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Fujiwhara et al.

[11] **3,888,680**

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[54] **LIGHT-SENSITIVE SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL CONTAINING BIS-PYRAZOLONE COUPLERS**

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[22] Filed: **Dec. 26, 1973**

[21] Appl. No.: **428,207**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 207,796, Dec. 14, 1971, abandoned.

[30] **Foreign Application Priority Data**

Dec. 18, 1970 Japan 45-113100

[52] **U.S. Cl.** ..... **96/100;** 260/310 A

[51] **Int. Cl.** **G03c 1/40**

[58] **Field of Search** 96/100, 56.5

[56] **References Cited**

UNITED STATES PATENTS

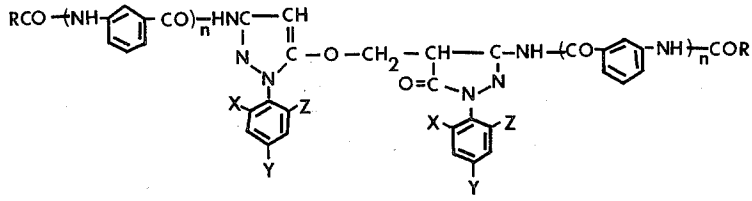
2,294,909	9/1942	Jennings	96/100
2,403,040	7/1946	Bavley	96/100
3,468,666	9/1969	Shiba et al.	96/100

Primary Examiner—J. Travis Brown

Attorney, Agent, or Firm—Bierman & Bierman

[57] **ABSTRACT**

A light-sensitive silver halide color photographic material is disclosed which comprises a bis-type coupler of the following general formula:



wherein R is alkyl, aralkyl or aryl X, Y and Z are individually hydrogen, halogen or alkyl or alkoxyl group having 1 to 4 carbon atoms, one of X and Z being a halogen atom; and n is zero or 1.

4 Claims, No Drawings

LIGHT-SENSITIVE SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL CONTAINING BIS-PYRAZOLONE COUPLERS

This application is a continuation-in-part of application Ser. No. 207,796 filed Dec. 14, 1971, now abandoned, and it claims priority of Japanese application No: 113100/1970 filed Dec. 18, 1970.

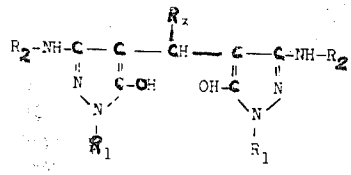
This invention relates to a light-sensitive color photographic material containing a novel coupler of the pyrazolone type for forming a magenta color photograhpic image.

For the formation of color photographic images according to the conventional substractive color photography, there have been used, in general, couplers capable of forming yellow, magenta and cyan dye images by coupling with an oxidation product of N,N'-disubstituted p-phenylenediamine type developing agent. Particularly in the so-called internal color photography in which the above-mentioned couplers are incorporated into photographic emulsions to develop colors, there are two processes; a process in which a hydrophilic coupler containing in the molecule a non-diffusing group and a hydrophilic group such as a group of the formula —COOH or —SO_3H is dissolved in an alkali solution or the like and then dispersed in a photographic emulsion, and a process in which an oleophilic coupler, which contains no hydrophilic group in the molecule and which has been rendered oil-soluble by introduction of an oleophilic group (e.g. a higher alkyl group), is dispersed to extremely fine oil drops in a high boiling solvent such as di-n-butyl phthalate or tricresyl phosphate and then incorporated into a photographic emulsion.

In the former case, the coupler is easily dispersible in an aqueous emulsion. However, a coupler having a sulfone group brings about a great variation in viscosity of the emulsion, and the control of film thickness at the time of coating the emulsion becomes extremely difficult. Further, a coupler having a carboxyl group is somewhat low in solubility for alkali solution and, in case the emulsion, which has been diluted before coating, becomes neutral or weakly acidic, the coupler deposits in the emulsion to deteriorate the transparency of the resulting image. In the latter case, the tendency of deposition of the coupler in the emulsion is greatly dominated by the extent of hydrophilic property of the coupler residue, the kinds and amounts of non-diffusing group and coupler solvent, etc. This tendency is observed as well in the case of a magenta coupler, and an internal oleophilic magenta coupler, which has a 5-pyrazolone, pyrazolinobenzimidazole, pyrazoloquinazolone or indazolone ring incorporated with a non-diffusing group such as a long chain alkyl, dialkylphenoxy or alkoxy group, is greatly dominated in said tendency by the extent of hydrophilic property of the coupler residue, the kind and amount of the non-diffusing group. Particularly, a coupler having a 5-

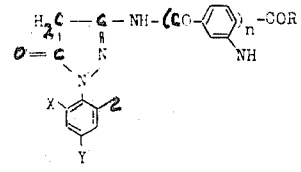
pyrazolone nucleus, with which is concerned the present invention, is low in solubility for high boiling solvent due to the hydrophilic property of the coupler residue, and undesirably deposits in a dispersion thereof or in the resulting film.

