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LIGHT SENSITIVE COLOR MATERIALS

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Int. Cl. C07c *103/33*
U.S. Cl. 260—559 **2 Claims**

The present invention relates to color photography and more particularly to a color coupler soluble in organic solvent and having an oil-solubilizing group.

In the formation of color photographic images by a subtractive color process, couplers capable of forming cyan, magenta and yellow dyes by coupling with the oxidation product of a developer of N,N-di-substituted paraphenylene diamine series have generally been used.

In a color photographic material wherein three such kinds of couplers are incorporated in three or more photographic emulsion layers having different spectral sensitivities, there has been adopted a process in which the couplers are converted to be water soluble by introducing molecules of the couplers alkali-solubilizing groups. The couplers are then incorporated in said three or more photographic emulsions as the aqueous solutions or the alkaline aqueous solutions thereof, and a process in which the couplers are converted to be oil-soluble by introducing into the molecules of the couplers oil-solubilizing groups. Then the couplers are incorporated in the photographic emulsions as the solutions thereof in an organic solvent.

It is well known that in order to obtain such a type of light sensitive color material capable of forming by color development a color image stable to light, heat and moisture, and having a good color reproducing property, and an excellent color tone, it is desirable to use couplers which introduce therein oil-solubilizing groups, or so-called protective couplers, which can be dispersed in emulsions as the solutions thereof in an organic solvent insoluble or weak-soluble in water. Hereinafter, such an organic solvent is called "coupler solvent."

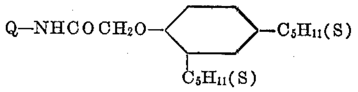
It is of course desirable, in the case of using such a protective coupler, that the coupler have an excellent coupling efficiency and the color image obtained from the coupler have excellent photographic properties such as color hue, but the particularly important factors for the couplers are that the coupler have a sufficient solubility to a coupler solvent, and have a good dispersibility in a photographic emulsion as well as in a photographic emulsion layer during or after coating on a support, which prevents the coupler being deposited or aggregated. Accordingly, there are provided various protective couplers having oil-solubilizing groups in many patents, but many of them have no sufficient solubility to coupler solvents, or no sufficient dispersibility in emulsions and hence they are frequently deposited or aggragated.

An object of the present invention is to provide couplers capable of preventing the unevenness of coating and the reduction in image quality.

Another object of the present invention is to provide couplers having a sufficiently good solubility to coupler solvents, such as ethyl acetate, butyl phthalate, o-tricresylphosphate, or butylphosphate and causing neither deposition nor aggregation when they are dispersed in emulsions or incorporated in emulsion layers during or after coating the coupler-containing emulsions on a support, or when or after the color photographic material having the emulsion layers containing the couplers are subjected to color development.

Still another object of the present invention is to provide a color photographic material containing the abovementioned improved couplers.

The inventors have found that the abovementioned objects of this invention can be sufficiently accomplished by the couplers having the general formula:



$$Q\text{—NHCOCH}_2\text{O—C}_6\text{H}_3\text{—C}_5\text{H}_{11}(\text{S}) \quad (\text{C}_5\text{H}_{11}(\text{S}))$$

Q represents a coupler residual group capable of coupling with the oxidation product of a color developer, such as a compound having a phenolic hydroxyl group (e.g., phenol or naphtol), a compound having an active methylene group (e.g., pyrazolone, indazolone, or acylacetanilide), and the derivatives of them; and (S) means "secondary."

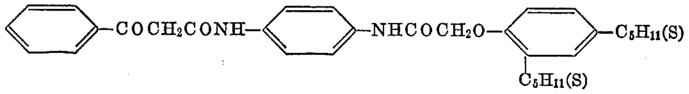
When Q is a phenol compound or a naphthaol compound, a coupler having the above formula can provide a cyan dye by coupling; when Q is a pyrazolone compound or a indazolone compound, the coupler provides a magenta dye by coupling; and when Q is an acylacetanilide compound, the coupler provide a yellow dye by coupling.

It has been well known that these couplers one of which however, composed of hydrogen atoms at the coupling positions is substituted with a halogen atom, a thiocyanide group or a sulfone group, have a merit that the amount of silver ions necesasry for forming dye with the coupler may be half the amount thereof in the case of the unsubstituted coupler, and further, the couplers substituted with an azo compound residual group or aromatic aldehyde residual group have the function of making color correction of unnecessary absorption of the cyan dye or the magenta dye. Furthermore, it has been known that the abovementioned coupler of which, however, one of hydrogen atoms at the coupling positions is substituted with an alkyl group or aryl group has the characteristics of coupling with the oxidation product of a color developer to form a colorless compound.

