United States Patent [15] **3,658,545**
Iwama et al. [45] **Apr. 25, 1972**

[54] LIGHT-SENSITIVE SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL CONTAINING CYAN COUPLERS

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[22] Filed: **Dec. 19, 1969**

[21] Appl. No.: **886,779**

[30] **Foreign Application Priority Data**

Dec. 20, 1968 Japan..................................43/93070

[52] **U.S. Cl.**..**96/100,** 96/9
[51] **Int. Cl.**..**G03c 1/40**
[58] **Field of Search**......................................96/9, 56.1, 100

[56] **References Cited**

UNITED STATES PATENTS

2,521,908	9/1950	Glass et al.	96/56.1
2,808,329	10/1957	Whitmore	96/9
3,034,892	5/1962	Gledhill et al.	96/100

Primary Examiner—J. Travis Brown
Attorney—Waters, Roditi, Schwartz & Nissen

[57] **ABSTRACT**

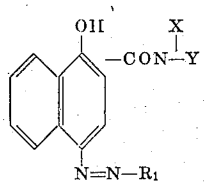
New colored cyan couplers useful in color photography can be obtained by substitution of a cyan coupler of the 1-hydroxy-2-naphtamide type at its 4-position with a particular new arylazo group. These colored cyan couplers provide light-sensitive silver halide color-photographic material, which exhibits high photographic speed and which is free from color tone deviation over a wide pH range.

2 Claims, No Drawings

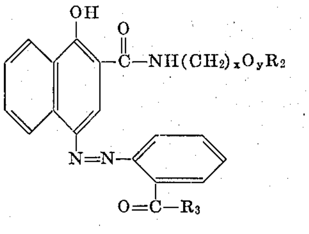
LIGHT-SENSITIVE SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL CONTAINING CYAN COUPLERS

The present invention relates to a light-sensitive silver halide color photographic material containing cyan coupler which has appreciable solubility in a water-immiscible high boiling solvent (hereinafter known as coupler solvent), said cyan coupler falling within the class of so-called colored couplers which provide auto-masking mechanism for the light-sensitive silver halide color photographic material so as to compensate for the deficient color reproductivity of said material. Almost all the cyan couplers used as color former in color photography are compounds of 1-naphthol-2-carboxylic acid or aminophenol type. Where these coupler compounds are intended for use in photographic emulsions, a long chain alkyl group or a dialkylphenoxy group should preferably be introduced as a diffusion-preventing group into their molecule so that diffusion of the couplers from photographic layers can be prevented.

Among the cyan couplers, those which have an arylazo group at their 4-position have been known as colored couplers provided with auto-masking mechanism so as to compensate for deficiencies in color reproduction of color photographic materials concerned. See U.S. Pat. Nos. 2,449,966 and 2,455,169. Particularly, a coupler of the 1-hydroxy-4-arylazo-2-naphthoamide or naphthoanilide type, having the formula



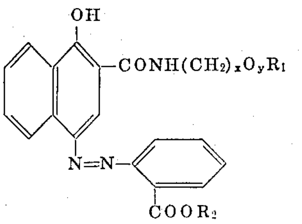
wherein X is hydrogen or alkyl, Y is a mononuclear aryl or aralkyl radical and R_1 is a mononuclear aryl radical (cf. U.S. Pat. No. 2,521,908), or X is hydrogen, Y is a mononuclear aryl radical substituted in a position ortho to the amido group with either halogen, alkoxy or mononuclear aryloxy radical and R is a mononuclear aryl radical (U.S. Pat. No. 2,706,684), and a coupler having the formula



wherein x is an integer in the range of 0–4, y is 0 or 1, R_2 is a member selected from the group consisting of phenyl radical, alkyl radical having from six to 15 carbon atoms, alkyl-substituted phenyl radical and alkyl-substituted phenoxy-phenyl radical, and R_3 is an alkyl group of one to four carbon atoms in either straight or branched chains (cf. U.S.. Pat. No. 3,034,892), are well known as good couplers.