With an aim to overcome the above-mentioned drawbacks, the synthesis of bis-pyrazolone type couplers has been attempted, and Japanese Patent Publication No. 26,589/1969 discloses a process for preparing light-sensitive photographic materials incorporated with said couplers. However, the couplers of this type, which has the chemical structure



are not only undesirable in solubility as shown in the test example set forth later, but also slow in color developing rate at the time of color development and low in sensitivity of green light sensitive layer, so that the independent use thereof is difficult.

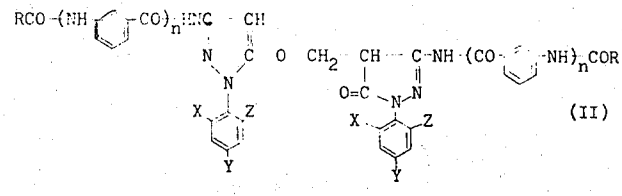
As the result of extensive studies, we have found magenta couplers which have been improved in solubility and deposition property at the time of dispersion and coating and which can give spectral absorption characteristics suitable for color reproduction. That is, we have found new couplers of the bis-pyrazolone type, obtained by condensing a coupler of the general formula (I)



(I)

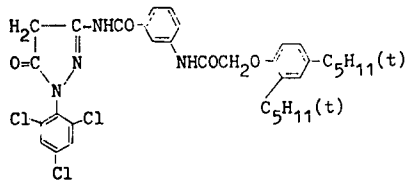
wherein R is an alkyl, aralkyl or aryl group; X, Y and Z are individually a hydrogen or halogen atom, or an alkyl or alkoxy group having 1 to 4 carbon atoms, either one of said X and Z being necessarily a halogen atom; and *n* is zero or 1, with formaldehyde in acetic acid.

The above-mentioned couplers have the following chemical structure:

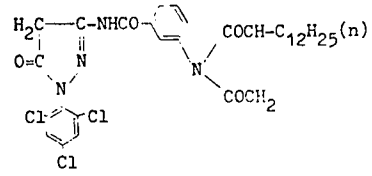


(II)

Among the couplers of the above general formula (I), those which can give new couplers of the general formula (II) displaying particularly excellent properties are compounds of the following structure:



(1)



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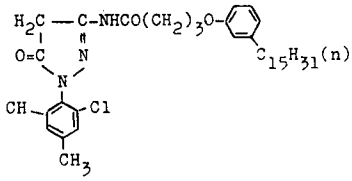

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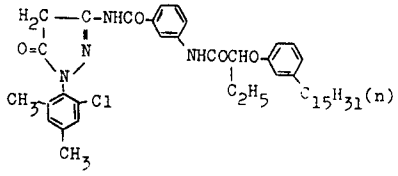

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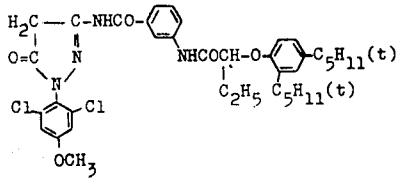
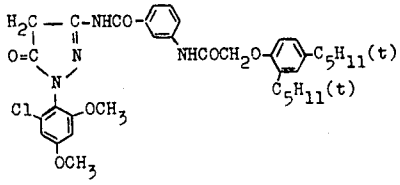
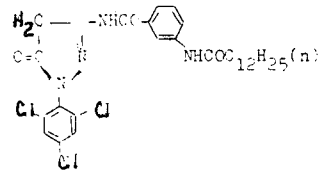


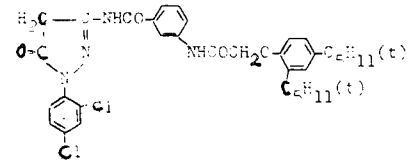
(5)



(6)



(7)



(8)

It is to be noted that compounds usable in the present invention are not limited to the above-mentioned compounds.

