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3,458,315

CYAN COUPLERS FOR COLOR PHOTOGRAPHY
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No Drawing. Filed Oct. 24, 1965, Ser. No. 504,994

Int. Cl. G03c 1/40

U.S. Cl. 96—56.2

12 Claims

ABSTRACT OF THE DISCLOSURE

Two-equivalent couplers containing a 4-hydroxy-1-naphthyl group wherein the hydrogen atom in the 1-position of the said naphthyl group has been replaced with an imido group react with the oxidation product of an aromatic amino color developing agent to form a cyan dye and are advantageously incorporated in color developer compositions and photographic elements for color photography.

This invention relates to color photography and more particularly to new and improved cyan-dye-forming coupler compounds for use in image-forming systems, and to processes utilizing such couplers for the formation of images. In a more specific aspect, my invention relates to two-equivalent coupler compounds for forming cyan dye images in color photography.

The formation of color photographic images by the image-wise coupling of oxidized aromatic primary amino developing agents with color-forming or coupling compounds to form indoaniline, indophenol, and azomethine dyes is well known. In these processes, the subtractive process of color formation is ordinarily used and the image dyes customarily formed are cyan, magenta, and yellow, the colors that are complementary to the primary colors, red, green, and blue, respectively. Usually phenol or naphthol couplers are used to form the cyan dye image; pyrazolone or cyanoacetyl derivative couplers are used to form the magenta dye image; and acylacetamide couplers are used to form the yellow dye image.

In these color photographic systems, the color-forming coupler may be either in the developer solution or incorporated in the light-sensitive photographic emulsion layer so that, during development, it is available in the emulsion layer to react with the color developing agent that is oxidized by silver image development. Diffusible couplers are used in color developer solutions. Nondiffusing couplers are incorporated in photographic emulsion layers. When the dye image formed is to be used in situ, couplers are selected which form nondiffusing dyes. For image transfer color processes, couplers are used which will produce diffusible dyes capable of being mordanted or fixed in the receiving sheet.

Most of the couplers which have been used in the various color photographic systems described above are four-equivalent couplers, that is, they require reduction of 4 moles of silver halide for the formation of 1 mole of dye. Certain of the prior-art couplers are two-equivalent couplers, i.e., they require reduction of only 2 moles of silver halide for the formation of 1 mole of dye. However, some of the prior-art couplers exhibit serious disadvantages such as low reactivity, formation of an unacceptably high level of color fog, and other undesirable side reactions.

It is an object of my invention to provide new and improved two-equivalent 1-naphthol couplers capable of forming a dye on coupling with the oxidation product of an aromatic amino developing agent, said couplers being characterized from prior art cyan forming couplers by having an imido group in the coupling position.

It is a second object to provide such couplers having a materially reduced tendency to produce unwanted color density in the nonimage areas during color development.

It is another object of this invention to provide such two-equivalent couplers with greatly reduced propensity to unwanted side reactions during color development and hence higher dye yield.

It is a further object of this invention to provide new and improved two-equivalent cyan couplers which have good reactivity, thereby obviating prolonged or forced development.

It is another object of my invention to provide improved color photographic image-forming layers containing my novel couplers dispersed in a colloidal film-forming binder.

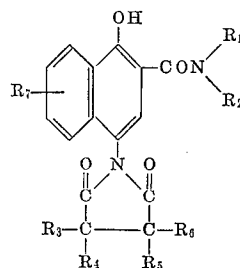
It is another object of my invention to provide a simple, economical, and reproducible process for preparing these couplers in high yield.

It is a further object to provide photographic silver halide-gelatin emulsion layers containing these new couplers for use in color photography.

It is another object of my invention to provide improved photographic cyan dye images by the use of these couplers.

These and other objects will appear from the following description of my invention. These and other objects are accomplished according to my invention by the preparation and use of my two-equivalent 1-naphthol couplers, in which the 4-position, that is, the coupling position is substituted with an imido group, preferably a 2,5-diketopolyhydropyrrole group having from two to four hydrogen atoms, said group being attached to the 4-position of the naphthol ring through the nitrogen atom in the pyrrole ring. The said imido group can be either monofunctional having one coupler moiety attached to it as described, or bifunctional with the nitrogen of each imido function attached to the carbon atom in the coupling position of separate coupler moieties. My couplers are derived from any of the known four-equivalent 1-naphthol couplers.

