

**3,761,274**  
**Patented Sept. 25, 1973**

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**3,761,274**  
**LIGHT-SENSITIVE COLOR PHOTOGRAPHIC**  
**MATERIAL**

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Claims priority, application Japan, July 10, 1970,

45/59.863

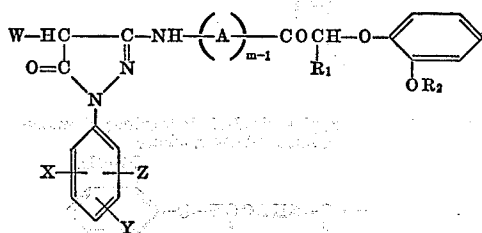
**Int. Cl. G03c 1/40**

**U.S. Cl. 96—100**

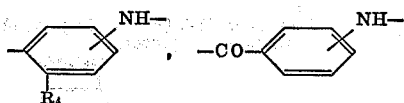
## 5 Claims

## ABSTRACT OF THE DISCLOSURE

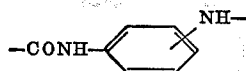
A light-sensitive silver halide color photographic material containing a compound of the general formula,



where W is a hydrogen atom, or a phenylazo group; X, Y and Z, which may be same or different, are individually a hydrogen or halogen atom, a lower alkyl group, a lower alkoxy group, a phenoxy group or a group of the formula COOR<sub>3</sub> (where R<sub>3</sub> is a lower alkyl group); A is a divalent group of the formula

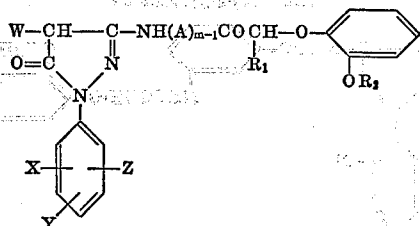


or



(where  $R_4$  is a hydrogen or halogen atom);  $m$  is an integer of 1 or 2;  $R_1$  is a hydrogen atom or a lower alkyl group; and  $R_2$  is an aliphatic hydrocarbon residue having 8 to 16 carbon atoms.

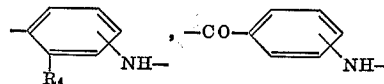
This invention relates to a light-sensitive silver halide color photographic material. More particularly, the invention pertains to a color photographic material containing, as a coupler of the so-called protect type (which is insoluble or difficultly soluble in water and which is used by dissolving the coupler in a difficultly water-miscible high boiling solvent and dispersing the resulting solution in a photographic emulsion), a novel coupler for forming a red color image which has the general formula,



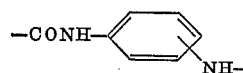
wherein X, Y and Z, which may be same or different, are individually a hydrogen or halogen atom, a lower alkyl group, a lower alkoxy group, a phenoxy group or a

2

group of the formula  $\text{COOR}_3$  (where  $\text{R}_3$  is a lower alkyl group); A is a divalent group of the formula



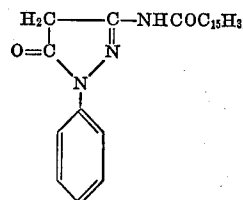
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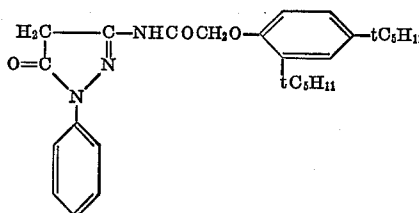
(where  $R_4$  is a hydrogen or halogen atom);  $m$  is an integer of 1 or 2;  $R_1$  is a hydrogen atom or a lower alkyl group;  $W$  is a hydrogen atom or a phenylazo group; and  $R_2$  is an aliphatic hydrocarbon residue having 8 to 16 carbon atoms.

Heretofore, many compounds have been proposed as protect type couplers. These couplers, however, have various drawbacks, and there have scarcely been known those which can be prepared at lower cost with higher purity.

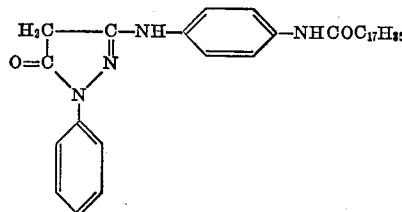
For example, the coupler disclosed in U.S. Pat. No. 2,428,054 which has the general formula,



the coupler disclosed in U.S. Pat. No. 2,694,703 which has the general formula,



and the coupler disclosed in Japanese patent publication No. 28,114/1964 which has the general formula,



can be synthesized easily and at relatively low cost. These couplers, however, have low solubility in high boiling solvents and are readily crystallizable, so that it is extremely difficult to use them as couplers of the protect type.

