# United States Patent [19]

**Inoue et al.**

[11] **3,832,386**

[45] **Aug. 27, 1974**


[54] **COLOR PHOTOGRAPHIC MATERIAL**


[75] Inventors: **Isaburo Inoue; Teruo Hanzawa; Takaya Endo; Hidetaka Deguchi,** all of Tokyo, Japan

[73] Assignee: **Kanishiroku Photo Industry Co., Ltd.**



[22] Filed: **May 13, 1971**

[21] Appl. No.: **143,241**

[30] **Foreign Application Priority Data**

May 14, 1970 Japan ..... 45-40492

[52] **U.S. Cl.** ..... **260/471 R,** 96/100, 260/326.3, 260/404.5, 260/558 R, 260/559 R

[51] **Int. Cl.** ..... **C07c 103/30**

[58] **Field of Search** ..... 260/471 R, 404.5



[56] **References Cited**

UNITED STATES PATENTS

3,644,498 2/1972 Loria ..... 260/471 R

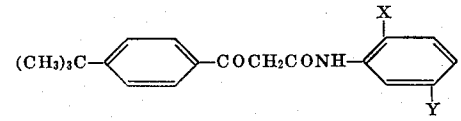


*Primary Examiner*—Lorraine A. Weinberger
*Assistant Examiner*—L. A. Thaxton
*Attorney, Agent, or Firm*—Waters, Roditi, Schwartz & Nissen

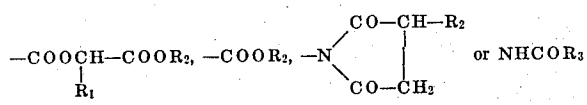


[57] **ABSTRACT**

A yellow color image-forming coupler, useful as a protect type coupler in a light-sensitive silver halide color photographic emulsion. The coupler has the general formula



wherein X is hydrogen, halogen, a lower alkoxy group, a lower alkyl group or an aryloxy group; and Y is

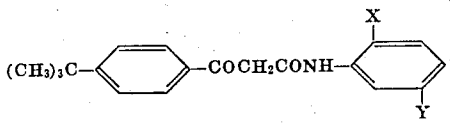


where $R_1$ is a lower alkyl group; $R_2$ is a hydrocarbon residue having eight to 18 carbon atoms; and $COR_3$ is an acyl group having nine to 20 carbon atoms.

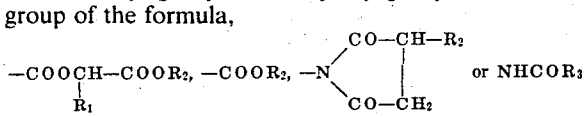

**2 Claims, No Drawings**

# COLOR PHOTOGRAPHIC MATERIAL

This invention relates to a light-sensitive color photographic material. More particularly, the invention pertains to a color photographic material containing a yellow color image-forming novel coupler belonging to the so-called protect type coupler, i.e., a water-insoluble or difficulty water-soluble coupler to be used by dissolving the same in a difficulty water-miscible high boiling solvent and dispersing the resulting solution in a photographic emulsion. The novel yellow coupler is represented by the general formula,



wherein X is hydrogen, halogen, a lower alkoxy group, a lower alkyl group or an aryloxy group; and Y is a group of the formula,



where $R_1$ is a lower alkyl group; $R_2$ is a hydrocarbon residue having eight to 18 carbon atoms; and $COR_3$ is an acyl group having nine to 20 carbon atoms.

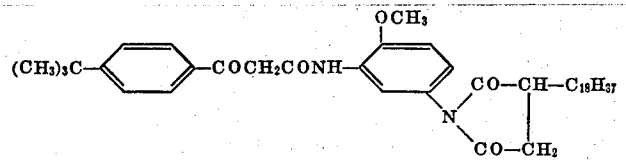
Heretofore, many compounds have been proposed as protect type yellow couplers. However, they have various drawbacks in spectral absorption characteristic, light and moisture fastness of the resulting images, and those which have satisfactory characteristics are not many.