However, colored cyan couplers of the 4-arylazo-substituted 1-hydroxy-2-naphthoamide type generally are not so good in solubility in coupler solvents, and this has been appreciated as a great disadvantage in the production of light-sensitive color photographic materials. Further, almost all of these couplers have an aryl group at the 2-position of their naphthol nucleus. The introduction of an aryl group at the 2-position of the naphthol nucleus causes a decrease in solubility of said couplers in coupler solvents, whereby the couplers become difficult to be prepared in dispersion and tend to cause undesired crystallization in photographic emulsions. Accordingly, many attempts have been made to improve their solubility, but they are not successful.

In view of the state of the prior art, we have made extensive studies and have found that a novel compound of the general formula

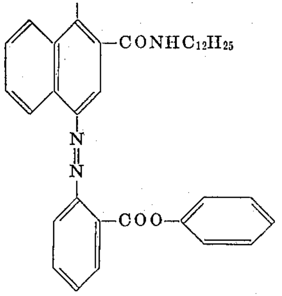


(wherein x is an integer in the range of 0–4, y is 0 or 1, R_1 is phenyl radical, alkyl or alkenyl radical having four to 15 carbon atoms in either straight or branched chain, alkyl-substituted phenyl radical, alkyl-substituted phenoxyphenyl radical, alkylsuccinimido or alkoxycarbonylalkyl radical, and R_2 is substituted or non-substituted aryl or aralkyl radical) is excellent as colored cyan coupler.

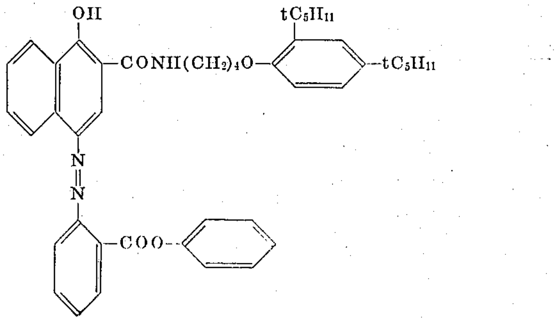
The above compounds have good solubility in coupler solvents and have good dispersibility in photographic emulsions. Further, the photographic emulsions containing the above coupler compounds have high relative speed and are excellent in color shade of the resulting color image and in photographic properties, e.g. fog, etc. Density and spectral characteristics of the colored cyan coupler which may remain unreacted are not changed through the overall process of color development, while said coupler can provide an image having sufficient color density. Thus, a light-sensitive color photographic material having said coupler incorporated therein has good color reproductivity and is quite satisfactory in photographic properties.

Typical concrete examples of the above-mentioned couplers employed in the present invention are shown below, but couplers usable in the invention are not limited only to these.

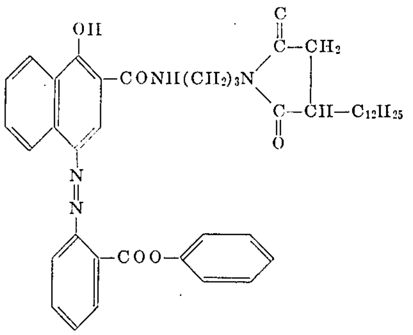
(1) 1-hydroxy-4-(2-carbophenoxyphenylazo)-N-dodecyl-2-naphthamide



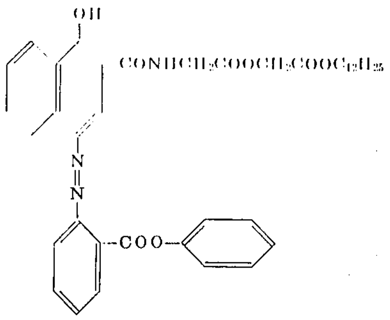
(2) 1-hydroxy-4-(2-carbophenoxyphenylazo)-N-[δ-(2,4-di-tert-amyl-phenoxy)-butyl]-2-naphthamide



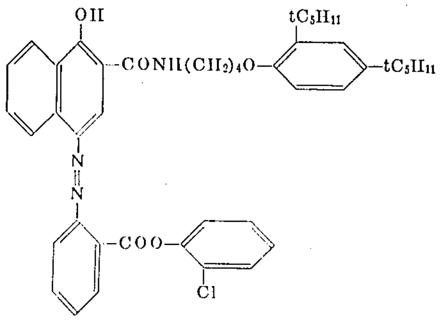
(3) 1-hydroxy-4-(2-carbophenoxyphenylazo)-2-N-[γ-(n-dodecylsuccinimide)-propyl]-naphthamide