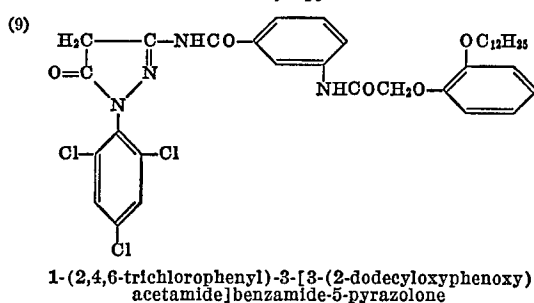
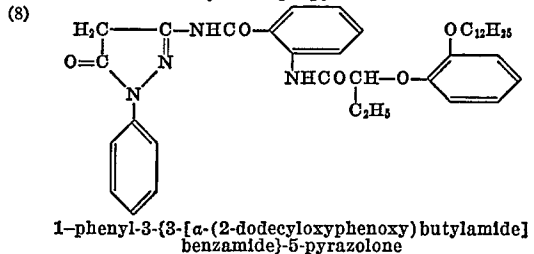
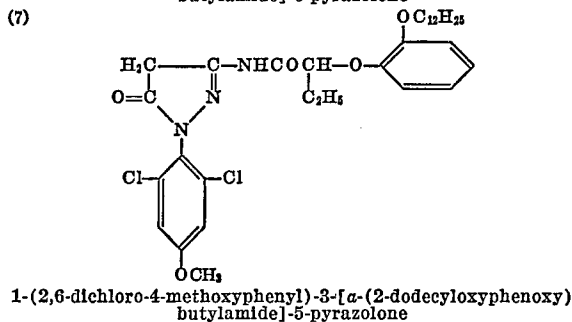
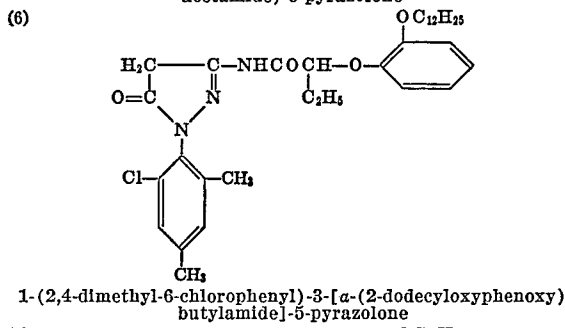
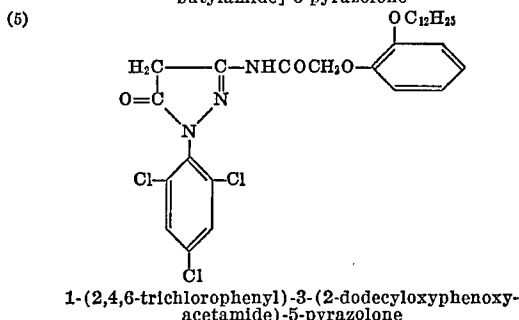
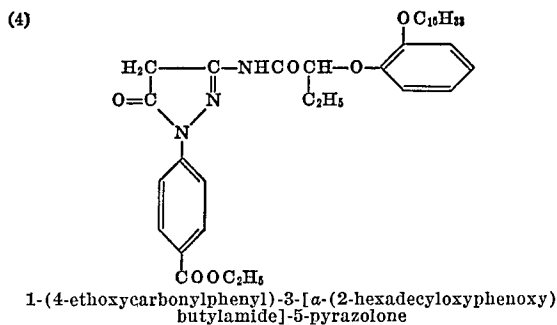
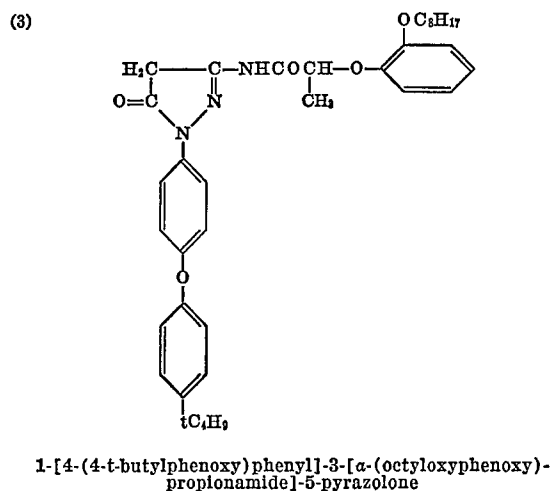
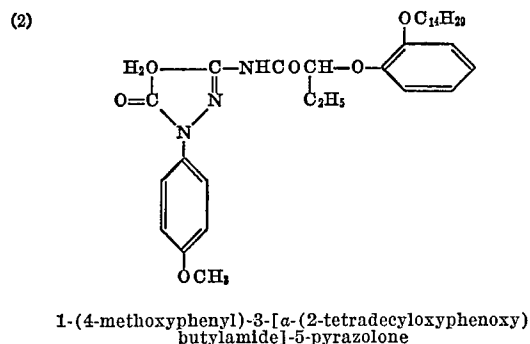
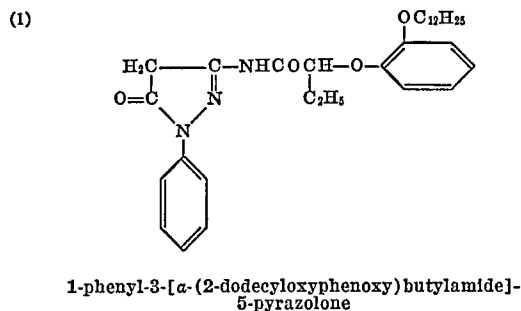
In contrast thereto, the coupler of the aforesaid general formula which is used in the present invention can be prepared simply and economically by utilizing a certain color-forming nucleus and by using as starting materials alkyl bromide and catechol which can be obtained commercially with ease and at low cost. The thus prepared coupler is easily soluble in a high boiling solvent such as phthalate or tricresyl phosphate, so that the amount of solvent for the coupler can be decreased to make it possible to obtain a highly concentrated dispersion. Moreover, the coupler synthesized in the above manner has a low melting point and hence has the characteristic that