As the color developer there have generally been used mainly p-phenylenediamine and the derivatives thereof, such as N,N - diethylaminoaniline, N,N-diethylaminotoluidine, N-ethyl - N - hydroxyethylaminotoluidine, N-ethyl-N-methylsulfoneaminoethylamino-toluidine, and the salts thereof.

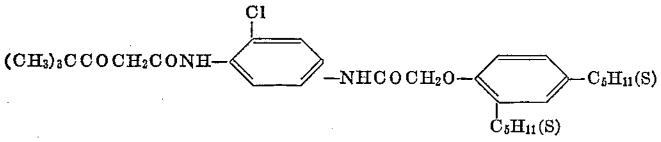
As shown above, the feature of the coupler to be used in the present invention is that it has 2,4-di-secondary-amyl-phenoxyacetamino group as the oil-solubilizing group and Q of the aforementioned formula may be any compound capable of coupling with the oxidation product of a color developer.

Examples of the coupler to be used in this invention are as follows:



$$\text{C}_6\text{H}_5\text{—COCH}_2\text{CONH—C}_6\text{H}_4\text{—NHCOCH}_2\text{O—C}_6\text{H}_3\text{—C}_5\text{H}_{11}(\text{S}) \quad (\text{C}_5\text{H}_{11}(\text{S}))$$

(1)



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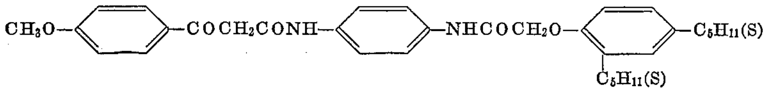

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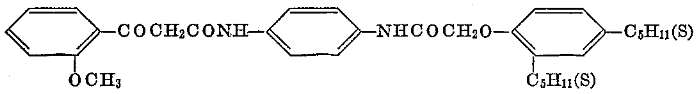

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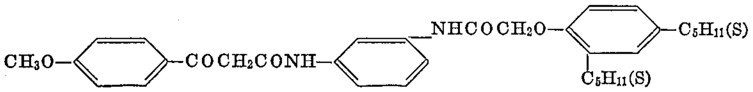

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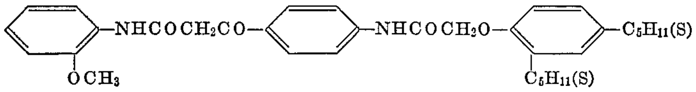

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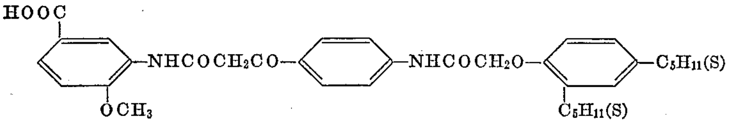

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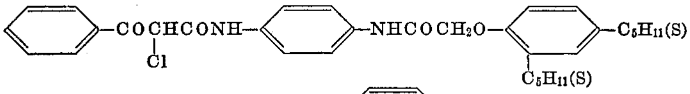

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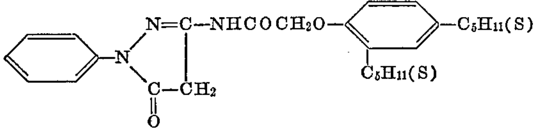

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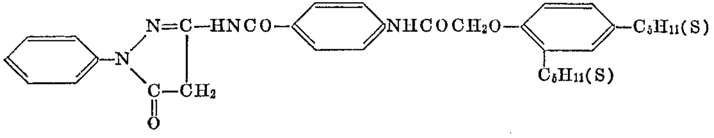

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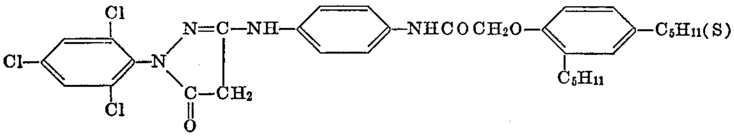