Included among the outstanding 4-imido-substituted couplers according to my invention are 4-cyclic imido derivatives of 1-hydroxy-2-naphthamides of the general formula:



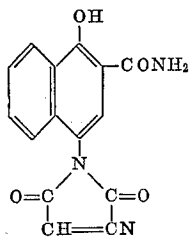
in which R₁ and R₂ represent any combination of hydrogen, an alkyl radical having either a straight or a branched chain of from 1 to 30 carbon atoms, a mono- or bicyclic alkyl radical such as cyclohexyl, terpenyl, e.g., a norbornyl radical, etc., an aryl radical (e.g., phenyl, tolyl, naphthyl, etc.), a heterocyclic radical having from 5 to 6 members in the heterocyclic ring (e.g., benzimidazolyl, benzoxazolyl, benzoselenazolyl, benzothiazolyl, thiazolyl, pyridyl, quinolyl, etc.), or together R₁ and R₂ provide the non-metallic atoms necessary to complete with the nitrogen atom between them, a heterocyclic group having 5 to 6 members in the ring, e.g., morpholine, piperidine, pyridine, pyrrolyl, etc. These groups, that is, alkyl, aryl, and heterocyclic as defined above may contain substituent groups such as halogen (e.g., chlorine, bromine, etc.), cyano, hydroxyl, carboxyl, amino, substi-

tuted amino (e.g., alkylamino, dialkylamino, anilino, N-alkylanilino, etc.), a carboxyl ester (e.g., a carboalkoxy, a carboaryloxy, etc.), an amido (e.g., acetamido, butyramido, ethylsulfonamido, N-methyl-benzamido, N-propylbenzamido, 4-t-butylbenzamido, etc.), a carbamyl (e.g., carbamyl, N-octadecylcarbamyl, N,N-dihexylcarbamyl, N-methyl-N-phenylcarbamyl, 3-pentadecylphenylcarbamyl, etc.), a sulfamyl (e.g., sulfamyl, N-propylsulfamyl, N-tolylsulfamyl, etc.), an alkoxy (e.g., ethoxy, octadecoxy, etc.), an aryloxy (e.g., phenoxy, tolyloxy, naphthylloxy, etc.), sulfo, sulfonyl, a substituted sulfonyl (e.g., methylsulfonyl, octadecylsulfonyl, ethoxysulfonyl, decoxysulfonyl, phenylsulfonyl, tolylsulfonyl, phenoxy-sulfonyl, etc.), and in which R₃, R₄, R₅, and R₆ may represent any combination of hydrogen, halogen (e.g., chlorine, bromine, etc.), alkyl having from 1 to 30 carbon atoms, alkoxy having from 1 to 30 carbon atoms, aryl, and aryloxy groups which may be unsubstituted or substituted by any of the groups described as substituents for the R₁ and R₂ groups, and R₄ and R₅ together may comprise a valence bond between the two carbon atoms to which they are attached and R₃, R₄, R₅, and R₆ may together comprise the atoms necessary to complete an isocyclic or heterocyclic ring, saturated or unsaturated, such, for example, as benzene, pyridine, cyclohexane, cyclohexene, furane, bicycloheptane, bicycloheptene, etc. The R₇ group represents hydrogen, lower alkyl having from 1 to 4 carbon atoms, lower alkoxy having from 1 to 4 carbon atoms, an amido group having from 1 to 4 carbon atoms, etc.

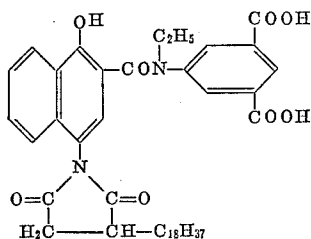
My novel couplers are characterized by an imido substituent in the coupling position, have good coupling reactivity and other valuable properties. Thus they induce unusually low levels of unwanted color fog upon color development, and they show good stability. Good coupling reactivity is obtained with couplers of my invention when incorporated in emulsion layers without the use of high-boiling coupler solvents. When high-boiling solvents are used to disperse these couplers, high dye yield and low color fog are attained over a wide range of coupler-to-solvent ratios. When the diffusible couplers of my invention are used in color developing solution, good reactivity and dye yield are achieved.

Included among my novel couplers are the following typical examples which are used to illustrate but not limit my invention:

(1) 1-hydroxy-4-maleimido-2-naphthamide



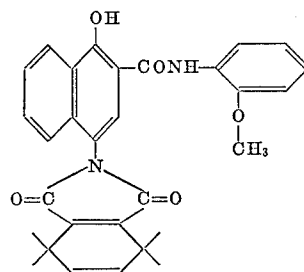
(2) 1-hydroxy-4-(octadecylsuccinimido)-N-ethyl-3',5'-dicarboxy-2-naphthanilide



(3) 1-hydroxy-4-succinimido-N-[δ-(4-t-butylphenoxy)-butyl]-2-naphthamide

(4) 1-hydroxy-4-maleimido-N-ethyl-2-naphthamide

(5) 1-hydroxy-4-(cis-4-cyclohexenyl-1,2-dicarboximido)-2'-methoxy-2-naphthanilide



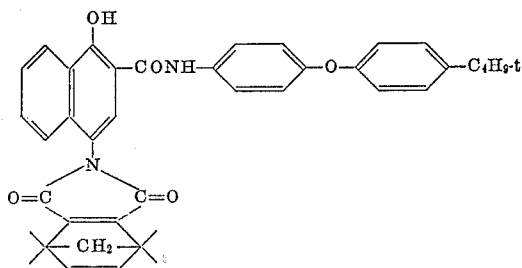
(6) 1-hydroxy-4-(1,2-cyclohexyldicarboximido)-N-(β-phenylethyl)-2-naphthamide