In contrast thereto, the coupler of the aforesaid general formula, which is used in the present invention, has a t-butyl group substituted in the p-position of the benzoyl portion, so that it can overcome the above-mentioned drawbacks of the conventional couplers and gives such effects that the resulting color image becomes unexpectedly excellent in color reproduction and comes to be improved in stability as well. These effects are considered to be ascribable to the branched tertiary alkyl group in the p-position. Further, the coupler is easily soluble in such a high boiling solvent as dibutyl phthalate or tricresyl phosphate, so that the amount of solvent for the coupler can be decreased to give a high concentration dispersion, which is difficultly crystallized in a photographic emulsion or a film formed by coating and drying the emulsion. Thus, the coupler of the present invention has greatly overcome the drawbacks of the conventional couplers.

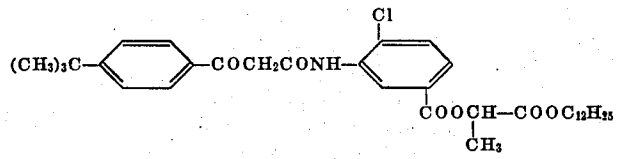
Typical examples of the compound of the aforesaid general formula are set forth below, but couplers usable in the present invention are not limited only to these.

(1)



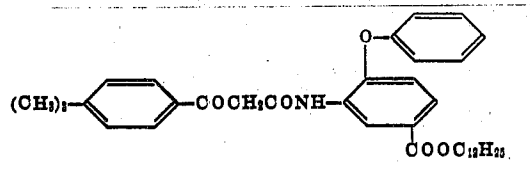
α-(4-t-Butylbenzoyl)-2-methoxy-5-octadecylsuccinimide acetanilide

(2)



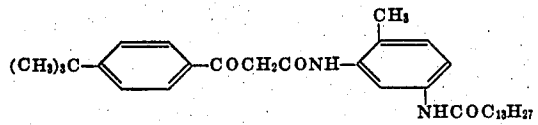
α-(4-t-Butylbenzoyl)-2-chloro-5-(α-dodecyloxycarbonyl ethoxycarbonyl) acetanilide

(3)



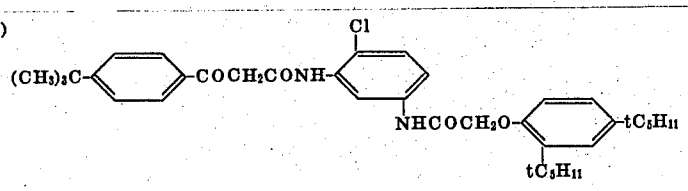
α-(4-t-Butylbenzoyl)-2-phenoxy-5-dodecyloxycarbonyl acetanilide

(4)



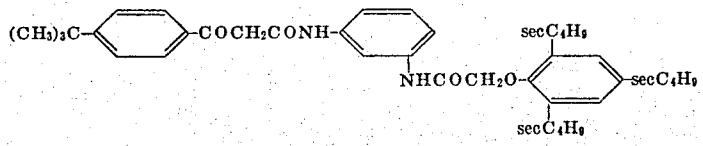
α-(4-t-Butylbenzoyl)-2-methyl-5-myristamide acetanilide

(5)



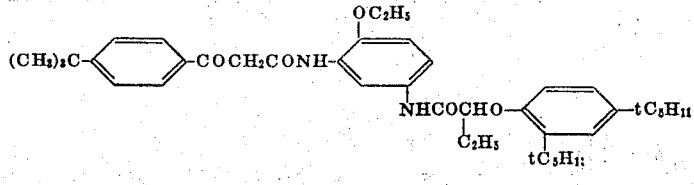
α-(4-t-Butylbenzoyl)-2-chloro-5-(2,4-di-tert-amylphenoxy acetamide) acetanilide

(6)



