United States Patent Office

3,667,956
Patented June 6, 1972

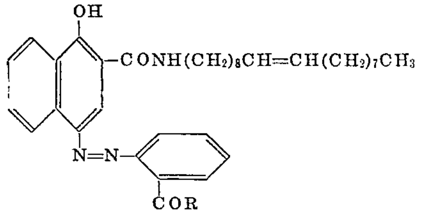
3,667,956

LIGHT-SENSITIVE SILVER HALIDE COLOR PHOTOGRAPHIC MATERIALS CONTAINING CYAN COUPLERS

No Drawing. Filed Feb. 18, 1970, Ser. No. 12,476
Claims priority, application Japan, Feb. 24, 1969, 44/13,216
Int. Cl. G03c *1/40*
U.S. Cl. 96—100 **4 Claims**

ABSTRACT OF THE DISCLOSURE

A compound of the general formula

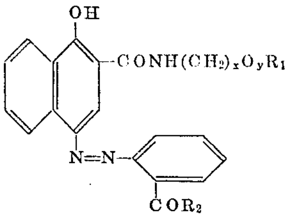


wherein R is a lower alkyl group, a lower alkoxy group, or a phenoxy or aralkoxy group which may have a substituent selected from alkyl, alkoxy and halogen is found to be useful as a cyan coupler providing auto-masking mechanism for light-sensitive color photographic materials so as to compensate the deficient color reproductivity of said materials.

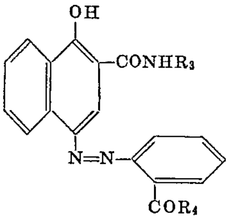
This invention relates to a light-sensitive rolor photographic material containing a cyan coupler usable in the form of a solution in an organic solvent, said cyan coupler falling within the class of so-called colored cyan couplers which provide auto-masking mechanism for the light-sensitive color photographic material so as to compensate for the deficient color reproductivity of said material.

Almost all of the cyan couplers to be used as color formers in light-sensitive color photographic materials are compounds of the 1-naphthol-2-carboxylic acid or aminophenol type. Further, these couplers have been incorporated with a diffusion-preventing group such as a long chain alkyl group or a dialkylphenoxy group so that when they are used in photographic emulsions, diffusion or exudation thereof from photographic layers can be prevented.

Among such cyan couplers, those having 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 United States Pats. 2,449,966 and 2,455,169). Particularly, a coupler having the formula



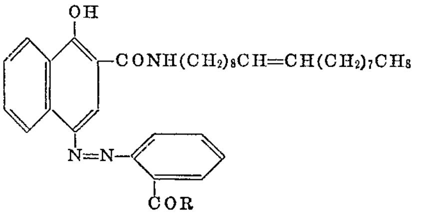
wherein *x* is an integer of 0–4, *y* is 0–1, R_1 is phenyl, C_6–C_{15} alkyl, alkyl-substituted phenyl, or alkyl-substituted phenoxyphenyl, and R_2 is straight or branched C_1–C_4 alkyl, (cf. United States Pat. 3,034,892), and a coupler having the formula



wherein R_3 is branched alkyl of C_6 or more, and R_4 is lower alkyl (cf. Japanese patent publication No. 11,-304/1967), have been well known as good couplers.

Generally, however, these couplers of the 1-hydroxy-4-arylazo-2-naphthoamide type, in which the 4-position has been substituted with an arylazo group, are low in solubility in tricresyl phosphate, dibutyl phthalate or similar water-immiscible high boiling solvent (hereinafter referred to as "the coupler solvent"). Accordingly, they are difficultly formed into dispersion and tend to cause undesirable crystallization or deposition in photographic emulsions, and this has been a great disadvantage in the production and photographic properties of light-sensitive color photographic materials. Many attempt have therefore been made in order to improve the solubility of said couplers, but no satisfactory couplers have yet been obtained. For example, the introduction of a dialkylphenoxyphenyl or dialkylphenoxyalkyl group into the 2-position of the naphthol nucleus of said coupler has been attempted, with the result that the solubility of the coupler is considerably improved but is not yet sufficient. Moreover, such coupler is complex in structure and is quite difficultly synthesizable. Thus, the atempt requires much expense not only in the starting materials but also in the synthesis operations.