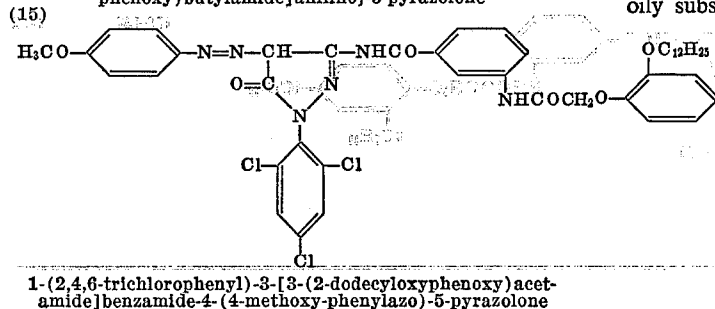
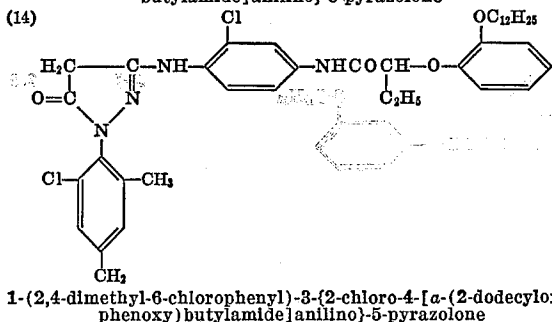
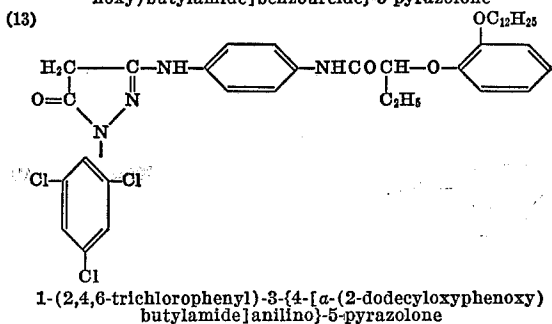
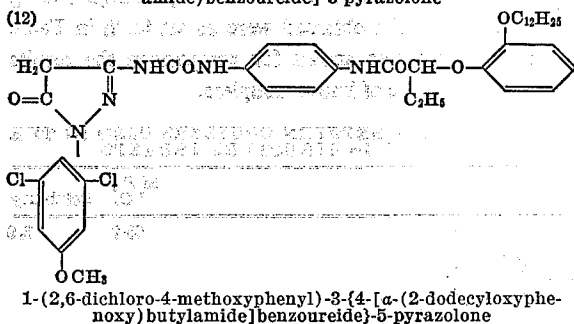
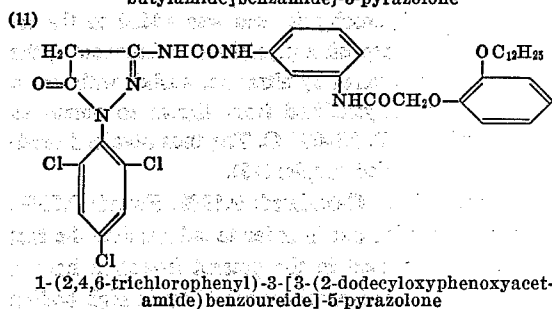
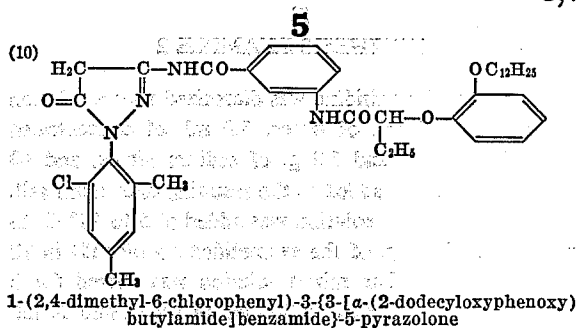
it is difficultly crystallized in a photographic emulsion or in a film formed by coating and drying the emulsion. Further, the light-sensitive color photographic material according to the present invention which has been incorporated with said coupler is favorable in durability and easily soluble in a high boiling solvent, so that the photographic material is excellent in spectral absorption characteristic and can give a color image which is favorable in transparency and high in density.