The accompanying drawing shows variations in density due to amounts of exposure of dye images obtained by subjecting to color development two light-sensitive color photographic materials containing, respectively, a coupler according to the present invention and a known coupler.

Procedures for synthesizing the magenta couplers used in the present invention are set forth below with reference to synthesis examples.

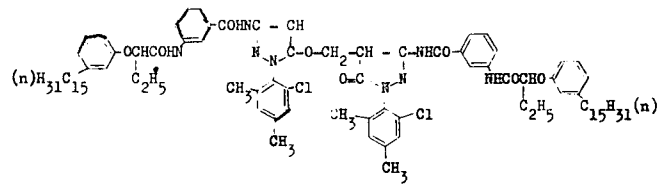
SYNTHESIS EXAMPLE 1

To a solution of 7.3 g. (0.01 mole) of 1-(6-chloro-2,4-dimethylphenyl)-3-(α-3-n-pentadecylphenoxy) butyrylamide-benzamide-5-pyrazolone (the compound 4) in 30 ml. of acetic acid was added 1.5 ml. of 37% formaldehyde, and the resulting mixture was stirred at room temperature and concentrated under reduced pressure to form a gelatinous substance. To this substance was further added a solution of 7.3 g. (0.01 mole) of the said coupler in 30 ml. of acetic acid, and the resulting mixture was boiled under reflux for 20 minutes and then concentrated under reduced pressure. The concentrate was recrystallized from acetonitrile to obtain 12.0 g. (81.6% on theoretical basis) of white crystals, m.p. 107.5°–108.5°C.

Elementary analysis:

	C	H	N	Cl
Calculated (%)	71.05	7.81	7.62	4.82
Found (%)	70.95	7.63	7.44	4.81

Structural formula:



SYNTHESIS EXAMPLE 2

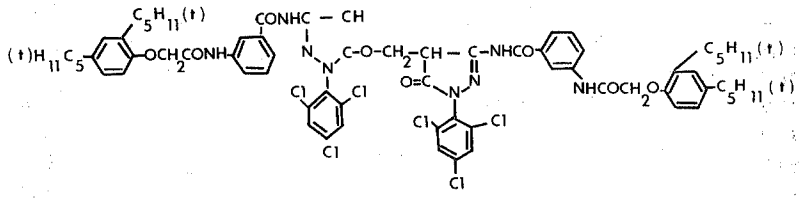
To a solution of 13.4 g. (1/50 mole) of 1-(2,4,6-trichlorophenyl)-3-[3-(2.4-di-t-amylphenoxy) acetamide-bezamide]-5-pyrazolone (the compound 1) in 50 ml. of acetic acid was added 3 ml. of 37% formaldehyde, and the resulting mixture was stirred for 30 minutes at room temperature (25°–27°C.) and then con-

centrated under reduced pressure to form a gelatinous substance. To this substance was further added a solution of 13.4 g. (0.02 mole) of the said coupler, and the resulting mixture was boiled under reflux for 30 minutes and then concentrated under reduced pressure. The concentrate was recrystallized from ether to obtain 21.3 g. (79.5% on theoretical basis) of pale yellow crystals, m.p. 238°–242°C.

Elementary analysis:

	C	H	N	Cl
Calculated (%)	61.20	5.36	8.28	15.71
Found (%)	60.95	5.21	8.45	16.03

Structural formula:



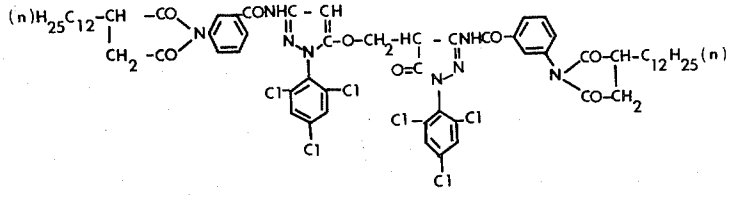
SYNTHESIS EXAMPLE 3

13 Grams (0.02 mole) of 1-(2,4,6-trichlorophenyl)-3-(3-n-dodecylsuccinimide-benzamide)-5-pyrazolone (the compound 2) was treated in the same manner as in Synthesis Example 1 to synthesize a crude bis-type coupler. This crude product was recrystallized from methanol to obtain 10.5 g. (80.4% on theoretical basis) of a white powder, m.p. 120°–122°C.