(7) 1-hydroxy-4-succinimido-N-[β-(2-acetamidophenyl)-ethyl]-2-naphthamide

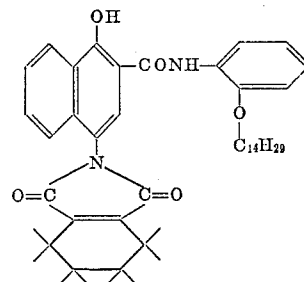
(8) 1-hydroxy-4-(4-carboxyphthalimido)-N-{β-[4-(α-(2,4-di-t-amylphenoxy)acetamido)phenyl]ethyl}-2-naphthamide

(9) 1-hydroxy-4-(4-methyl-4-cyclohexenyl-1,2-dicarboximido)-N,N-diethyl-2-naphthamide

(10) 1-hydroxy-4-(bicyclo[2,2,1]-5-heptenyl-2,3-dicarboximido)-4'-(4-t-butylphenoxy)-2-naphthanilide



(11) 1-hydroxy-4-(1,2-cyclohexyldicarboximido)-2'-tetradecyloxy-2-naphthanilide



(12) 1-hydroxy-4-(octadecylsuccinimido)-3',5'-dicarboxy-2-naphthanilide

(13) 1-hydroxy-4-(1,2-cyclohexyldicarboximido)-3'-[α-(3-pentadecylphenoxy)butyramido]-2-naphthanilide

(14) 1-hydroxy-4-(octadecylsuccinimido)-N-methyl-4'-sulfo-2-naphthanilide sodium salt

(15) 1-hydroxy-4-phthalimido-N-octadecyl-3',5'-dicarboxy-2-naphthanilide

(16) 1-hydroxy-4-maleimido-N-{β-[4-[2-(2,4-di-t-amylphenoxy)-5-(3,5-disulfo-2-naphthanilide)benzamido]-phenyl]ethyl}-2-naphthamide disodium salt

(17) 1-hydroxy-4-[4-(4-hydroxyphenylazo)phthalimido]-4'-(4-t-butylphenoxy)-2-naphthanilide

(18) 1-hydroxy-4-(cis-4-cyclohexenyl-1,2-dicarboximido)-N-octadecyl-2-naphthamide

(19) 1-hydroxy-4-succinimido-2-naphthomorpholide

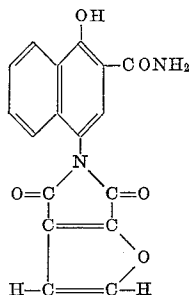
(20) 1-hydroxy-4-(4-methyl-4-cyclohexenyl-1,2-dicarboximido)-N-cyclohexyl-2-naphthamide

(21) 1-hydroxy-4-succinimido-N-methyl-N-(β-sulfoethyl)-2-naphthamide sodium salt

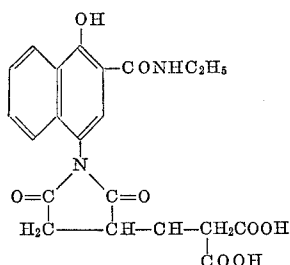
(22) 1-hydroxy-4-phthalimido-N-[B-(2-acetamidophenyl)ethyl]-2-naphthamide

(23) 1-hydroxy-4-(1,2-cyclohexyldicarboximido)-N-methyl-4'-sulfo-2-naphthanilide sodium salt

- (24) 1-hydroxy-4-(dodecenylsuccinimido)-N-ethyl-3',5'-dicarboxy-2-naphthanilide
 (25) 1-hydroxy-4-phthalimido-N-ethyl-3',5'-disulfo-2-naphthanilide disodium salt
 (26) 1-hydroxy-4-(4-carboxyphthalimido)-N-(2-benzimidazolyl)-2-naphthamide
 (27) 1-hydroxy-4-phthalimido-N-methyl-N-(β -sulfoethyl)-2-naphthamide sodium salt
 (28) 1-hydroxy-4-maleimido-N,N-(dicarboxymethyl)-2-naphthamide
 (29) 1-hydroxy-4-phthalimido-2-naphthamide
 (30) 1-hydroxy-4-phthalimido-N-[δ -(2,4-di-t-amylphenoxy)-butyl]-2-naphthamide
 (31) 1-hydroxy-4-(dodecenylsuccinimido)-N-[δ -(2,4-di-t-amylphenoxy)butyl]-2-naphthamide
 (32) 1-hydroxy-4-(1,2-cyclohexyldicarboximido)-N-[δ -(2,4-di-t-amylphenoxy)butyl]-2-naphthamide
 (33) 1-hydroxy-4-(bicyclo-[2,2,1]-5-heptenyl-2,3-dicarboximido)-N-[δ -(2,4-di-t-amylphenoxy)butyl]-2-naphthamide
 (34) 1-hydroxy-4-maleimido-N-[δ -(2,4-di-t-amylphenoxy)-butyl]-2-naphthamide
 (35) 1-hydroxy-4-(4-methyl-4-cyclohexenyl-1,2-dicarboximido)-N-[δ -(2,4-di-t-amylphenoxy)butyl]-2-naphthamide
 (36) 1-hydroxy-4-succinimido-N-[δ -(2,4-di-t-amylphenoxy)butyl]-2-naphthamide
 (37) 1-hydroxy-4-(cis-4-cyclohexenyl-1,2-dicarboximido)-N-[δ -(2,4-di-t-amylphenoxy)butyl]-2-naphthamide
 (38) 1-hydroxy-4-(4-carboxyphthalimido)-N-[δ -(2,4-di-t-amylphenoxy)butyl]-2-naphthamide
 (39) 1-hydroxy-4-(2,3-furyldicarboximido)-2-naphthamide