In view of such actual circumstances as mentioned above, the present inventors made extensive studies to find that a novel compound represented by the general formula



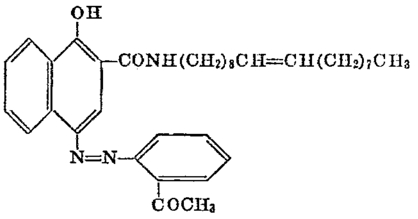
wherein R is lower alkyl, lower alkoxy, substituted or non-substituted phenoxy, or substituted or non-substituted aralkoxy, is an excellent colored cyan coupler, and a light-sensitive color photographic material incorporated therewith has excellent photographic properties.

The above- mentioned compound is not only so excellent in solubility in the coupler solvent as to easily form a dispersion thereof but also has good dispersibility in a photographic emulsion, so that it is possible to obtain a reddish orange, red light-sensitive color photographic material having good transparency. Further, a photographic emulsion containing the above-mentioned compound has high relative speed and is excellent in color shade of the resulting image and in photographic properties, e.g. fog, etc. Moreover, the density and spectral characteristic of the colored cyan coupler which may remain unreacted are not changed throughout the overall process of color development, thereby providing an image sufficient in color density.

Thus, the light-sensitive color photographic materials of the present invention which have been incorporated with the aforesaid compounds are prominent in color reproductivity and have excellent photographic properties. Furthermore, the couplers employed in the present invention can be prepared according to extremely simple synthesis procedures using easily obtainable inexpensive starting materials, as will be described in the synthesis examples set forth later.

The above-mentioned couplers employed in the present invention include those of the cis and trans types, and typical examples of the couplers represented by the aforesaid general formula are as shown below, but couplers usable in the present invention are not limited to these.

(1)



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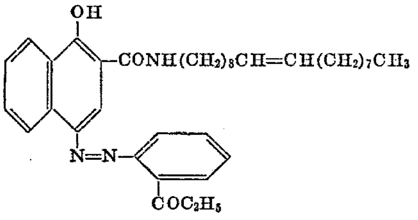

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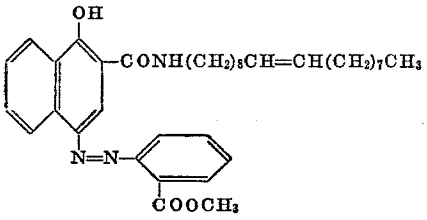

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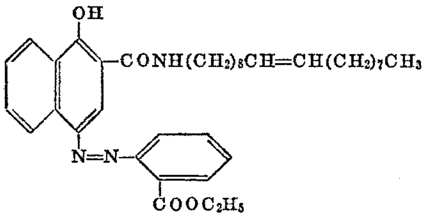

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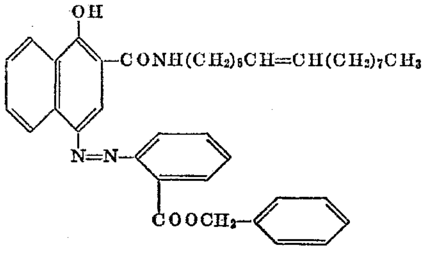

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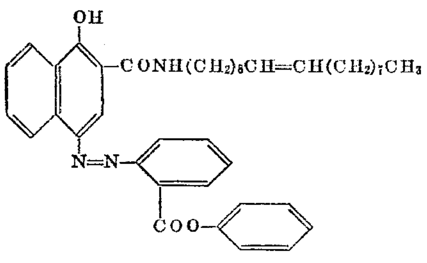

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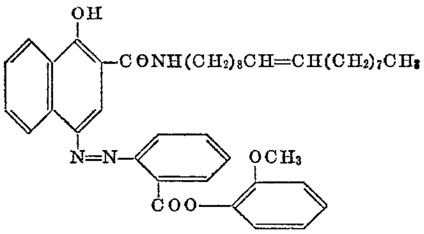


Concrete procedures for synthesizing several couplers employed in the present invention are illustrated below with reference to synthesis examples.