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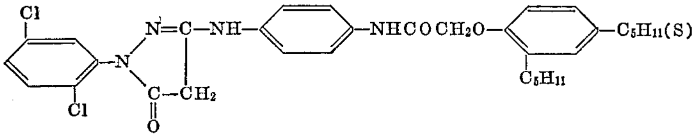

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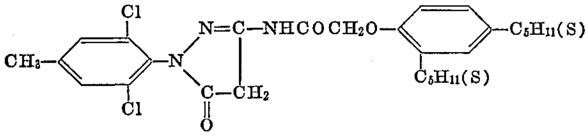

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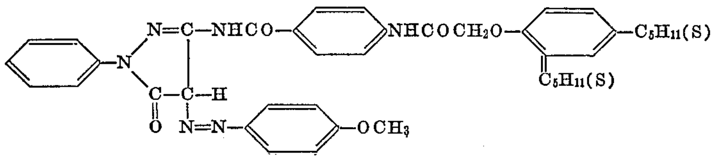

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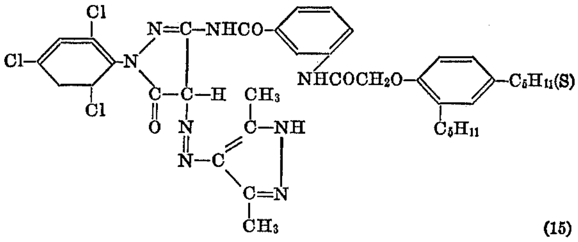

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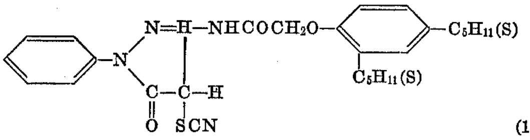

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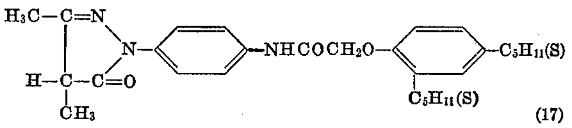

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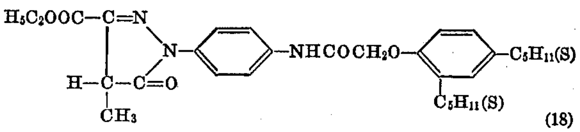

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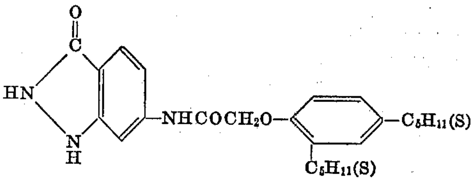

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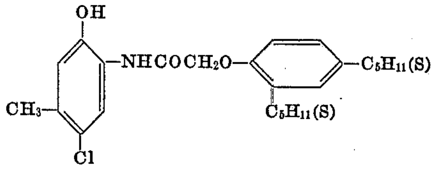

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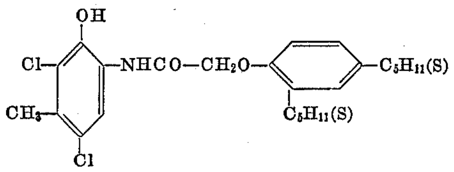

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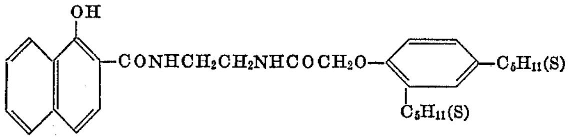

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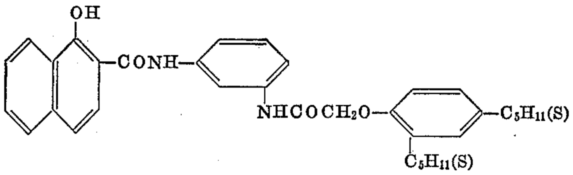

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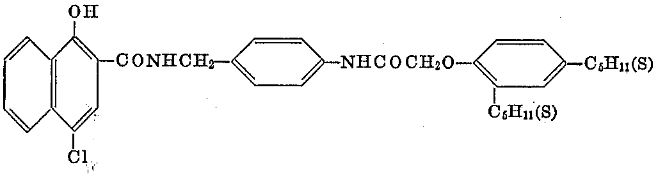