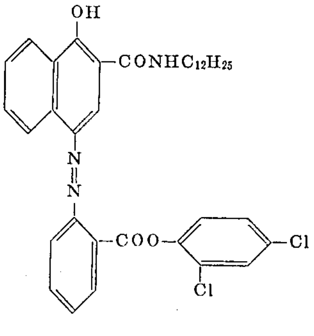
(4) 1-hydroxy-4-(2-carbophenoxyphenylazo)-2-N-[γ-(n-dodecyloxycarbonyl-methoxy)-carbonylmethyl]-naphthamide



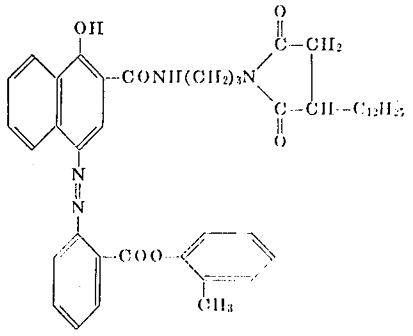
(5) 1-hydroxy-4-[2-carbo-(2-chlorophenoxy)phenylazo]-N-[γ-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide



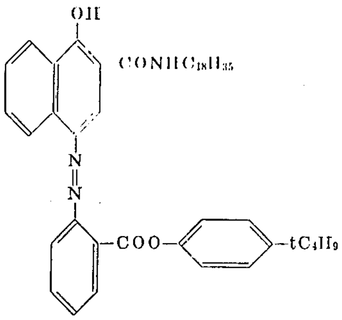
(6) 1-hydroxy-4-[2-carbo-(2,4-dichlorophenoxy)phenylazo]-N-dodecyl-2-naphthamide



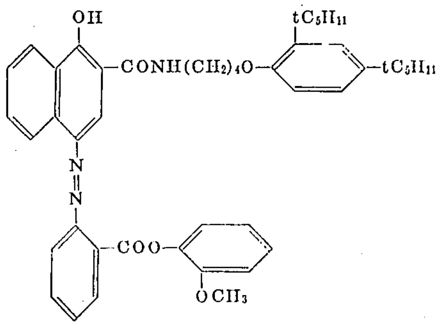
(7) 1-hydroxy-4-[2-carbo-(2-methylphenoxy)phenylazo]-2-N-[γ-(n-dodecylsuccinimide)propyl]-naphthamide



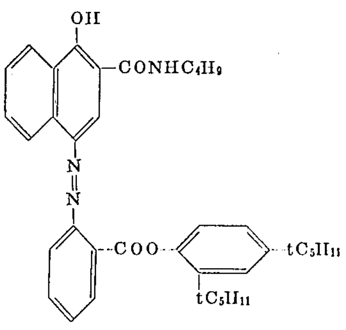
(8) 1-hydroxy-4-[2-carbo-(4-tert-butylphenoxy)-phenylazo]-N-octadecenyl-2-naphthamide



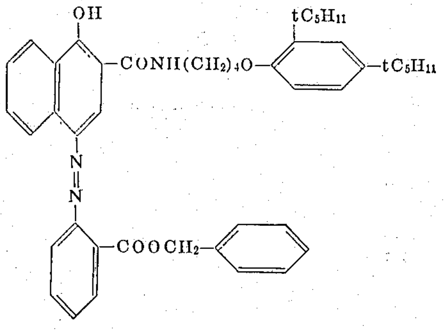
(9) 1-hydroxy-4-[2-carbo-(2-methoxyphenoxy)phenylazo]-N-[δ-(2,4-di-tert-amylphenoxy)]butyl-2-naphthamide



(10) 1-hydroxy-4-[2-carbo-(2,4-di-tert-amylphenoxy)-phenylazo]-N-butyl-2-naphthamide



(11) 1 - hydroxy - 4 - (2 - carbobenzyloxyphenylazo) - N - [δ - (2, 4 - di - tert-amylphenoxy) butyl]-2-naphthamide



Concrete procedures for synthesizing several couplers employed in the present invention are illustrated below with reference to synthesis examples.