SYNTHESIS EXAMPLE 1

Synthesis of 2 - (N - octadecenylcarbamoyl) - 4 - (2-acetophenylazo)-1-naphthol [the coupler of exemplification (1)]

21 g. of o-aminoacetophenone suspended in 70 ml. of water was treated with 70 ml. of concentrated hydrochloric acid. The resulting solution was diazotized by adding to the solution at below 5° C. a solution of 10 g. of sodium nitrite in 20 ml. of water. Subsequently, the thus treated solution was added at below 8° C. to a solution of 44 g. of 2-(N-octadecenylcarbamoyl)-1-naphthol in 1,000 ml. of pyridine to effect coupling. Thereafter, 1,000 ml. of water was added to the solution to deposit crystals, which were then collected by filtration, washed successively with 1,000 ml. of water, 50 ml. of hydrochloric acid and 2,000 ml. of water, recrystallized from 800 ml. of ethanol, and then washed with 100 ml. of methanol to obtain 46 g. of the desired compound, yield 80%, M.P. 101–103° C.

Elementary analysis.—Found (percent): C, 76.30; H, 8.43; N, 7.05. Calculated (percent): C, 76.12; H, 8.46; N, 7.20.

SYNTHESIS EXAMPLE 2

Synthesis of 2-(N-octadecenylcarbamoyl)-4-(2-carboethoxyphenylazo)-1-naphthol [the coupler of exemplification (4)]

Synthesis Example 1 was repeated, except that 2-carboethoxyaniline was used in place of the o-aminoacetophenone, to obtain the desired compound, yield 81%, M.P. 122–124° C.

Elementary analysis.—Found (percent): C, 74.43; H, 8.53; N, 6.98. Calculated (percent): C, 74.35; H, 8.38; N, 6.85.

SYNTHESIS EXAMPLE 3

Synthesis of 2-(N-octadecenylcarbamoyl)-4-(2-carbobenzyloxyphenylazo)-1-naphthol [the coupler of exemplification (5)]

Synthesis Example 1 was repeated, except that 2-carbobenzyloxyaniline was used in place of the o-aminoacetophenone, to obtain the desired compound, yield 85%, M.P. 109–111° C.

Elementary analysis.—Found (percent): C, 76.63; H, 7.94; N, 6.07. Calculated (percent): C, 76.41; H, 7.90; N, 6.22.

SYNTHESIS EXAMPLE 4

Synthesis of 2-(N-octadecenylcarbamoyl)-4-(2-carbophenoxy-phenylazo)-1-naphthol [the coupler of exemplification (6)]

Synthesis Example 1 was repeated, except that 2-carbophenoxyaniline was used in place of the o-aminoacetophenone, to obtain the desired compound, yield 83%, M.P. 139–140° C.

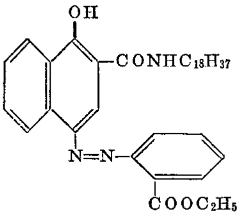
Elementary analysis.—Found (percent): C, 76.41; H, 7.90; N, 6.44. Calculated (percent): C, 76.21; H, 7.77; N, 63.5.

Comparison in solubility in the coupler solvent between the couplers employed in the present invention and control couplers will be shown with reference to the following test example:

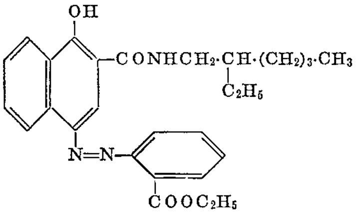
TEST EXAMPLE

1 g. of each of the couplers employed in the present invention and the control couplers set forth below was dissolved in 10 ml. of dibutyl phthalate with stirring at 60° C. and was allowed to stand at 20° C., and the time required for initiation of crystal deposition was measured and was regarded as a measure for the comparison in solubility. In this case, the longer the time required for obvious deposition, the better the coupler in solubility in the coupler solvent. The results obtained were as shown in the table below. Provided that the control coupler (A) was quite difficultly soluble in the coupler solvent, so that 1 g. of the coupler was dissolved at 80° C. in 25 ml. of dibutyl phthalate and was then treated in the same manner as above.