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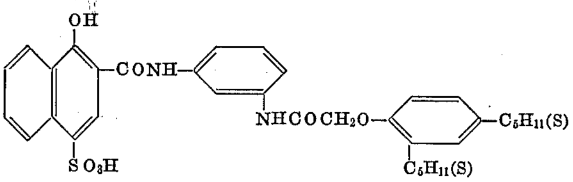

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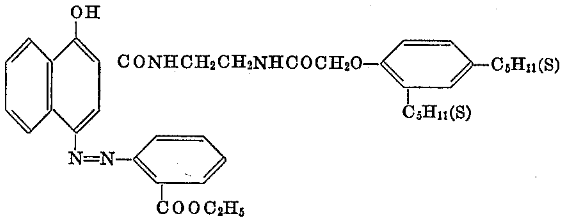

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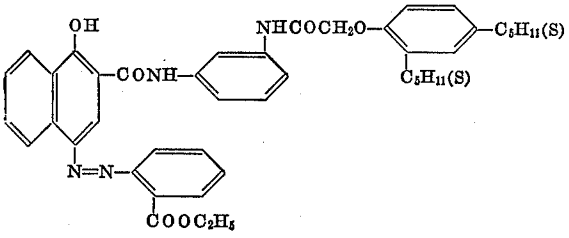


(27)

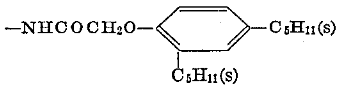
Since the coupler of this invention having the oil-solubilizing group may be prepared by using, as the starting material, inexpensive and easily available 2,4-di-secondary amylphenol, the cost of a coupler so prepared is low, and as shown in the following examples of preparation, it can be produced very profitably.

About the typical examples of the couplers to be used in the present invention, the solubilities thereof in a coupler solvent, ethyl acetate at 25° C. are shown in Table 1 together with those of control couplers having an oil-solubilizing group (2,4-di-tertiary-amyl-phenoxyacetamino group) having the similar structure to the group of this invention.

TABLE 1

	Coupler of this invention (I)		Control coupler (II)		
Mother nuclear structure of coupler	M.P., ° C.	Solubility (A), percent	M.P., ° C.	Solubility (B), percent	(A)/(B)
(a)	165	2.7	185	0.27	10.0
(b)	110	>30	140	4.7	6.4
(c)	120	29.2	149	3.7	7.9
(d)	135	19.1	223	1.9	10.0
(e)	140–142	22.4	185–186	2.9	7.7
(f)	190	9.8	220	3.1	3.1
(g)	150–152	2.4	201–203	0.3	8.0
(h)	25–27	28.7	158	12.2	2.4
(j)	120–122	18.5	144–146	7.1	2.6

(I):



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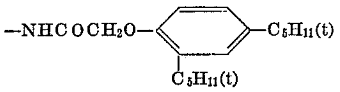

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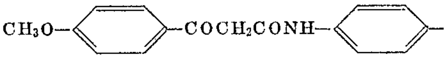

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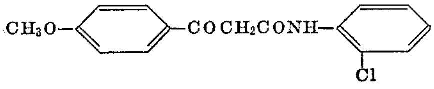

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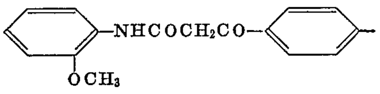

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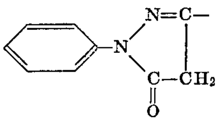

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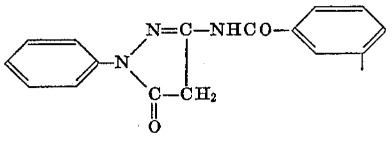

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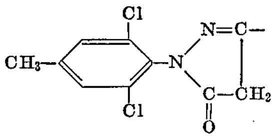
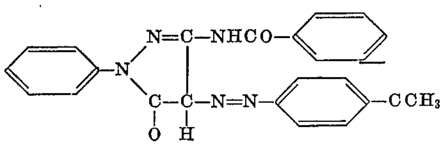


(g):



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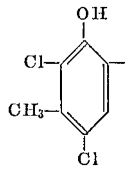

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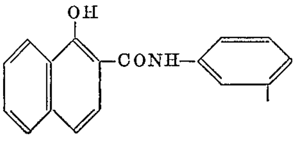


From Table 1 it will be understood that although the 2,4-di-tertiary-amyl-phenoxyacetamino group is generally used as an oil-solubilizing group, the melting point of the coupler in this invention is about 20° C. lower than that of the conventional coupler having such a known group. Further, solubility of the coupler of this invention in the coupler solvent is about, in average, 7 times as large as that of the corresponding conventional coupler. Moreover, the coupler used in this invention can be dissolved very highly in an ester type organic solvent such as a phthalic acid ester, a phosphoric acid ester, and an acetic acid ester, and hence, when the organic solution of the coupler is maintained at a super cooled state, the deposition of the crystal of coupler and the aggregation thereof are very slow, which makes the use of the coupler extremely profitable.