The coupler used in the present invention may be synthesized according to, for example, the following procedures:

A long chain alkyl bromide and catechol are condensed with in dimethylformamide in the presence of potassium bicarbonate to form a catechol monoalkyl ether, which is then condensed with a halogeno-fatty acid to obtain a long chain alkoxyphenoxy fatty acid. Subsequently, this acid is treated with phosphorus pentachloride to form the corresponding acid chloride, which is then condensed with a coupler component having an amino group, whereby the coupler used in the present invention can be synthesized.

Typical examples of the coupler having the aforesaid general formula are set forth below, but couplers usable in the present invention are not limited to these examples.





Concrete synthesis examples of typical couplers among those having the aforesaid general formula are set forth below.

- (a) A mixture comprising 110 g. of catechol, 500 ml. of dimethylformamide, 140 g. of potassium carbonate and 280 g. of dodecyl bromide was stirred at 110° to 120° C. for 3 hours and then poured into water. The oily layer formed was extracted with ether, and the extract was washed with water and then dried with anhydrous sodium sulfate. Subsequently, the ether was removed by distillation, and the residue was subjected to distillation to obtain a fraction of catechol monododecyl ether, B.P. 203–205° C./2 mm. Hg. yield 65%.

In the same manner as above, there were obtained catechol monooctyl ether, B.P. 180–3° C./4 mm. Hg; decyl ether, B.P. 192–3° C./4 mm. Hg; tetradecyl ether, B.P. 220–5° C./4 mm. Hg; and hexadecyl ether, B.P. 225–8° C./3 mm. Hg.

- (b) A solution of 13.8 g. of metallic sodium in 300 ml. of alcohol was mixed with 86.5 g. (0.3 mole) of catechol monododecyl ether, and the resulting mixture was boiled for 30 minutes. Thereafter, the mixture was charged with 50.5 g. (0.3 mole) of α-bromobutyric acid, boiled for 3 hours, poured into ice water with stirring and then acidified with hydrochloric acid to form a precipitate. This precipitate was recovered by filtration, dried and then recrystallized from hexane to obtain α-(2-dodecyloxyphenoxy) butyric acid, M.P. 74–6° C., yield 75%.

In the same manner as above, there were obtained long chain alkoxyphenoxy fatty acids to be used in the synthesis examples shown later. For example, 2-dodecyloxyphenoxy acetic acid, M.P. 68–70° C., was synthesized from catechol monododecyl ether and monochloroacetic acid; α-(2-tetradecyloxyphenoxy)butyric acid, M.P. 80–3° C., from resorcinol monotetradecyl ether and α-bromobutyric acid; α-(2-octyloxyphenoxy)propionic acid, M.P. 64–7° C., from resorcinol monooctyl ether and α-bromopropionic acid; and α-(2-hexadecyloxyphenoxy)butyric acid, M.P. 85–8° C., from resorcinol monohexadecyl ether and α-bromobutyric acid.

(c) The thus obtained long chain alkoxyphenoxy fatty acid is formed into an acid chloride by treatment with phosphorus pentachloride. For example, a suspension of 36.4 g. of 2-dodecyloxyphenoxy acetic acid in 100 ml. of chloroform is charged with 23 g. of phosphorus pentachloride, allowed to stand for 30 minutes and then heated for 30 minutes in a water bath kept at 60° C. Thereafter, by-produced phosphorus oxychloride and chloroform are removed by distillation under reduced pressure, and the residual chloride is used in the subsequent acylation step.

#### SYNTHESIS EXAMPLE 1

- A mixture comprising 7.02 g. of 1-phenyl-3-amino-5-pyrazolone, 21 ml. of acetonitrile, 4 ml. of pyridine and 14.60 g. of the chloride described in the abovementioned item (c) was refluxed for 1 hour and then poured into a liquid mixture consisting of 210 ml. of water and 21 ml. of concentrated hydrochloric acid to deposit a brown oily substance.