Control coupler (A):



Control coupler (B), (the coupler disclosed in Japanese Patent Publication No. 11,304/1967):

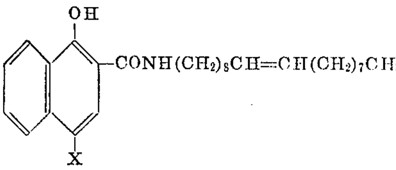


Coupler:	Time required for deposition
Control coupler (A)	3 min.
Control coupler (B)	15 min.
Coupler of exemplification (4) similar in structure to the above couplers	1 hr. and 30 min.
Couplers of exemplification (1)	3 hr. and 30 min.
Coupler of exemplification (5)	4 hr. and 30 min.

As is clear from the above table, the coupler of exemplification (4) which is similar in structure to the control couplers is far more excellent in solubility than the control couplers. Accordingly, light-sensitive color photographic materials incorporated with these couplers employed in the present invention do not suffer from deposition of the couplers during the production step and during the storage thereof and are not deteriorated in photographic properties due to deposition of the couplers.

The production of light-sensitive color photographic materials by use of these couplers may be carried out according to the prior art process. For example, the coupler is dissolved in dibutyl phthalate, tricresyl phosphate, dibutyl lauramide or the like water-immiscible high boiling solvent having a boiling point of about 180° C., either singly or in admixture with ethyl acetate, butyl acetate, butyl propionate or the like low boiling solvent. 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 a 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 coupled employed is desirably within the range of 10–100 g. per mole of the 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 case, the coupler according to the present invention is further enhanced in solubility and the resulting photographic material is improved in photographic properties. Particularly, it is desirable to use the coupler of the invention in combination with a coupler of the formula



wherein X is hydrogen or halogen.

Emulsions usable in the present invention include various silver salts such as silver chloride, silver iodide, silver chlorobromide, etc., and may contain chemical sensitizers such as, for example, sulfur sensitizers and reduction sensitizers, and noble metal salts. Further, they may contain common photographic additives such as, for example, fog inhibitors, stabilizers, contamination-preventing agents, coating aids, etc. They can further be incorporated with carbocyanine dyes and merocyanine dyes known as optical sensitizers for emulsions.

Light-sensitive color photographic materials of the present invention which are obtained in the above manner do not suffer from crystallization of couplers and are excellent in transparency. When these materials are exposed to light and are then subjected to ordinary color development, the resulting dye images exhibit desirable spectral absorption characteristics and provide excellent photographic properties.

The present invention is illustrated below with reference to examples.

EXAMPLE 1

1.2 parts of the coupler of exemplification (4) was dissolved in 10 parts of tricresyl phosphate with stirring at 80° C. and was added to 100 parts of a 10% aqueous gelatine solution kept at 60° C., and the mixed solution was charged with 2 parts of a 10% 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 5 times at intervals of 1 minute to prepare a coupler dispersion. 13 parts of the thus prepared 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, to obtain a red light-sensitive color photographic material.

The thus obtained material was exposed to red light through an optical wedge and was subjected to ordinary color development using 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).

Thereafter, the material was bleached and fixed by use of 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.

Fixing solution:
- Hypo: 200 g.
- Sodium sulfiite: 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).

In the above manner, there were simultaneously obtained a cyan colored negative image and a reddish orange positive image comprising unreacted residual coupler. The film was quite excellent in transparency, which is considered ascribable to the fact that the coupler was excellent in solubility, difficulty crystallized and favorable in dispersibility. The absorption maximum wave length of the reddish orange positive image was 506 mμ.

Separately, the control coupled (A) 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 maintained at above 80° C. and the temperature of the aqueous gelatine solution at the time of dispersion should be maintained at above 70° C. The thus prepared coupler dispersion was treated in the same manner as above to obtain a red light-sensitive color photographic material. This material was exposed to red light through an optical wedge and was then subjected to color development, bleaching and fixing to obtain a cyan colored negative image and a reddish orange positive image containing unreacted residual coupler which were hazy and somewhat opaque.

EXAMPLE 2

The coupler of exemplification (4) was treated in the same manner as in Example 1, except that di-n-butyl phthalate was used in place of the tricresyl phosphate, to obtain a red light-sensitive color photographic material. This material was exposed to red light and was treated in the same manner as in Example 1 to obtain simultaneously a cyan colored negative image and a reddish orange positive image. This film was markedly excellent in transparency.