The solubility of the coupler shown in Table 1 is at a normal temperature (25° C.) but the solubility is rapidly increased as the increase of temperature, and hence, a large quantity of the coupler can be dissolved in a small proportion of coupler solvent. Such properties of the coupler, that the solubility of the coupler to coupler solvents is high, and the deposition of the coupler crystal and the aggregation thereof are very slow, are very important for the process wherein the coupler is incorporated in a photographic emulsion after dissolving it in the coupler solvent and then dispersing the solution in a gelatin solution. Further, it will be clear that by using the coupler of this invention having such important properties, the color hue, the transparency and the density of the color image of the color photographic material obtained from the coupler, as well as the stability thereof to light, heat and moisture are remarkably improved.

The coupler of this invention may be added as a solution of a high boiling point solvent, a low boiling point solvent or a mixture of both solvents. Further, the coupler of this invention is usually added in a photographic emulsion, as mentioned above, after dissolving on the coupler solvent and then dispersing the solution in gelatin, but the coupler may be added therein by other method. For example, if the melting point of the coupler is low the coupler is melted by heating and the melt is dispersed in a gelatin solution, or the coupler may be added in a photographic emulsion as a solution thereof in an alkaline aqueous solution. These methods will be explained practically in below examples.

The color photographic material prepared by applying to a support the photographic silver halide emulsion obtained by the abovementioned various methods is exposed and developed in a color developer mainly consisting of N-N-di-substituted-p-phenylene diamine series developer, which confirms the light sensitive color element having a good photographic property.

Further, the use of the coupler of this invention is not limited to only usual color photographic materials, but the coupler may be utilized to obtain two-color images or mono-color images and may be used for printing as well.

The following examples illustrate the preparations of the couplers to be used in this invention.

PREPARATION 1

2,4-di-secondary-amyl-phenoxyacetyl chloride

Metallic sodium was dissolved in ethanol and into the solution was added commercially available 2,4-di-secondary-amyl-phenol to form sodium phenolate and thereafter excessive ethanol was distilled off under a reduced pressure. The product was added with toluene, ethylchloro acetate was added into the mixture with stirring, and the system was reacted for about two hours under refluxing. After removing by filtration the produced sodium chloride and distilling off toluene under reduced pressure, ethyl-2,4-di-secondary-amyl-phenoxy acetate was obtained from the reaction mixture by distillation under a reduced pressure. The yield of the product was 78% and the boiling point thereof was 150–162° C./2.5 mm. Hg.

Thus obtained ethyl-2,4-di-secondary-amyl-phenoxy acetate was added into a diluted sodium hydroxide solution and after boiling for about two hours hydrochloric acid was added into the solution to form an oily mass, which was separated and extracted. By distilling the extract under a reduced pressure, 2,4-di-secondary-amyl-phenoxy acetic acid was obtained. The yield and the boiling point thereof were 75% and 150–167° C./1.5 mm. Hg respectively.

The obtained 2,4-di-secondary-amyl-phenoxy acetic acid was caused to react with thionyl chloride by a conventional manner and then by distilling the reaction product under a reduced pressure, 2,4-di-secondary-amyl-phenoxyacetyl chloride was obtained. The yield and the boiling point thereof were 71% and 150–155° C./200 mm. Hg respectively.

PREPARATION 2

2-methoxy-(4-(2,4-di-secondary-amyl-phenoxyacetamino) benzoyl) acetanilide: Formula 6

In a flask were charged 28 g. of 2-methoxy-(4-aminobenzoyl)-acetanilide, 10 g. of anhydrous sodium acetate, and 300 ml. of glacial acetic acid and while stirring at room temperature 31 g. of the above-prepared 2,4-di-secondary-amyl-phenoxyacetyl chloride was added into the mixture. After reacting the system for about five hours with stirring, undissolved matters were removed by filtration and the resultant solution was added into ice water to deposit crystals. The crystals were recovered by filtration, washed with water, dried and then recrystallized from ethanol solution thereof to provide the objective acetanilide. The yield of the product was 54% (30 g.), the melting point thereof was 120–121° C. and the nitrogen analytical value was found to be 5.21% (calculated 5.02%).