SYNTHESIS EXAMPLE 1

Synthesis of 1-hydroxy-4-(2-carbophenoxyphenylazo)-N-dodecyl-2-naphthamide [the coupler of exemplification (1)]:

Into a solution of 167.1 g. of o-nitrobenzoic acid in 250 ml. of pyridine was dropped with stirring at room temperature 353.2 g. of benzenesulfonyl chloride. Subsequently, 94.1 g. of phenol was added with cooling, and the mixture was stirred for 1 hour. This reaction liquid was introduced into ice water, and a white precipitate deposited was filtered, water-washed, dried and then recrystallized from n-hexane to obtain a phenyl o-nitrobenzoate ester. 121.6 g. of the thus obtained ester was dissolved in 1.2 l of 80 percent acetic acid, and the solution was charged with 89.6 g. of iron powder and then stirred for 1 hour. This reaction liquid was subjected to filtration to recover a precipitate, which was then washed with 200 ml. of hot 80 percent acetic acid. To the filtrate was added 2.4 l of water, and a deposited crystal was recovered by filtration, water-washed and then dried to obtain a phenyl 2-aminobenzoate ester. 23.4 g. of this ester was dissolved in 300 ml. of 10 percent hydrochloric acid, and the solution was stirred with cooling. During the stirring, a solution of 7.94 g. of sodium nitrite in 20 ml. of water was dropped into said solution, and the mixed solution was reacted for 30 minutes. This solution was dropped into a solution comprising 35.5 g. of 1-hydroxy-N-dodecyl-2-naphthamide and 1.5 l of pyridine, and was then stirred with cooling for 2 hours to form a red precipitate. This reaction liquid was charged into a solution comprising 2 l of concentrated hydrochloric acid and 2 kg. of ice, and the deposited red precipitate was recovered by filtration, water-washed, dried and then recrystallized from propyl alcohol, whereby a crystal was obtained. The thus obtained crystal was washed with methyl alcohol and then dried to obtain 50 g. of 1-hydroxy-4-(2-carbophenoxyphenylazo)-N-dodecyl-2-naphthamide, yield about 85 percent, m.p. 164° – 166° C.

SYNTHESIS EXAMPLE 2

Synthesis of 1-hydroxy-4-(2-carbophenoxyphenylazo)-N-[δ-(2,4-di-tert-amylphenoxy)-butyl]-2-naphthamide [the coupler of exemplification (2)]:

Synthesis Example 1 was repeated, except that 1-hydroxy-N-[δ-(2,4-di-tert-amylphenoxy) butyl]-2-naphthamide was used in place of the 1-hydroxy-N-dodecyl-2-naphthamide, whereby the above-mentioned compound was obtained, yield about 80 percent, m.p. 149° – 150° C.

SYNTHESIS EXAMPLE 3

Synthesis of 1-hydroxy-4-[2-carbo-(2-methylphenoxy)-phenylazo]-2-N-[γ-(n-dodecylsuccinimide) propyl]-naphthamide [the coupler of exemplification (7)]:

Using o-cresol in place of the phenol employed in Synthesis Example 1, the same treatment as in Synthesis Example 1 was effected to obtain (2-methylphenyl) 2-aminobenzoate ester as intermediate. Thereafter, the same procedures as in Synthesis Example 1 were repeated, using the above-mentioned ester in place of the phenyl 2-aminobenzoate ester and using 1-hydroxy-N-[γ-(n-dodecylsuccinimide) propyl]-2-naphthamide in place of the 1-hydroxy-N-dodecyl-2-naphthamide, whereby the above-mentioned compound was obtained, yield 85 percent, m.p. 116° – 117° C.

According to these synthesis examples, the couplers represented by the aforesaid structural formulas can be synthesized. Physical properties of the exemplified couplers synthesized in the above manner are set forth in the table below.