After removing the mother liquor by decantation, the oily substance was dissolved in ethyl acetate and dried

with anhydrous sodium sulfate, and then the solvent was removed by distillation under reduced pressure. The residual brown oily substance was dissolved in 200 ml. of hexane to deposit a white precipitate, which was then recovered by filtration, washed with a small amount of hexane and then dried to obtain 12.0 g. (57.4%) of a white powder, M.P. 66-7° C.

The thus obtained product was the exemplified Compound 1.

In the same manner as above, the exemplified Compounds 2 to 14 could be synthesized by the condensation of acid chloride having a different alkyl chain with nuclei having different substituents.

The melting points and nitrogen analysis values of the exemplified compounds were as set forth below.

Exemplified coupler	M.P. (° C.)	Nitrogen analysis values (percent)	
		Calculated	Found
1.....	66-7	8.06	7.82
2.....	70-2	7.25	7.04
3.....	53-4	7.20	6.97
4.....	80-1	6.80	6.65
5.....	48-50	7.03	6.79
6.....	Oil	7.19	7.00
7.....	Oil	6.77	6.70
8.....	67-8	8.74	8.85
9.....	45-7	7.82	7.71
10.....	53-4	7.96	7.83
11.....	Oil	9.57	9.40
12.....	57-8	9.28	9.03
13.....	62-3	7.82	7.70
14.....	65-7	7.89	7.73

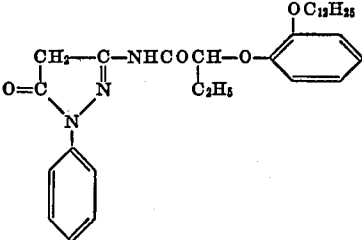
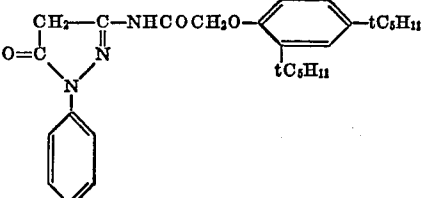
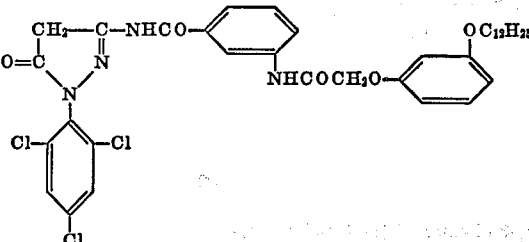
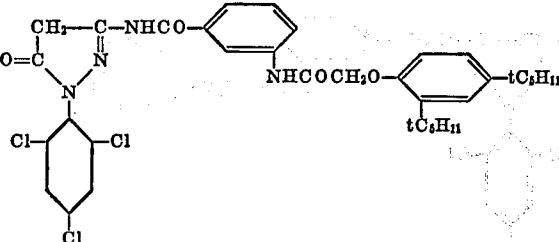
## SYNTHESIS EXAMPLE 2

1.8 grams of p-anisidine was diazotized with a solution comprising 20.0 ml. of water, 5.0 ml. of concentrated hydrochloric acid and 1.2 g. of sodium nitrite, and 40 ml. of alcohol was added to the resulting diazonium salt. This diazonium salt solution was added at 5 to 10° C. to a solution of 7.2 g. of the exemplified coupler (9) in 72 ml. of pyridine. The mixed solution was stirred for 3 hours and then diluted with 300 ml. of water, and 80 ml. of concentrated hydrochloric acid was added to the resulting dilution to deposit a precipitate. Subsequently, the precipitate was recovered by filtration, washed with water, dried and then recrystallized from ligroin to obtain an orange powder, M.P. 58-60° C. The thus obtained product was the exemplified coupler (15).

Nitrogen analysis: Calculated: 9.88%. Found: 9.70%.

Tests were carried out in order to substantiate the fact that the couplers used in the present invention have a low melting point and excellent solubility in high boiling solvents. The results obtained were as set forth in Table 1, in which are also shown for comparison the results obtained in the case of known couplers.

TABLE 1.—COMPARISON OF MELTING POINT AND SOLUBILITY BETWEEN COUPLERS USED IN THE PRESENT INVENTION AND KNOWN COUPLERS SIMILAR IN STRUCTURE THERETO

Coupler	Structure	M.P. ° C.	Solubility
Exemplified coupler (7).....		66-7	3.0
Coupler disclosed in U.S. Pat. 2,694,703.		204-6	(1)
Exemplified coupler (9).....		45-7	2.0
Coupler disclosed in U.S. Pat. 2,618,641.		138-139	11.0

<sup>1</sup> Substantially insoluble.

In Table 1, the solubility in high boiling solvent is represented by the amount (ml.) of dibutyl phthalate necessary to dissolve 1 g. of each coupler.