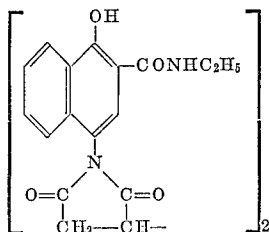


(40) 1-hydroxy-4-[3-(1,2-dicarboxyethyl)succinimido]-N-ethyl-2-naphthamide



The following coupler will serve to illustrate my couplers that are derived from a prior art four-equivalent coupler and contains a bifunctional imido group.

3,3' - bis[1 - (3-ethylcarbamy1-4-hydroxynaphthyl)succinimide]



Although this coupler contains two identical coupler moieties, the two coupler moieties can be different if this is desired.

Among still further couplers that are used to advantage according to my invention are included the following:

- 5 1-hydroxy-4-(octadecylsuccinimido)-N-ethyl-3',5'-acetoxy-2-naphthanilide,
 1-hydroxy-4-(octadecylsuccinimido)-N-ethyl 2',4',6'-trichloro-2-naphthanilide,
 10 1-hydroxy-4-(octadecylsuccinimido)-N-ethyl-3'-cyano-2-naphthanilide,
 1-hydroxy-4-succinimido-N-[β -(2-dimethylaminophenyl)ethyl]-2-naphthamide,
 1-hydroxy-4-succinimido-N-methyl-N-(β -sulfamylethyl)-2-naphthamide,
 15 1-hydroxy-4-(octadecylsuccinimido)-N-methyl-4'-methylsulfamyl-2-naphthanilide,
 1-hydroxy-4-succinimido-N-methyl-N-(β -ethylcarbamy1ethyl)-2-naphthamide,
 20 1-hydroxy-4-(methoxysuccinimido)-N-ethyl-3',5'-dicarboxy-2-naphthanilide,
 1-hydroxy-4-(phenylsuccinimido)-N-ethyl-3',5'-dicarboxy-2-naphthanilide,
 1-hydroxy-4-(chlorosuccinimido)-N-ethyl-3',5'-dicarboxy-2-naphthanilide, etc.

In the couplers of my invention, which are distinguished by their high coupling reactivity and the reduced tendency to produce color fog during color development, the imido groups provide a means of attaching other substituents such as, for example, preformed dyes useful in color correction, dye transfer processes, and the like. Additional ballasting groups can be introduced conveniently in the imido groups; these ballasting groups are then eliminated during the coupling reaction with oxidized color developer which forms the image dyes.

The diffusible couplers of my invention, such as couplers 1, 4, 5, 6, 7, 19, 20, 21, 22, 23, 25, 26, 27, 28, 29, and 39, are employed advantageously in color developing solutions used to color develop light-sensitive color photographic elements which do not contain the color-forming coupler. Any of the well known primary aromatic amino color-forming silver-halide developing agents such as the phenylenediamines, e.g.,

- 45 diethyl-p-phenylenediamine hydrochloride,
 monomethyl-p-phenylenediamine hydrochloride,
 dimethyl-p-phenylenediamine hydrochloride,
 2-amino-5-diethylaminotoluene hydrochloride,
 2-amino-5-(N-ethyl-N-laurylamino)toluene,
 50 N-ethyl-N-(β -methanesulfoamidoethyl)-3-methyl-4-aminoaniline,
 4-[N-ethyl-N-(β -hydroxyethyl)amino]aniline, etc.,

the p-aminophenols and their substitution products in which the amino group is unsubstituted, are used in the alkaline developing solution with my couplers. Various other materials may be included in the developer solutions depending upon the particular requirements, for example, an alkali metal sulfite, carbonate, bisulfite, bromide, iodide, etc., and the thickening agents used in viscous developer compositions such as carboxymethylcellulose, carboxyethyl cellulose, gelatin, etc. The following is a typical developer solution given to illustrate but not limit my invention.