PREPARATION 3

1-phenyl-3-3(3-(2,4-di-secondary-amyl-phenoxyacetamino) benzamido)-5-pyrazolone: Formula 10

In a flask 29 g. of 1-phenyl-3-(3-aminobenzamide)-5-pyrazolone, 10 g. of triethylamine and 100 ml. of acetone were charged, and while stirring at room temperature 31 g. of 2,4-di-secondary-amyl-phenoxyacetyl chloride was added into the mixture. After reacting the system for about 30 minutes, undissolved matters were removed by filtration and then 500 ml. of petroleum ether was added into the reaction mixture to precipitate crystals, which were recovered by filtration and recrystallized from a mixed solvent of benzene and ethanol to provide 35 g. of the objective pyrazolone. The yield and the melting point of the product were 62% and 140–142° C. respectively and the nitrogen analytical value of it was found to be 9.33% (calculated 9.85%).

PREPARATION 4

1-phenyl-3-(3-(2,4-di-secondary-amyl-phenoxyacetamino) benzamido)-4-(4-methoxyphenylazo)-5-pyrazolone: Formula 14

6 g. of p-anisidine was dissolved into 40 ml. of water and 20 ml. of concentrated hydrochloric acid, and dropwise into the mixture a solution of 4 g. of sodium nitrate in 40 ml. of water was added at a temperature lower than 5° C. The above prepared 1-phenyl-3-(3-(3,4-di-secondary-amyl-phenoxyacetamino) benzamino)-5-pyrazolone (24 g.) was dissolved into 400 ml. of pyridine and into the resulting solution was added dropwise into the abovementioned diazotized solution at a temperature lower than 5° C. After reacting the system for about 30 minutes, the product was poured into water and the resulting crystals were collected by filtration. The crystals were washed with concentrated hydrochloric acid and then recrystallized from ethanol to provide 24 g. of the objective pyrazolone. The yield and the melting point of the product were 81% and 150–152° C. respectively. The nitrogen analytical value was 12.22% (calculated 11.97%).

PREPARATION 5

2,4-di-chloro-3-methyl-5-(2,4-di-secondary-amyl-phenoxyacetamino) phenol: Formula 21

In a flask 23 g. of the hydrochloride of 2,4-di-chloro-3-methyl-5-aminophenol, 31 g. of 2,4-di-secondary-amyl-phenoxyacetyl chloride, and 400 ml. of acetonitrile were charged and the system was boiled for about two hours under refluxing. After removing by filtration undissolved matters, the precipitated crystals were recovered by filtration and recrystallized from acetonitrile to provide the objective phenol (25 g.). The yield and the melting point of the product were 54% and 25–27° C. respectively and the nitrogen analytical value thereof was 2.87% (calculated 3.00%).

PREPARATION 6

1-hydroxy-2-(3-(2,4-di-secondary-amyl-phenoxyacetamido)-naphthanilide: Formula 23

Into 150 ml. of acetonitrile was dissolved 15 g. of 1-hydroxy-2-(3-amino)naphthanilide while boiling under refluxing and into the solution was added 17.5 g. of 2,4-di-secondary-amyl-phenoxyacetyl chloride. After reacting for about three hours, acetonitrile was distilled off under a reduced pressure, and 200 ml. of petroleum ether was added into the reaction mixture. Thus precipitated crystals were recovered by filtration, boiled in petroleum ether for washing, and recrystallized from ethanol to provide the objective naphthanilide (18 g.). The yield and the melting point of the product were 60% and 120–122° C. respectively and the nitrogen analytical value thereof was 5.29% (calculated 5.07%).

The invention will, now, be explained referring to the following examples.

EXAMPLE 1

Into 4 g. of dibutyl phthalate was added 2 g. of the coupler having the aforementioned structural Formula 6 and dissolved therein by heating. The coupler containing solution was added into 30 ml. of a 7% aqueous gelatin solution containing 0.1 g. of sodium dodecylbenzene sulfonate and emulsion-dispersed therein by stirring at high speed for 10 minutes in a homo-blender at 60° C.