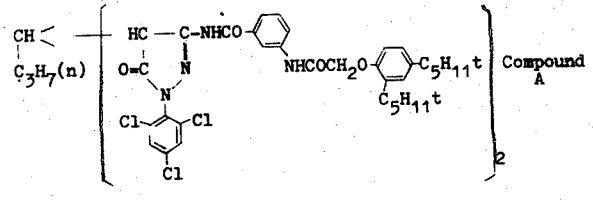
Elementary analysis:

	C	H	N	Cl
Calculated (%)	59.31	5.76	8.65	16.41
Found (%)	59.18	5.86	8.89	16.15

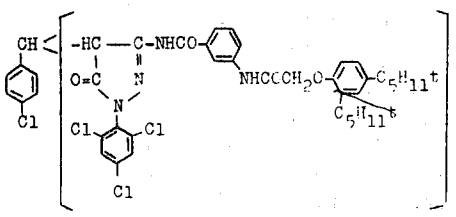
Structural formula:



The couplers synthesized according to the above-mentioned procedures are excellent in solubility and favorable in deposition property after storage as compared with such known alkylidene-bis compound (compound A disclosed in Japanese Patent Publication No. 26,589/1969) and arylidene-bis compound (compound B disclosed in U.S. Pat. No. 2,618,641) as shown below, and with the known mono-type compounds (the compounds 1 and 4)



Compound A



Compound B

TEST EXAMPLE

The above-mentioned compounds were compared each other in solubility for high boiling solvent and in deposition property after storage by measuring the amount of di-n-butyl phthalate used to dissolve 100 mg. of each coupler in said solvent at 60°C. and the time required for deposition of the coupler when the coupler solution was allowed to stand at 25° to 27°C. The results obtained were as set forth in Table 1.

Table 1

Coupler	Amount of di-n-butyl phthalate used	Time required for deposition
Compound A	1.2 ml.	20 hrs.
Compound B	2.0 ml.	18 hrs.
compound (1)	1.9 ml.	20 hrs.
Formalin-bis derivative of compound (1) (Coupler of Synthesis Example 2)	0.15 ml.	Non-deposition
Compound (4)	0.8 ml.	20 hrs.
Formalin-bis derivative of compound (4)	0.5 ml.	Non-deposition
(Coupler of Synthesis Example 1) Compound 1 1 part Coupler of Synthesis Example 2 1 part	0.4 ml.	Non-deposition

As is clear from Table 1, the compounds of the present invention are excellent in solubility for high boiling solvent. Moreover, the compounds A and B are extremely low in color developing rate at the time of color development, so that the independent use thereof is considerably difficult, whereas the compounds of the present invention are markedly excellent in color developing rate (refer to the accompanying drawing) and display prominent photographic properties (refer, for example, to Table 2).

Applications of the couplers used in the present invention are set forth below with reference to examples.

EXAMPLE 1

10 Grams of the coupler synthesized in Synthesis Example 1 was completely dissolved at 60°C. in a mixed solvent comprising 10 ml. of di-n-butyl phthalate and 20 ml. of ethyl acetate. This solution was mixed with a 10% aqueous solution of Alkanol B (trade name for a surface active agent produced by Du Pont) and with 200 ml. of a 5% aqueous gelatin solution, and then subjected to a colloid mill to form a dispersion. The thus formed dispersion was added to and dispersed in 1,000 ml. of a green sensitive silver iodobromide emulsion, which was then coated on a film base and dried to obtain a green sensitive color photographic material. This film was exposed and then developed with a developer of the following composition:

N,N-Diethyl-p-phenylenediamine hydrochloride	2.0 g.
Sodium sulfite (anhydrous)	2.0 g.
Sodium carbonate (monohydrate)	82.0 g.
Potassium bromide	2.0 g.
Water to make	1,000 ml.

The developed film was subjected to ordinary fixing and water-washing and then treated for 5 minutes with a bleaching solution of the following composition:

Potassium ferricyanide	100 g.
Potassium bromide	50 g.
Water to make	1,000 ml.

Subsequently, the film was fixed for 5 minutes with a fixing solution comprising 200 g. of sodium thiosulfate (pentahydrate) and 1,000 of water, washed with water for 20 to 30 minutes and then dried. The film gave a fine-grain magenta color image excellent in transparency and having an absorption maximum at 546 mμ.

EXAMPLE 2

Example 1 was repeated, except that the coupler used was replaced by the coupler synthesized in Synthesis Example 2, to obtain a film. This film gave a fine-grain magenta color image excellent in transparency and having an absorption maximum at 556 mμ.