	G.
65 2-amino-5-diethylaminotoluene HCl	2.0
Sodium sulfite (anhydrous)	2.0
Sodium carbonate monohydrate	20.0
Potassium bromide	1.0
70 Coupler	2.0
Water to 1000.0 ml.	

Couplers 21, 23, 25, 27, and 28 are diffusible couplers which form diffusible dyes on coupling with oxidized color developer, and are used to advantage in photographic emulsion layers.

The other coupler examples used to illustrate my invention are nondiffusing and are used to advantage in photographic emulsion layers. Couplers, such as 2, 8, 12, 14, 15, 16, 24, and 38, illustrate those that are incorporated as Fischer-type couplers. The other nondiffusing couplers, e.g., 9, 10, 11, 13, 18, 30, 31, 32, 33, 34, 35, 36, and 37, are incorporated in emulsion layers by methods such as are described by Mannes et al., U.S. Patent 2,304,939, issued December 15, 1942, Jelley et al., U.S. Patent 3,322,027, issued June 15, 1943, etc., in which high-boiling organic solvents are used to dissolve the coupler, and by methods described in Vittum et al., U.S. Patent 2,801,170 and Fierke et al., U.S. Patent 2,801,171, both issued July 30, 1957, and Julian, U.S. Patent 2,949,360, issued Aug. 16, 1960, in which low-boiling or water-soluble organic solvents are used with or in place of the high-boiling solvent. The use of such coupler dispersions permits thinner emulsion layers. These thinner layers are very desirable because they cause less light scattering, consequently, they produce sharper images.

The nondiffusing couplers 2, 12, 14, and 24 contain free acid groups (i.e., carboxy and sulfo) so that the dyes formed by these couplers are rendered diffusible. This valuable property enables these couplers to be used to advantage in image-transfer processes and as incorporated, diffusible-dye-forming competing couplers in conventional color films.

Coupler 17 contains a preformed dye attached to the coupler moiety through the imido group. This dye is eliminated during the coupling of the coupler with an oxidized color developer and diffuses out of the film. This coupler is used to advantage as a yellow-colored coupler for the purpose of correcting for the unwanted blue absorption of the cyan image dyes, i.e., that formed from the coupler itself as well as that formed from other cyan couplers. Generally, such a coupler as this would be used in combination with another image-forming cyan coupler in the same layer.

My couplers are used to advantage in the color development of photographic hydrophilic colloid-silver halide emulsion layers of the developing-out type in the emulsion layer or a contiguous layer. The emulsions may contain silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide, etc., as the light-sensitive material.

Any of the hydrophilic colloids used in making photographic emulsions can be used to advantage including gelatin, colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound, etc.

The emulsions used in the photographic element of my invention can be chemically or optically sensitized by methods well known in the art.

The couplers of my invention are also used to advantage in image-forming layers, either alone or with image-forming compounds other than silver halide, such as ZnO, ZnS, CdS, CdSe, NiS, etc., either with or without binders such as gelatin, polyvinyl alcohol, etc.

Usually my emulsions are coated on photographic supports in the form of multilayer color photographic elements wherein at least three differently sensitized emulsion layers are coated over one another on the support. Usually the support is coated in succession with a red-sensitive layer, a green-sensitive layer, and a blue-sensitive layer either with or without a Carey Lea silver yellow filter layer between the blue-sensitive and green-sensitive layers. The three differently color sensitized layers may be arranged in any other order over one another that is desirable; however, the Carey Lea filter layer obviously would not be put over the blue-sensitive layer. Preferably, these light-sensitive layers are arranged on the same side of the support.

Elements made for image transfer processing may use a separate reception sheet which is contacted with the light-sensitive layer during its development or the recep-

tion layer may be an integral part of the light-sensitive element. Any of the support materials mentioned previously may be used as the support for a separate reception sheet. The reception layer comprises a hydrophilic colloid layer containing a cationic mordant, e.g., the polymers of amino guanidine derivatives of vinyl methyl ketone such as described in Minsk U.S. Patent 2,882,156, granted Apr. 14, 1959.

My invention is further illustrated by the following typical examples.

Example 1

Samples of a single layer gelatin silver bromoiodide coating were exposed (i.e., for $\frac{1}{25}$ second on a 1B intensity scale sensitometer). These strips were then processed to color positives by the following process; all process temperatures were 68°.

	Minutes
MQ developer	5
Kodak F-5 fixing bath	5
Reexposure (i.e., 12" 100 watt bulb)	1
Color developer (formula below)	10
Kodak F-5 fixing bath	5
Water wash	5
Bleach (ferricyanide)	5
Water wash	5
Kodak F-5 fixing bath	5
Water wash	10
Drying.	

A conventional MQ Developer comprising an alkaline solution of hydroquinone and 4-methylaminophenol sulfate was used. The bleach was conventional, comprising aqueous alkali metal ferricyanide.