EXAMPLE 3

The coupler of exemplification (1) was treated in the same manner as in Example 1 to prepare a red light-sensitive color photographic material. This material was exposed to red light and was treated in the same manner as in Example 1, whereby a cyan colored negative image and a reddish orange positive image were simultaneously obtained. This film was markedly excellent in transparency.

EXAMPLE 4

The coupler of exemplification (5) was treated in the same manner as in Example 1 to prepare a red light-sensitive color photographic material. This material was exposed to red light and was treated in the same manner as in Example 1, whereby a cyan colored negative image and a reddish orange positive image were simultaneously obtained. This film was markedly excellent in transparency.

EXAMPLE 5

The coupler of exemplification (7) was treated in the same manner as in Example 1 to prepare a red light-sensitive material. This material was exposed to red light and was treated in the same manner as in Example 1, whereby a cyan colored negative image and a reddish orange positive image were simultaneously obtained. This film was markedly excellent in transparency.

EXAMPLE 6

A mixture comprising 1 part of the coupler of exemplification (4) and 3 parts of 2-(N-octadecenylcarbamoyl)-1-naphthol was dissolved in 5 parts of di-n-butyl phthalate with stirring at 80° C. and was added to 100 parts of a

10% aqueous gelatine solution kept at 60° C., and the mixed solution was further charged with 2 parts of a 10% aqueous sodium alkylbenzenesulfonate solution. Subsequently, the liquid was stirred and dispersed at about 65° C. for 5 minutes by use of a high speed rotary mixer. This operation was repeated 5 times at intervals of 1 minute to prepare a coupler dispersion.

Separately, a mixture comprising 1 part of the control coupler (A) and 3 parts of 2-(N-octadecenylcarbamoyl)-1-naphthol was dissolved in 10 parts of di-n-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 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 2 kinds of light-sensitive color photographic materials.

In the same manner as in Example 1, these 2 kinds of color photographic materials were exposed to red light through an optical wedge and were subjected to color development, bleaching and fixing to simultaneously obtain cyan colored negative images and red and reddish orange positive images.

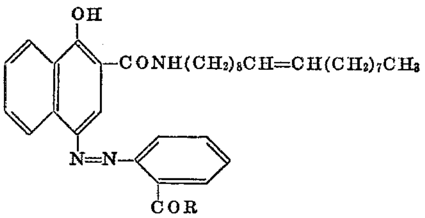
The film using the coupler of exemplification (4) was markedly excellent in transparency, whereas the film using the control coupler (A) was hazy and somewhat opaque.

The absorption maximum wavelengths and photographic speeds of film positive images obtained by subjecting said two photographic materials to exposure and then to bleaching and fixing are shown below.

Coupler	Absorption maximum wave length	Photographic speed, percent
Coupler of exemplification (4)	502	100
Control coupler (A)	502	85

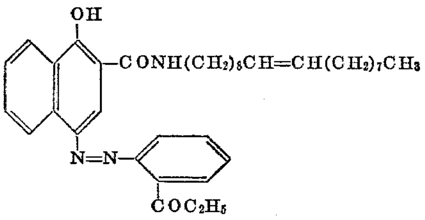
What we claim is:

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

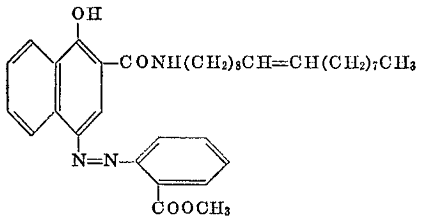


wherein R is a lower alkyl, lower alkoxy, phenoxy, or aralkoxy group.

2. A light-sensitive silver halide color photographic material according to claim 1, wherein said coupler is a compound of the formula



3. A light-sensitive silver halide color photographic material according to claim 1, wherein said coupler is a compound of the formula



4. A light-sensitive silver halide color photographic material according to claim **1** wherein the phenoxy group is substituted with a lower alkoxy group.

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J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

96—9, 56.1

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,667,956 Dated June 6, 1972

Inventor(s) Masakuni Iwama, et. al.

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

In the heading to the printed specification, between lines 4 and 5, insert -- 1. Masakuni Iwama, 2. Mitsuto Fujiwara, 3. Tamotsu Kojima, 4. Koichi Takabe and 5. Toshihiko Yamamoto, Tokoyo, Japan --

Signed and sealed this 26th day of December 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)