As is clear from Table 1, it is understood that the couplers used in the present invention have a low melting point and excellent solubility in high boiling solvents as compared with the known couplers, and hence are quite useful as protect type couplers.

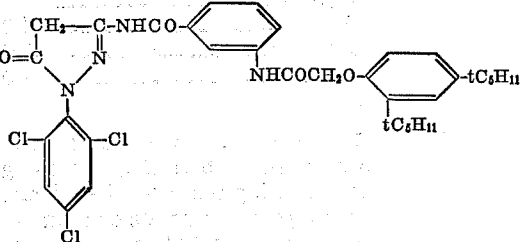
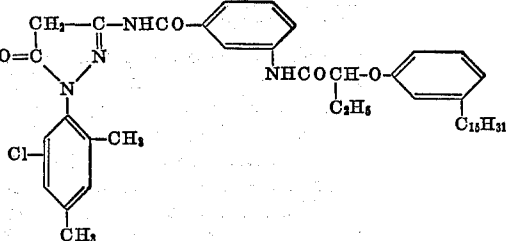
In the next place, test results showing the fact that the couplers according to the present invention give color images excellent in spectral absorption characteristics are set forth in Table 2.

In Table 2,  $\Delta\lambda_1$  is the difference between the absorption wave length  $\lambda_1$  (m $\mu$ ) at [D]=0.2 and  $\lambda_{max}$  (m $\mu$ ) at [D]=1.0 in the long wave side adsorption zone, and  $\Delta\lambda_2$  is the difference between the absorption wave length  $\lambda_2$  at [D]=0.4 and  $\lambda_{max}$  at the short wave side absorption zone.

$$\Delta\lambda_1 = \lambda_1 - \lambda_{max}$$

$$\Delta\lambda_2 = \lambda_{max} - \lambda_2$$

TABLE 2

	$\lambda_{max}$	$\Delta\lambda_1$	$\Delta\lambda_2$
Known coupler			
	555	80	64
Known coupler			
	546	77	64
Exemplified coupler:			
(9) -----	555	76	63
(10) -----	546	73	61

The results set forth in Table 2 are measured values of color images formed according to Example 1.

From the results of Table 2, it is understood that the couplers used in the present invention give color images excellent in spectral absorption characteristic.

For incorporation of the couplers used in the present invention into light-sensitive color photographic materials, there may be adopted any of the known procedures. For example, the couplers are dissolved either singly or in combination in a high boiling solvent having a boiling point of more than 175° C., such as tricresyl phosphate or dibutyl phthalate, a low boiling solvent such as butyl acetate or butyl propionate, or a mixture of said two solvents. Subsequently, the resulting solution is mixed with an aqueous gelatin solution containing a surfactant and then emulsified by means of a high speed rotary mixer or a colloid mill. Thereafter, the resulting emulsion is directly incorporated into a light-sensitive silver halide photographic emulsion and coated on a support such as a glass plate, synthetic resin plate, film base or laminated paper, and then a major proportion of the low boiling solvent is removed by drying to prepare a light-sensitive color photographic material. Alternatively, the said coupler emulsion is once set, finely cut, freed from the

low boiling solvent by water-washing or the like treatment and incorporated into a silver halide photographic emulsion, which is then coated on such a support as mentioned above and dried to prepare a light-sensitive color photographic material.

The above-mentioned incorporation procedure is illustrative and is not limitative. In the above case, the amount of the coupler to be incorporated into the photographic emulsion is ordinarily 10 to 100 g. per mole of the silver halide contained therein, but is not always limited to said range and is variable according to application purposes.

Further, the coupler may be incorporated into two or more different emulsion layers of a multi-layered light-sensitive color photographic material. The emulsion used in the present invention may contain any of various silver halides such as silver chloride, silver iodobromide and silver chlorobromide, and may have been incorporated with a chemical sensitizer, e.g. sulfur sensitizer, a natural sensitizer present in gelatin, a reducing sensitizer or

a noble metal salt. The emulsion may further contain ordinary photographic additives such as, for example, antifoggant, stabilizer, anti-stain agent, anti-irradiation agent, physical property-improving high polymer additive, film hardener, coating aid, etc. Furthermore, the emulsion may contain a known carbocyanine dye, merocyanine dye or the like as an optical sensitizer for the emulsion.

The thus obtained light-sensitive color photographic material is exposed to radio active rays such as  $\alpha$ -rays,  $\beta$ -rays, etc., visible rays, infrared rays or the like, developed with a developer containing a p-phenylenediamine type developing agent, and then subjected to bleaching, desilvering and fixing treatments to obtain a high density color image excellent in spectral absorption characteristic and durability and favorable in transparency.

