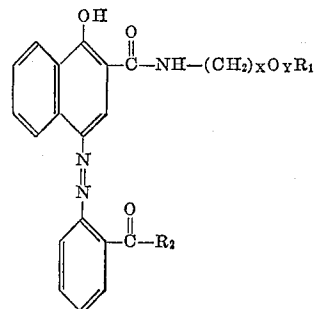
and



wherein X is an integer in the range of from 0 to 4; Y is an integer of from 0 to 1; R₁ is a member selected from the group consisting of alkyl radicals containing from 6 to 15 carbon atoms, phenyl radicals, alkphenyl radicals in which the alkyl group contains from 1 to 15 carbon atoms, alkphenoxy radicals in which the alkyl group contains from 1 to 15 carbon atoms, and alkphenoxyphenyl radicals in which the alkyl group contains from 1 to 15 carbon atoms; R₂ is an alkyl group having from 1 to 4 carbon atoms; and R₃ is an alkyl group having 1 to 12 carbon atoms.

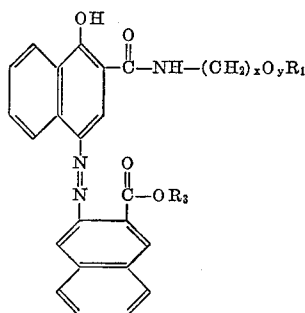
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2. A photographic silver halide emulsion containing a magenta-colored cyan-forming coupler of the formula:



wherein X is an integer of from 0 to 4; Y is an integer from 0 to 1; R₁ is a member selected from the class consisting of alkyl radicals containing from 6 to 15 carbon atoms, phenyl radicals, alkphenyl radicals in which the alkyl group contains from 1 to 15 carbon atoms, alkphenoxy radicals in which the alkyl group contains from 1 to 15 carbon atoms and alkphenoxyphenyl radicals in which the alkyl group has from 1 to 15 carbon atoms; and R₂ is an alkyl group having from 1 to 4 carbon atoms.

3. A photographic silver halide emulsion containing a magenta-colored cyan-forming coupler compound of the formula:



wherein X is an integer from 0 to 4; Y is an integer from 0 to 1; R₁ is a member selected from the group consisting of alkyl radicals containing from 6 to 15 carbon atoms, phenyl radicals, alkphenyl radicals in which the alkyl group contains from 1 to 15 carbon atoms, alkphenoxy radicals in which the alkyl group contains from 1 to 15 carbon atoms and alkphenoxyphenyl radicals in which the alkyl group contains from 1 to 15 carbon atoms; and R₃ is an alkyl group having from 1 to 12 carbon atoms.

4. A photographic gelatino silver halide emulsion containing 1-hydroxy-4-(2-acetyl phenylazo)-N-[δ -(2,4-di-tertiary-amylphenoxy)butyl]-2-naphthamide.

5. A photographic gelatino silver halide emulsion containing 1-hydroxy-4-(2-acetyl phenylazo) - N - [4(p-tertiary-butyl phenoxy)phenyl]-2-naphthamide.

6. A photographic gelatino silver halide emulsion containing 1-hydroxy-4-(3-carbethoxy - 2 - naphthylazo)-N-[4 - (2,4-di-tertiary-amylphenoxy)phenyl]-2-naphthamide.

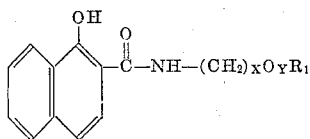
7. A photographic gelatino silver halide emulsion containing 1 - hydroxy-4-(3-carbododecoxy-2-naphthylazo)-N-[δ -(2,4-di-n-amylphenoxy)butyl]-2-naphthamide.

8. A photographic gelatino silver halide emulsion containing 1 - hydroxy-4-(3-carbethoxy-2-naphthylazo)-N-[δ -(2,4-di-tertiary-amylphenoxy)butyl]-2-naphthamide.

9. A photographic silver halide emulsion containing, in combination, a magenta-colored cyan-forming coupler compound as defined in claim 1 and an uncolored cyan-forming coupler which forms the same cyan dye as formed from the magenta-colored cyan-forming coupler upon coupling with the development product of a primary aro-

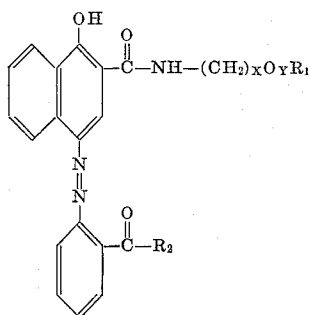
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matic amino developing agent, said uncolored coupler having the general formula:

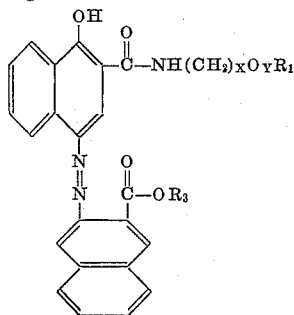


wherein X is an integer of from 0 to 4; Y is an integer from 0 to 1; and R₁ is a member selected from the group consisting of alkyl radicals containing from 6 to 15 carbon atoms, phenyl radicals, alkphenyl radicals in which the alkyl group contains from 1 to 15 carbon atoms, alkphenoxy radicals in which the alkyl group contains from 1 to 15 carbon atoms, alkphenoxyphenyl radicals in which the alkyl group contains from 1 to 15 carbon atoms.

10. A photographic silver halide emulsion containing in combination (a) a magenta-colored cyan-forming coupler compound selected from the class consisting of those having the formula:



and those having the formula:



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wherein X is an integer in the range of 0 to 4, Y is an integer from 0 to 1; R₁ is a member selected from the group consisting of alkyl radicals containing from 6 to 15 carbon atoms, phenyl radicals, alkphenyl radicals in which the alkyl group contains from 1 to 15 carbon atoms, alkphenoxy radicals in which the alkyl group contains from 1 to 15 carbon atoms, and alkphenoxyphenyl radicals in which the alkyl group contains from 1 to 15 carbon atoms; R₂ is an alkyl group containing from 1 to 4 carbon atoms; and R₃ is an alkyl group containing from 1 to 12 carbon atoms; and (b) an uncolored cyan-forming coupler which forms a dye upon coupling with the oxidation products of a primary aromatic amino developing agent.

11. The method of producing a cyan dye image against a magenta dye background in a latent image bearing silver halide emulsion layer containing an incorporated magenta-colored cyan-forming coupler of claim 1 comprising the steps of developing said layer in a primary aromatic amino developer to produce a combined silver and cyan dye image against a magenta dye and silver halide background and subsequently converting the silver to silver halide by bleaching, and then removing the silver halide by fixing said layer.

12. The method of producing a cyan dye image against a magenta dye background in a latent image bearing gelatino-silver halide emulsion layer containing the magenta-colored cyan-forming coupler 1-hydroxy-4-(2-acetylphenylazo)-2-naphthanilide comprising the steps of developing said layer in a primary aromatic amino developer to produce a combined silver and cyan dye image against a magenta dye and silver halide background and subsequently converting the silver to silver halide by bleaching, and then removing the silver halide by fixing said layer.

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