EXAMPLE 3

Example 1 was repeated, except that the coupler used was replaced by a mixture comprising 5 g. of the coupler synthesized in Synthesis Example 2 and 5 g. of the exemplified compound (1), to obtain a film. This film gave a fine-grain magenta color image having an absorption maximum at 556 mμ.

When the films obtained in the above examples are compared in photographic properties with photographic films incorporated with any of the compounds A, B, (1) and (4), it is understood that the films according to the present invention are extremely high in durability of dye image and in density of developed color, as seen in Table 2.

Table 2

	λmax (mμ)	^{D}max	Light fastness (%)
Coupler of Synthesis Example 1	544	2.5	92
Coupler of Synthesis Example 2	556	3.0	93
Compound A	554	1.3	75
Compound B	553	1.2	78
Compound (1)	556	2.1	88
Compound (4)	546	2.2	79
Compound (1) 1 part Coupler of Synthesis Example 2 1 part	555	2.5	91

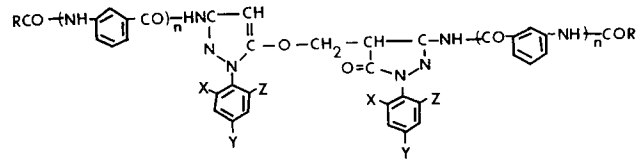
"Light fastness" in Table 2 represents the ratio of residual color after exposing the film to light for 20 hours by use of Fade-O-meter.

Characteristic curves of the compound A and the compound of Synthesis Example 2 are shown in the accompanying drawing, in which the solid line shows the case of the compound A and the dotted line shows the case of the compound of Synthesis Example 2.

As is clear from Table 2 and the drawing, the couplers of the present invention are excellent not only in color developability but also in storability, and hence are quite useful couplers.

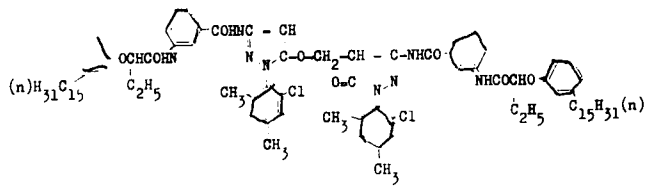
What we claim is:

1. A light-sensitive silver halide color photographic material containing a bis-type coupler of the general formula,

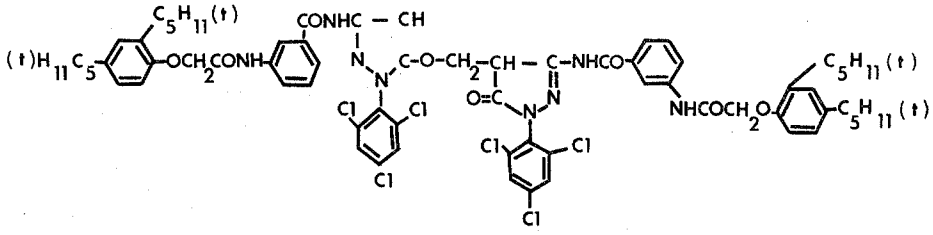


wherein R is an alkyl, aralkyl or aryl group; X, Y and Z are individually a hydrogen or halogen atom or an alkyl or alkoxy group having 1 to 4 carbon atoms, either one of said X and Z being necessarily a halogen atom; and *n* is zero or 1.

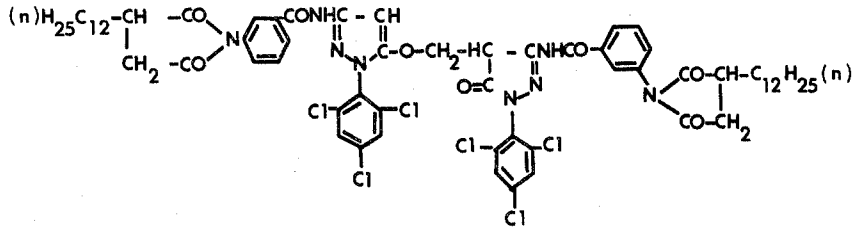
2. A light-sensitive silver halide color photographic material as claimed in claim **1**, wherein said bis-type coupler is a compound of the structural formula



3. A light-sensitive silver halide color photographic material as claimed in claim 1, wherein said bis-type coupler is a compound of the structural formula



4. A light-sensitive silver halide color photographic material as claimed in claim 1, wherein said bis-type coupler is a compound of the structural formula



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