Furthermore, a color photographic material containing the coupler of the present invention can give a color image of improved durability when the photographic material is incorporated with an ultraviolet absorber of the benzophenone type, e.g. 2-hydroxy-4-dodecyloxybenzophenone, or of the triazole type, e.g. 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)benzotriazole.

## 11

Typical examples of the developing agent used for development of the light-sensitive color photographic material of the present invention are sulfates, sulfites and hydrochlorides of the following:

N,N-diethyl-p-phenylenediamine,  
N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline,  
N-ethyl-N-hydroxyethyl-p-phenylenediamine,  
N-ethyl-N-hydroxyethyl-2-methyl-p-phenylenediamine  
and  
N,N-diethyl-2-methyl-p-phenylenediamine.

Further, the color developer used for development of the photographic material may contain, in addition to the above-mentioned developing agent, a development-controlling agent such as citrazinic acid or the like.

The present invention is illustrated in further detail below with reference to examples, but the examples are illustrative and it is needless to say that the invention is not limited only to these examples.

## EXAMPLE 1

10.0 grams of the exemplified coupler (9) was added to a mixed solvent comprising 10 ml. of dibutyl phthalate and 30 ml. of butyl acetate and then heated to 60° C., whereby the coupler was completely dissolved to form a solution. This solution was mixed with 5 ml. of a 10% aqueous solution of Alkanol B (alkylnaphthalene sulfonate produced and sold by Du Pont) and with 100 ml. of a 5% aqueous gelatin solution, and the mixed solution was subjected to a colloid mill to prepare a dispersion.

This coupler dispersion was incorporated into 1 kg. of a high speed light-sensitive gelatinous silver iodobromide photographic emulsion, which was then coated on a film base and dried to obtain a light-sensitive photographic film.

The thus obtained photographic film was exposed according to an ordinary procedure and then developed at 20° C. for 10 minutes with a developer of the following composition:

	G.
3-sodium N-ethyl-N-β-methane-sulfonamidoethyl-3-methyl-4-aminoanilate.12H <sub>2</sub> O	5.0
Anhydrous sodium sulfite	2.0
Benzyl alcohol	3.8
Sodium carbonate (monohydrate)	50.0
Potassium bromide	1.0
Caustic soda	0.55
Water to make 1,000 ml.	

Subsequently, the developed photographic film was subjected to ordinary stopping and fixing treatments, washed with water for 10 to 15 minutes and then treated for 5 minutes with a bleaching solution of the following composition:

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

Thereafter, the thus treated photographic film was washed with water for 5 minutes, fixed for 5 minutes in a fixing bath comprising 250 g. of sodium thiosulfate and 1,000 ml. of water, washed with water for 20 to 25 minutes and then dried to obtain a clear magenta color image having an absorption maximum at 550 mμ.

## EXAMPLE 2

10 grams of the exemplified coupler (8) was added to a mixed solvent comprising 10 ml. of tricresyl phosphate and 30 ml. of butyl acetate, and then heated to 50° C., whereby the coupler was completely dissolved to form a solution. This solution was mixed with 5 ml. of a 10% aqueous solution of Alkanol B and with 800 ml. of a 5% aqueous gelatine solution, and the mixed solution was

## 12

subjected to a colloid mill to prepare a coupler dispersion.

This dispersion was incorporated into 500 g. of a gelatin silver iodobromide emulsion, which was then coated on a film base and dried to obtain a photographic film.

The thus obtained photographic film was exposed and then developed at 21° C. for 12 minutes with a developer of the following composition:

	G.
Metol	3.0
Anhydrous sodium sulfite	50.0
Hydroquinone	6.0
Anhydrous sodium carbonate	40.0
Potassium bromide	3.5
Potassium rhodanate	2.0
Water to make 1,000 ml.	

Subsequently, the developed photographic film was subjected to ordinary stopping, hardening and water-washing treatments, and then to secondary exposure by use of a white light. Thereafter, the photographic film was developed at 21° C. for 13 minutes with a developer of the following composition:

	G.
N,N-diethyl-2-methyl-p-phenylenediamine	3.0
Anhydrous sodium sulfite	4.0
Sodium carbonate (monohydrate)	20.0
Potassium bromide	2.0
Water to make 1,000 ml.	

The thus developed photographic film was subjected to ordinary stopping, water-washing, bleaching and fixing treatments, washed with running water for 20 minutes and then dried to obtain a positive magenta color image having an absorption maximum at 540 mμ which was excellent in transparency.

## EXAMPLE 3

10 grams of the exemplified coupler (1) was mixed with 20 ml. of dibutyl phthalate and then heated to 50° C., whereby the coupler was completely dissolved to form a solution. This solution was mixed with 5 ml. of a 10% aqueous solution of Alkanol B and with 200 ml. of a 5% aqueous gelatin solution, and the mixed solution was subjected several times to a colloid mill to prepare a coupler dispersion. This dispersion was incorporated into 500 g. of a gelatin silver chlorobromide emulsion, which was then coated on a baryta paper and dried to produce a light-sensitive photographic material.