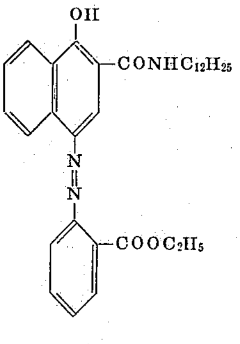
Structural formula	Melting point (° C.)	Yield (percent)	Absorption maximum (mμ)	Elementary analysis							
				Calculated				Found			
				C	H	N	Cl	C	H	N	Cl
(1)	164–166	85	495	74.58	7.13	7.25	--------	74.41	7.26	7.20	--------
(2)	149–150	80	496	75.51	7.06	6.00	--------	75.49	9.11	5.90	--------
(3)	138–139	85	497	71.84	7.01	7.79	--------	71.67	7.10	7.60	--------
(4)	131–132	90	498	69.04	6.52	6.04	--------	69.06	6.65	6.10	--------
(5)	145.5–146.5	80	495	71.96	6.58	5.72	482	71.77	6.73	5.62	499
(6)	148–149	90	495	66.66	6.06	6.47	1,093	66.57	6.19	6.60	1,106
(7)	116–117	80	497	72.10	7.15	7.65	--------	71.98	7.26	7.80	--------
(8)	124–126	90	495	76.95	8.28	6.85	--------	76.98	8.41	6.93	--------
(9)	141–142	90	490	74.04	7.04	5.75	--------	73.92	7.23	5.70	--------
(10)	124–125	80	495	75.09	7.46	6.91	--------	75.05	7.50	6.90	--------
(11)	117–119	80	497	75.70	7.20	5.89	--------	75.57	7.38	6.00	--------

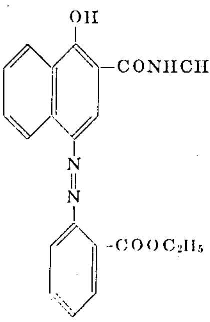
The following test example show a comparison in efficiency between couplers employed in the present invention and other couplers.

TEST EXAMPLE

A comparison in solubility for dibutyl phthalate (hereinafter abbreviated as D.B.P.) between couplers of the present invention and other couplers was effected in such a manner that 1 g. of each coupler was dissolved in D.B.P. at 60° C. and then set at room temperatures to measure the time required for initiation of crystallization of the coupler.

The results were as shown below.

Control couplers	Amount of D.B.P. used, ml.	Time of initiation of crystallization, min.
(A) 	10	4

(B) 	10	12
Couplers of the present invention		
Exemplification (1)	10 ml.	15 min.
Exemplification (2)	10 ml.	30 min.
Exemplification (7)	10 ml.	60 min.

As is clear also from the above-mentioned test example, it is understood that the colored cyan couplers employed in the present invention are longer in time of initiation of crystallization than other colored cyan couplers of this kind, and hence are markedly high in solubility for coupler solvents.

The production of light-sensitive color photographic materials by use of the couplers represented by the aforesaid structural formulas may be carried out according to the prior art process. For example, the coupler is dissolved in a water-immiscible high boiling solvent having a boiling point of above 180° C., such as dibutyl phthalate, tricresyl phosphate, dibutyl laurate or the like, either singly or, if necessary, in admixture with such low boiling solvent as ethyl acetate, butyl acetate, butyl propionate or the like. Thereafter, the solution is mixed with an aqueous gelatine solution containing a surface active agent, is emulsified by means of a high speed rotary mixer or a colloid mill, is directly added to a silver halide photographic emulsion, and is then coated onto a suitable support such as film base, or the like, followed by drying, whereby a light-sensitive color photographic material can be obtained. In this case, the amount of the coupler employed is desirably within the range of 10–100 g. per mole of silver halide, but is optionally variable according to the purpose of application, without being limited to said range. Further, when used in combination with a colorless cyan coupler, in the above-mentioned case, the coupler of the present invention is further enhanced in solubility and comes to be quite easily dispersible in the silver halide photographic emulsion.

Light-sensitive silver halide color photographic materials obtained in the above manner do not suffer from crystallization of couplers and are excellent in transparency. When these materials are subjected, after exposure, to ordinary developing treatment, the resulting dye images have desirable spectral absorption characteristics, good transparency and excellent photographic properties.