The Color Developer had the formula:

Benzy alcohol	ml	4.0
Sodium hexametaphosphate	g	0.5
Sodium sulfite, desiccated	g	2.0
Sodium hydroxide	g	0.16
Coupler ¹	g	2.0
4-amino-3-methyl-N-ethyl-N-[(β - (methanesulfonamido)ethyl]aniline sesquisulfate hydrate	g	5.0
Sodium carbonate monohydrate	g	50.0
Sodium bromide	g	0.2
Water to 1 liter.		
pH to 10.75.		

¹ The couplers used in the above mentioned developer formula were Couplers 1, 4, 5, 6, 7, 19, 20, 22, 26, 29, and 39, respectively.

Good cyan dye images were formed in each of the respective strips.

Example 2

Single layer gelatin silver bromoiodide coatings were prepared containing Couplers 3, 9, 10 11, and 13, respectively. Each of these couplers were dispersed in said coatings in the form of a finely-dispersed solution of the coupler in coupler solvent, di-n-butylphthalate. These coatings contained 10 parts of gelatin, 5 parts of silver, 2 parts of coupler, and 1 part of coupler solvent. Samples of the above mentioned coatings were given $\frac{1}{25}$ -second exposure on a 1B intensity scale sensitometer and processed in a conventional manner to color negatives, respectively, using the following developer solution:

Sodium sulfite (anhydrous)	g	2.0
2-amino-5-diethylaminotoluene HCl	g	2.0
Sodium carbonate monohydrate	g	20.0
Potassium bromide	g	2.0
Water to 1.0 l.		
pH to 10.86.		

Each of the processed strips contained high quality cyan dye images having good heat and light stability and low fog.

Example 3

Single layer gelatin silver bromiodide coatings containing Couplers 2, 12, 14, and 24, respectively, were prepared. These coatings were similar to those described in Example 2 above except that the couplers were dispersed directly in the gelatin. Samples of these coatings were exposed as described in Example 2 above, and processed by developing each of them for 5 minutes at 75° F. in contact with a receiving sheet containing a mordant which had been presoaked in the following developer solution:

	G.
Sodium carbonate monohydrate	22.0
Ascorbic acid	0.24
Potassium bromide	0.8
Sodium sulfite (anhydrous)	2.0
4-amino - N - ethyl-N-(β -hydroxyethyl)-aniline sulfite	11.0
Water to make 1.0 liter.	
pH adjusted to 12.5 using 20% sodium hydroxide solution.	

After the development period, samples of the film were removed from the mordant receiving sheet, in which sheets were contained the respective transferred and mordanted cyan dye images.

Example 4

Single layer camera speed gelatin silver bromiodide emulsions containing cyan-forming coupler and coupler solvent di-n-butyl phthalate were made for my couplers 30 to 35, respectively. The coatings contained 10 parts of gelatin, 5 parts of silver halide, 2 parts of coupler and 1 part of coupler solvent by weight.

Strips of the above coatings were given $\frac{1}{25}$ -second exposure on a 1B intensity scale sensitometer and processed through the following process:

Process step:	Time
Water dip	30"
Development	10'
Stop bath	5'
Ferricyanide beach	5'
Wash	5'
Fixing bath	5'
Wash	10'
Photo-Flo (wetting agent solution)	30"

The following developer solutions were used:

Developer 1

	Gm.
Sodium sulfite (anhydrous)	2
4-amino-N,N-diethyl-3-methylaniline hydrochloride	2
Sodium carbonate monohydrate	20
Potassium bromide	2
Water to 1 liter.	
pH 10.86.	

Developer 2

	ml.	Gm.
Benzyl alcohol	4.0	
Sodium sulfite (anhydrous)	2.0	
4 - amino - N - ethyl - 3 - methyl - N - [β - (methyl-sulfonamido)ethyl]aniline sesquisulfate hydrate	5.0	
Sodium carbonate, monohydrate	50.0	
Sodium bromide	0.86	
Sodium hydroxide (20% solution)	4.0	
Sodium hexameta phosphate	0.5	
Water to 1.0 liter.		
pH 10.75.		

The resulting cyan dye images were observed with a spectrophotometer to determine the λ -max values. The

photo data are given for the above mentioned processed strips below.

Coupler No.	Developer No.	λ -max
5 30	1	700
30	2	696
31	1	700+
31	2	698
32	1	697
32	2	687
33	1	700
33	2	688
10 34	1	700+
34	2	694
35	1	700
35	2	688

Similarly, other couplers of my invention are used to advantage in color photography as illustrated previously with representative couplers. Further, the couplers of my invention are valuable as cyan image-forming couplers in multilayer photographic color films containing other classes of couplers in the other layers of said film. Such other couplers are, for example, yellow image-forming couplers containing a methylene or substituted methylene group having two carbonyl groups directly attached thereto, and magenta image-forming couplers such as 5-pyrazolones, cyanoacetyl coumarones, etc.