The thus produced photographic material was exposed and then developed at 25° C. for 10 minutes in a bath of the following composition:

	g--
N-ethyl-N-β-methane-sulfonamidoethyl-3-methyl-4-aminoaniline sulfate	8.5
3-sodium sulfate.12H <sub>2</sub> O	15.0
Sodium metaborate	10.0
Anhydrous sodium sulfite	7.0
Hydroxylamine sulfate	2.0
Potassium bromide	0.5
6-nitrobenzimidazole nitrate	0.04
Benzyl alcohol	10
Diethylene glycol	20
Caustic soda	1.2
Water to make 1,000 ml.	

The developed photographic material was dipped for 2 to 4 minutes in a stopping and fixing bath of the following composition:

	g--
Ammonium thiosulfate	120
Potassium metabisulfite	20
Glacial acetic acid	10
Water to make 1,000 ml.	

## 13

The thus treated photographic material was washed with water for 5 minutes and then bleached at 25° C. for 3 minutes in a bath of the following composition:

	G.
Sodium nitrate .....	28.0
Potassium ferricyanide .....	10.0
Boric acid .....	7.5
Potassium bromide .....	7.5
Water to make 1,000 ml.	

Subsequently, the photographic material was washed with water for 10 minutes, dipped for 2 minutes in a stabilization bath and then dried to obtain a magenta color image having an absorption maximum at 540 mμ which was excellent in fastness to light and moisture.

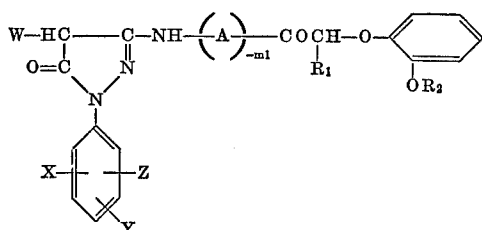
## EXAMPLE 4

2.0 grams of the exemplified coupler (15) was added to a mixed solvent comprising 2 ml. of dibutyl phthalate and 6 ml. of butyl acetate, and then heated to 60° C., whereby the coupler was completely dissolved to form a solution. This solution was mixed with 1 ml. of a 10% aqueous solution of Alkanol B and with 20 ml. of a 5% aqueous gelatin solution, and then emulsified to prepare a coupler dispersion. Subsequently, the coupler dispersion was incorporated into 100 g. of a high speed silver iodobromide photographic emulsion, which was then coated on a film base and dried to produce a light-sensitive photographic film.

This photographic film was exposed according to an ordinary procedure and then treated according to the same color development procedures as in Example 1 to obtain a yellow positive image having an absorption maximum at 440 mμ and a magenta color image having an absorption maximum at 550 mμ.

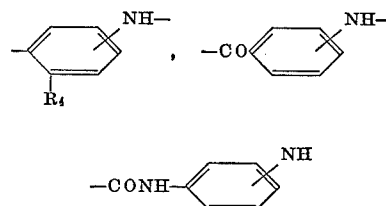
What we claim is:

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



## 14

wherein W is a hydrogen atom, or a phenylazo group; X, Y and Z, which may be same or different, are individually a hydrogen or halogen atom, a lower alkyl group, a lower alkoxy group, a phenoxy group or a group of the formula COOR<sub>3</sub> (where R<sub>3</sub> is a lower alkyl group); A is a divalent group of the formula



(where R<sub>4</sub> is a hydrogen or halogen atom); m is an integer of 1 or 2; R<sub>1</sub> is a hydrogen atom or a lower alkyl group; and R<sub>2</sub> is an aliphatic hydrocarbon residue having 8 to 16 carbon atoms.

2. The light-sensitive silver halide color photographic material of claim 1 wherein said compound is 1-(2,4,6-trichlorophenyl)-3-(2-dodecyloxyphenoxyacetamide)-5-pyrazolone.

3. The light-sensitive silver halide color photographic material of claim 1 wherein said compound is 1-(2,4-dimethyl-6-chlorophenyl)-3-[α-(2-dodecyloxyphenoxy)butylamide]-5-pyrazolone.

4. The light-sensitive silver halide color photographic material of claim 1 wherein said compound is 1-(2,4,6-trichlorophenyl)-3-[3-(2-dodecyloxyphenoxy)acetamide]benzamide-5-pyrazolone.

5. The light-sensitive silver halide color photographic material of claim 1 wherein said compound is 1-(2,4-dimethyl-6-chlorophenyl)-3-[3-[α-(2-dodecyloxyphenoxy)butylamide]benzamide]-5-pyrazolone.

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