The whole proportion of the emulsified dispersion was added in 100 g. of a photographic light-sensitive emulsion containing 5 g. of silver bromide and 6 g. of gelatin and the resulting emulsion was applied to a film base and dried to provide a color photographic material. Thus prepared photographic light sensitive film was exposed, color developed in a developer having the following composition, processed by using the bleaching solution and the mixing solution having the following composition, and dried.

Developer

2-methyl-4-N,N-diethylaminoaniline—2.0 g.
Sodium sulfite (anhydrous)—5.0 g.
Sodium carbonate (mono-hydrate)—20.0 g.
Potassium bromide—2.0 g.
Water to make 1 liter.

Bleaching solution

Potassium ferricyanate—100 g.
Potassium bromide—20 g.
Water to make 1 liter.

Fixing solution

Sodium thiosulfate—200 g.
Sodium sulfite—20 g.
Acetic acid (28%)—45 g.
Boric acid—7.5 g.
Potassium alum—20 g.
Water to make 1 liter.

Thus obtained yellow-colored film had its absorption maximum at 445 nm. and showed lemon yellow, having very few absorption in green portion. Further, the obtained yellow image was stable against heat and moisture and the transparency of the film was very good, and no deposition and aggregation of the coupler were observed.

EXAMPLE 2

Into a mixture of 2 g. of dibutyl phthalate and 4 ml. of ethyl acetate was dissolved by heating 2 g. of the coupler having afore-stated structural Formula 10 and the resulting solution was added into 30 ml. of a 7% aqueous gelatin solution containing 0.1 g. of sodium dodecylbenzene sulfonate and emulsion dispersed therein by stirring at a high speed in a homo-blender at 50° C.

The whole proportion of the emulsified dispersion was added into 100 g. of a gelatino silver iodo-bromide emulsion containing an orthornatic sensitizer and the resulting emulsion was applied to a baryta paper and dried to provide a color photographic material.

Color paper was exposed, color developed in the developer having the following composition:

Developer

2-methyl-4-N-ethyl-N-methylsulfonamino (ethylamino-aniline)—5.2 g.
Sodium carbonate (mono-hydrate)—30 g.
Sodium sulfite (anhydrous)—2 g.
Potassium bromide—1 g.
Benzyl alcohol—10 ml.
Hydroxylamine sulfate—2.4 g.
Water to make 1 liter.

Thus developed color paper was processed by using the bleaching solution having the following composition and the fixing solution as in Example 1, and dried.

Bleaching solution

Potassium nitrate—30 g.
Potassium ferricyanate—20 g.
Potassium bromide—10 g.
Boric acid—5 g.
Borax—2.5 g.
Water to make 1 liter.

Thus, a magenta image having sharp absorption curve with absorption maximum at 532 nm. was obtained. Further, no precipitation and aggregation of the coupler were observed during the whole processes for the production of the color photographic material, after processing, or in the color image.

EXAMPLE 3

The same procedure as in Example 2 was repeated using 6 ml. of ethyl acetate instead of dibutyl phthalate in the example and a color photographic material was obtained. The film was exposed, developed and processed as in Example 2.

Thus obtained magenta image has sharp absorption, and no precipitation or aggregation of the coupler was observed.

EXAMPLE 4

To grams of the coupler having aforementioned structural Formula 21 were melted by heating, added in 30 ml. of a 10% aqueous gelatin solution containing 0.2 g. of sodium dodecylbenzene sulfonate, and emulsion dispersed therein by stirring at a high speed in a homo-blender for 10 minutes at 50° C.

The whole amount of the emulsified dispersion was added into 100 g. of a gelatino silver iodo-bromide emulsion containing a panchromatic sensitizer and the resulting emulsion was applied to a film base followed by drying to provide a color photographic film. The film was exposed and developed and processed as in Example 1.

Thus, a cyan image having the sharp absorption curve with absorption maximum at 655 nm. as obtained. Further, during the whole processes as well as after processing, no precipitation or aggregation of the coupler was observed. The color image was also stable against heat and moisture and could be stored for a long period of time.