In general, my couplers are the product of the reaction of a 1-hydroxy-4-amino-2-naphthamide with the appropriately substituted anhydride.

The following preparation of Coupler 30 illustrates the method used to prepare the 1-hydroxy-4-imido couplers of my invention.

A mixture of 24.5 g. of Intermediate 2 below and 7.4 g. of phthalic anhydride were heated at reflux in 400 ml. of glacial acetic acid for 6 hours, after which time the solid which had separated was collected, washed on the funnel with water, and air dried. This solid was recrystallized from dioxane, yielding the product.

Intermediate 1: 1-hydroxy-4-(4-methoxyphenylazo)-N-[δ -(2,4-di-t-amylphenoxy)butyl]-2-naphthamide.—To a cold (5° C.) solution of 12 g. of p-anisidine in 25 ml. of concentrated hydrochloric acid and 75 ml. of water was added dropwise with stirring, a solution of 7.2 g. of sodium nitrite in 40 ml. of water. The resulting diazonium solution was added dropwise at a rapid rate with stirring to a solution of 47.5 g. of 1-hydroxy-N-[δ -(2,4-di-t-amylphenoxy)butyl]-2-naphthamide (U.S. Patent 2,474,293) in 700 ml. of pyridine at 5° C., after which time the temperature of the mixture was permitted to come to 25° C. This mixture was then poured with stirring into 3 liters of water. The solid which separated was collected and recrystallized successively from methyl alcohol and acetonitrile, yielding the product.

Intermediate 2: 1-hydroxy-4-amino-N-[δ -(2,4-di-t-amylphenoxy)butyl]-2-naphthamide.—A mixture of 12 g. of Intermediate 1 above in 100 ml. of ethanol was hydrogenated using the Parr hydrogenation apparatus at room temperature with Raney nickel as the catalyst. After the reduction was completed, the catalyst was removed by filtration and the filtrate was diluted with 100 ml. of water, whereupon a solid crystallized, was filtered, washed with water, and dried. It was then recrystallized from cyclohexane, yielding the product.

The bis type of couplers illustrated by 3,3'-bis[1-(3-ethylcarbonyl-4-hydroxynaphthyl)succinimide] are prepared to advantage by reacting the appropriate bifunctional anhydride (e.g., 4,4'-bis(succinic anhydride) in the immediate example) with the 4-amino derivative of the 1-naphthol coupler (e.g., 4-amino-1-hydroxy-N-ethyl-2-naphthamide in the immediate example).

Unsymmetrical couplers of my invention having two different coupler moieties per molecule are prepared to advantage by reacting the appropriate 4-(1',2'-dicarboxyethyl)succinic anhydride with the 4-amino derivative of one 1-naphthol coupler followed by appropriate treatment of the resulting coupler to remove a molecule of water from each of the 1,2-dicarboxyethyl groups to form

the corresponding anhydride and subsequently reacting this compound with the second 4-amino-1-naphthol coupler.

Similarly, the other couplers of my invention are readily prepared by the illustrative reactions described. The parent four-equivalent couplers and the appropriate acid anhydrides are prepared by methods well known in the art. Many of these compounds are available.

The two-equivalent image-forming couplers of my invention are distinguished from other two-equivalent couplers by having an imido group substituted on the coupling position of the coupler molecule. My couplers are characterized by not producing color fog, a problem with certain prior art two-equivalent couplers, and by having good coupling reactivity. These couplers are dispersed readily in emulsion layers as a coupler solvent solution having a wide range of coupler to solvent ratios.

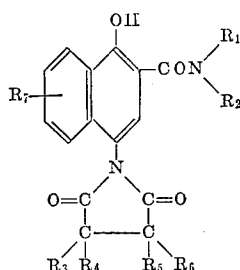
My couplers are not only valuable for the reasons cited, but because photographic emulsion layers color developed with them require only one-half the amount of silver halide required by four-equivalent couplers. Of particular value are certain of my nondiffusing couplers which have high coupling reactivity when dispersed in photographic emulsion layers without any high boiling solvent. These couplers are coated to advantage in particularly thin layers that produce good sharp images. The couplers of my invention may be used in emulsion layers either alone or admixed with other couplers, and the like.

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.

I claim:

1. An image-forming layer containing a two-equivalent coupler which is capable of forming a dye on coupling with the oxidation product of an aromatic amino developing agent, said coupler containing at least one 4-hydroxy-1-naphthyl group wherein the hydrogen atom of the 1-position of said naphthyl group has been replaced with an imido group.