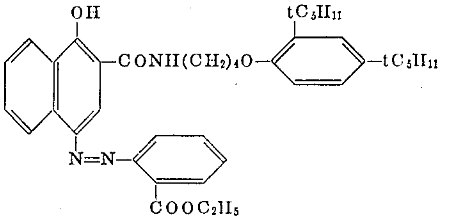
The present invention is illustrated below with reference to examples.

EXAMPLE 1

One part of the coupler of exemplification (2) was dissolved in 5 parts of D.B.P. with stirring at 80° C. and was added to 100 parts of a 10 percent aqueous gelatine solution kept at 60° C., and the mixed solution was further charged with 2 parts of a 10 percent aqueous sodium alkylbenzenesulfonate solution. Subsequently, the liquid was stirred at about 65° C. for 5 minutes by use of a high speed rotary mixer. This operation was repeated five times at intervals of 1 minute to prepare a coupler dispersion. 13.5 parts of the thus prepared coupler dispersion was added at 35° C. to 100 parts of a light-sensitive silver iodobromide emulsion containing a red light-sensitive sensitizing dye, and the mixture was stirred and was then coated onto a film support, followed by drying, whereby a red light-sensitive color photographic material was obtained.

Separately, 1 part of a control coupler of the structural formula (C) shown below was dissolved in 10 parts of D.B.P. and was treated in the same manner as above to prepare a coupler dispersion. In this case, it is necessary that the temperature at which the coupler is dissolved in the coupler solvent should be strictly maintained at above 80° C. and the temperature of the aqueous gelatine solution at the time of stirring should be strictly maintained at above 70° C. The thus prepared coupler emulsion was treated in the same manner as above to obtain a red light-sensitive color photographic material.

Control coupler (C):



The thus obtained two kinds of light-sensitive color photographic materials were exposed to red light—through an optical wedge and were treated with a color developer of the following composition:

Color developer:	
N,N-Diethyl-p-aminoaniline sulfate	2.0 g.
Sodium sulfite	2.0 g.
Sodium carbonate (monohydrate)	50.0 g.
Hydroxylamine hydrochloride	1.5 g.
Potassium bromide	1.0 g.
Water to make	1,000 ml.
	(pH 10.8 ± 0.1)

Subsequently, the materials were further treated with a bleaching solution and a fixing solution of the compositions shown below to remove undeveloped silver halide and by-produced reduced silver.

Bleaching solution:	
Red prussiate	100 g.
Potassium bromide	20 g.
Water to make	1,000 ml.
	(pH 6.9 ± 0.3)
Fixing solution:	
Hypo	200 g.
Sodium sulfite	20 g.
Acetic acid (28%)	45 ml.
Boric acid	7.5 g.
Potash alum	20 g.
Water to make	1,000 ml.
	(pH 4.5 ± 0.2)

From the color photographic material using the coupler of exemplification (2), there were simultaneously obtained a cyan colored negative image and a red positive image comprising residual coupler. The film was quite excellent in transparency, and the red positive image had a sufficiently red color. However, the color photographic material using the control coupler of the structural formula (C) gave a cyan colored negative image and a reddish orange positive image comprising unreacted residual coupler which were hazy and somewhat opaque. This is considered ascribable to partial crystallization and insufficient dispersibility of the control coupler.

The absorption maximum wave length and photographic speed of a film positive image, obtained by subjecting each of said two color photographic materials to exposure and then to bleaching and fixing, are shown below.

Structural formula	Absorption maximum wave length	Photographic Speed
Exemplification (2)	495	**100%**
Control (C)	505	**90%**

EXAMPLE 2

A mixture comprising 1 part of the coupler of exemplification (2) and 3 parts of 1-hydroxy-N-[δ-(2,4-di-tert-amylphenoxy)-butyl]-2-naphthamide was dissolved with stirring at 80° C. in 5 parts of di-n-butyl phthalate and was added to 100 parts of a 10 percent aqueous gelatine solution kept at 60° C., and the mixed solution was further charged with 2 parts of a 10 percent aqueous sodium alkylbenzene-sulfonate solution. Subsequently, the liquid was stirred at about 65° C. for 5 minutes by use of a high speed rotary mixer. This operation was repeated five times at intervals of 1 minute to prepare a coupler dispersion.