EXAMPLE 5

Into a mixture of 6 ml. of a 1 N aqueous sodium hydroxide solution and 18 ml. of methanol was dissolved heating 2 g. of the coupler having aforementioned Formula 25 and the solution was added with water to make 40 ml. of the aqueous solution. The whole proportion of the coupler containing solution was added into 100 g. of a gelatino silver iodo-bromide emulsion containing a panchromatic sensitizer, and after neutralizing the emulsion with the addtition of a 2% aqueous citric acid solution, the resulting emulsion was applied to a film base followed by drying to provide a color photographic film. The film was exposed and developed and processed as in Example 1.

Thus, a cyan image having sharp absorption curve with the absorption maximum at 695 nm. was obtained and no precipitation or aggregation of the coupler was observed.

EXAMPLE 6

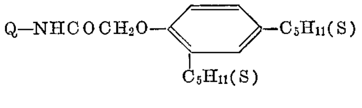
2 g. of the coupler having the aforementioned structural Formula 14 was dissolved into 16 g. of tricresyl diphosphate by heating. The coupler-containing solution was added into 160 ml. of a 10% gelatin solution containing 0.3 g. of sodium dodecylbenzene sulfonate and emulsion dispersed therein by repeating five times the high speed stirring for five minutes in a homo-blender at 65° C. and interruption for one mintue.

Into 100 g. of a gelatino silver iodo-bromide emulsion containing an orthomatic sensitizer was added 15 g. of the above prepared emulsion and the resulting mixture was applied to a film base followed by drying to provide a color photographic film. The film was exposed in green light and developed and processed as in Example 1.

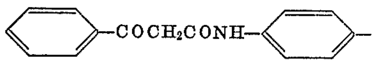
Thus, a magenta negative image and a yellow positive image having the absorption maximum at 435 nm. were obtained. The transparency of thus obtained film was very good and during the whole processes, no precipitation and aggregation of the coupler were observed.

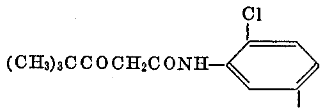
We claim:

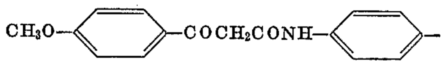
1. A color coupler compound represented by the formula

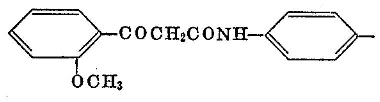


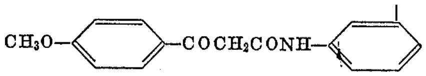
wherein Q represents a coupler residual group capable of coupling with the oxidation product of a color developer and (S) means "secondary," said residual group being selected from the group consisting of

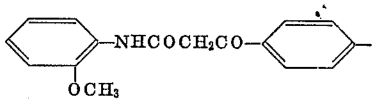


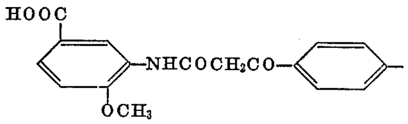


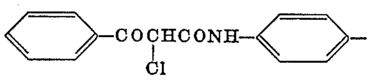


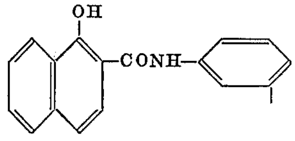


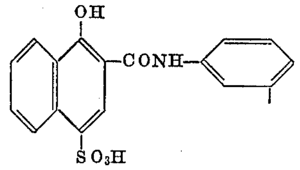


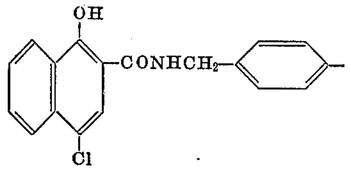


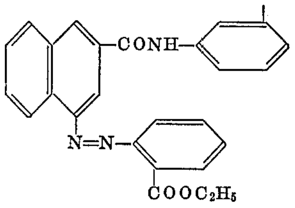


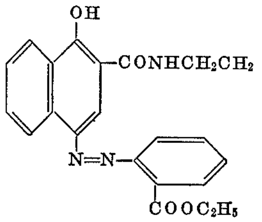




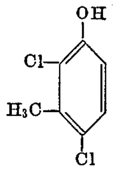




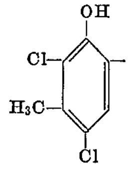




2. A color coupler compound represented by the formula:



wherein Q represents a coupler residual group capable of coupling with the oxidation product of a color developer and (S) means "secondary," said coupler residual group being represented by the formula:



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