2. An image-forming layer containing a coupler of the formula:



wherein R_1 and R_2 each represent a group selected from the class consisting of the hydrogen atom, an alkyl radical, an aryl radical, heterocyclic radical having 5 to 6 members in the ring, and, together, the nonmetallic atoms necessary to complete with the nitrogen atom between them a nitrogen containing heterocyclic ring having from 5 to 6 members in the ring; R_3 , R_4 , R_5 , and R_6 each represent a group selected from the class consisting of the hydrogen atom, an alkyl radical, an alkoxy radical, an aryl radical, an aryloxy radical, R_4 and R_5 taken together form a valence bond between the two carbon atoms, and R_3 , R_4 , R_5 , and R_6 taken together provide the atoms necessary to complete a ring selected from the class consisting of isocyclic and heterocyclic, and R_7 represents a group selected from the class consisting of hydrogen, lower alkyl, lower alkoxy, and a lower amido group.

3. An image-forming layer of claim 2 containing a silver halide emulsion.

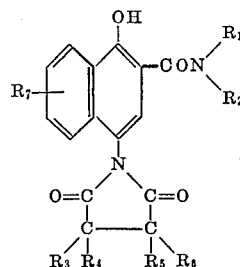
4. A light-sensitive hydrophilic colloid-silver halide emulsion containing 1-hydroxy-4-phthalimido-N-[δ -(2,4-di-t-amylphenoxy)butyl]-2-naphthamide.

5. A light-sensitive hydrophilic colloid-silver halide emulsion containing 1-hydroxy-4-(dodecylsuccinimido)-N-[δ -(2,4-di-t-amylphenoxy)butyl]-2-naphthamide.

6. A light-sensitive hydrophilic colloid-silver halide emulsion containing 1-hydroxy-4-(1,2-cyclohexyldicarboximido)-N-[δ -(2,4-di-t-amylphenoxy)butyl]-2-naphthamide.

7. In a multilayer multicolor element containing incorporated color-forming couplers, the improvement comprising the incorporation of a two-equivalent coupler which is capable of forming a dye on coupling with the oxidation product of an aromatic amino developing agent, said coupler containing at least one 4-hydroxy-1-naphthyl group wherein the hydrogen atom of the 1-position of said naphthyl group has been replaced with an imido group.

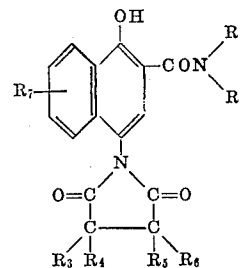
8. In a multilayer multicolor element containing incorporated color formers, the improvement comprising the incorporation of a coupler of the formula:



wherein R_1 and R_2 each represent a group selected from the class consisting of the hydrogen atom, an alkyl radical, an aryl radical, a heterocyclic radical having 5 to 6 members in the ring, and, together, the nonmetallic atoms necessary to complete with the nitrogen atom between them a nitrogen containing heterocyclic ring having from 5 to 6 members in the ring; R_3 , R_4 , R_5 , and R_6 each represent a group selected from the class consisting of the hydrogen atom, an alkyl radical, an alkoxy radical, an aryl radical, an aryloxy radical, R_4 and R_5 taken together form a valence bond between the two carbon atoms, and R_3 , R_4 , R_5 , and R_6 taken together provide the atoms necessary to complete a ring selected from the class consisting of isocyclic and heterocyclic, and R_7 represents a group selected from the class consisting of hydrogen, lower alkyl, lower alkoxy, and a lower amido group.

9. In an image-forming layer, the improvement comprising the use of a coupler which is capable of forming a dye on coupling with the oxidation product of an aromatic amino developing agent, said coupler containing at least one 4-hydroxy-1-naphthyl group wherein the hydrogen atom of the 1-position of said naphthyl group has been replaced with an imido group.

10. In an image-forming layer, the improvement comprising the use of a coupler of the formula:



wherein R_1 and R_2 each represent a group selected from the class consisting of the hydrogen atom, an alkyl radical, an aryl radical, a heterocyclic radical having 5 to 6 members in the ring, and, together, the nonmetallic atoms necessary to complete with the nitrogen atom between them a nitrogen containing heterocyclic ring having from 5 to 6 members in the ring; R_3 , R_4 , R_5 , and R_6 each repre-

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sent a group selected from the class consisting of the hydrogen atom, an alkyl radical, an alkoxy radical, an aryl radical, an aryloxy radical, R₄ and R₅ taken together form a valence bond between the two carbon atoms, and R₃, R₄, R₅ and R₆ taken together provide the atoms necessary to complete a ring selected from the class consisting of isocyclic and heterocyclic, and R₇ represents a group selected from the class consisting of hydrogen, lower alkyl, lower alkoxy, and a lower amido group.

11. A process for forming a cyan dye image in an image-forming layer comprising the step of contacting the said layer with an aqueous developer solution comprising an alkali and a primary aromatic amino developing agent in the presence of a coupler which is capable of forming a cyan dye on coupling with the oxidation product of an aromatic amino developing agent, said coupler containing at least one 4-hydroxy-1-naphthyl group

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wherein the hydrogen atom of the 1-position of said naphthyl group has been replaced with an imido group.

12. A process according to claim 11 in which the image-forming layer contains a silver halide emulsion.

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U.S. Cl. X.R.

96—55