A mixture comprising 1 part of the control coupler of the structural formula (C) and 3 parts of 1-hydroxy-N-[δ-(2,4-di-tert-amylphenoxy)-butyl]-2-naphthamide was dissolved in 10 parts of butyl phthalate and was treated in the same manner as above to prepare a coupler dispersion. In this case, it is necessary that the temperature at which the coupler is dissolved in the coupler solvent should be strictly maintained at above 80° C. and the temperature of the aqueous gelatine solution at the time of stirring should be strictly maintained at above 70° C.

Each 10 parts of the thus prepared coupler dispersions were individually added to 100 parts of a light-sensitive high speed silver iodobromide emulsion containing a red light-sensitive sensitizing dye, and the mixtures were treated in the same manner as in Example 1 to obtain two kinds of light-sensitive color photographic materials.

In the same manner as in Example 1, the thus obtained two kinds of color photographic materials were subjected to exposure, color development, bleaching and fixing to simultaneously obtain cyan colored negative images and red and reddish orange positive images. The film using the coupler (2) was good in transparency, whereas the film using the control coupler (C) was opaque and was extremely hazy, and the difference between the two materials was greater than in the case of Example 1.

The absorption maximum wave length and photographic speed of a film positive image, obtained by subjecting each of said two photographic materials to exposure and then to bleaching and fixing, are shown below.

Structural formula	Absorption maximum wave length	Photographic speed
Exemplification (2)	495	**100%**
Control (C)	500	**85%**

EXAMPLE 3

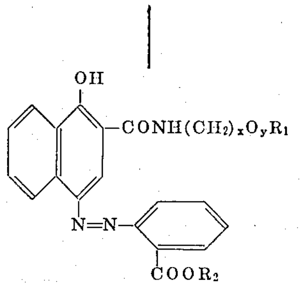
The coupler of exemplification (7) was treated in the same manner as in Example 1 to prepare a red light-sensitive photographic material. This material was treated in the same manner as in Example 1 to obtain simultaneously a cyan colored negative image and a red color positive image. This film was excellent in transparency and the red color positive image had a sufficiently red color. Further, the film was satisfactory in photographic speed.

EXAMPLE 4

The coupler of exemplification (9) was treated in the same manner as in Example 1 to prepare a red light-sensitive photographic material. This material was treated in the same manner as in Example 1 to obtain simultaneously a cyan colored negative image and a red color positive image. This film was excellent in transparency and the red positive image had a sufficiently red color. Further, the film was satisfactory in photographic speed.

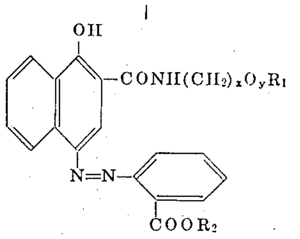
What we claim is:

1. A light-sensitive silver halide color photographic material, characterized by containing a compound represented by the formula



wherein x is an integer in the range of 0–4, y is 0 or 1, R_1 is phenyl radical, alkyl or alkenyl radical having four to 15 carbon atoms in either straight or branched chain, alkyl-substituted phenyl radical, alkyl-substituted phenoxyphenyl radical, alkylsuccinimide radical or alkoxycarbonylaklyl radical, and R_2 is an aryl or aralkyl radical which may be substituted with at least one member selected from the group consisting of halogen, lower alkyl or lower alkoxy.

2. A light-sensitive silver halide color photographic emulsion which contains as cyan color coupler a compound of the formula



wherein x is an integer in the range of 0–4 , y is 0 or 1, R_1 is phenyl radical, alkyl or alkenyl radical having four to 15 carbon atoms in either straight or branched chain, alkyl-substituted phenyl radical, alkyl-substituted phenoxyphenyl radical, alkylsuccinimide radial or alkoxycarbonylalkyl radial, and R_2 is an aryl or aralkyl radical which may be substituted with at least one member selected from the group consisting of halogen, lower alkyl or lower alkoxy.

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