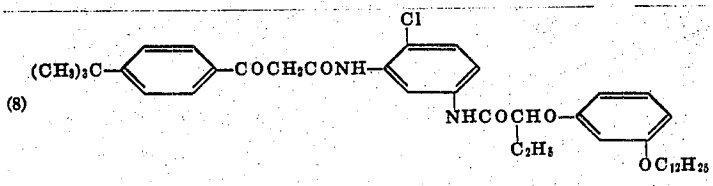
α-(4-t-Butylbenzoyl)-3-(2,4,6-tri-sec-butylphenoxy-acetamide) acetanilide

(7)



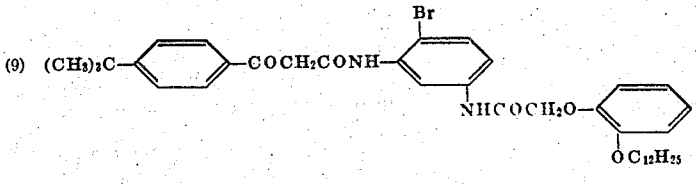
α-(4-t-Butylbenzoyl)-2-ethoxy-5-(α-2,4-di-tert-amylphenoxy butylamide) acetanilide

(8)



α-(4-t-Butylbenzoyl)-2-chloro-5-(α-3-dodecyloxyphenoxy butylamide) acetanilide

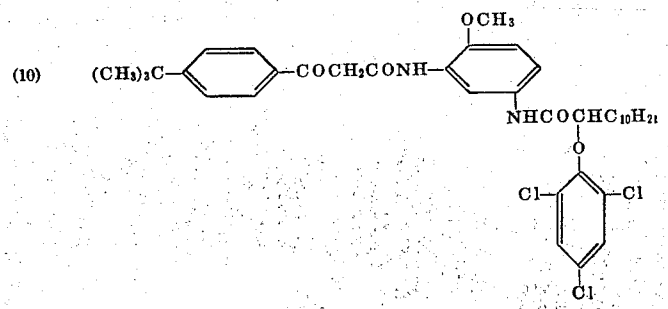
(9)





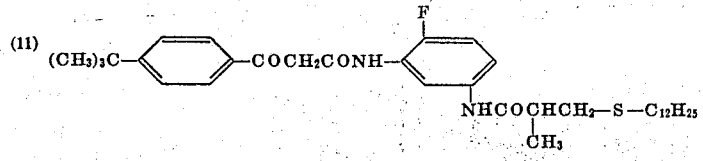
α-(4-t-Butylbenzoyl)-2-bromo-5-(2-dodecyloxyphenoxy acetamide) acetanilide

(10)



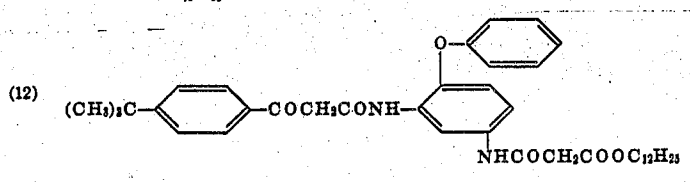
α-(4-t-Butylbenzoyl)-2-methoxy-5-(α-2,4,6-trichlorophenoxy lauramide) acetanilide

(11)



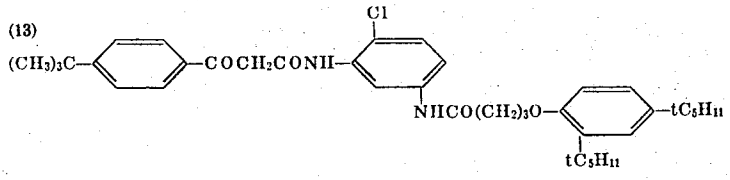
α-(4-t-Butylbenzoyl)-2-fluoro-5-(α-methyl-β-dodecylthiopropionamide) acetanilide

(12)



α-(4-t-Butylbenzoyl)-2-phenxoy-5-(β-dodecyloxycarbonyl propionamide) acetanilide

(13)



α-(4-t-Butylbenzoyl)-2-chloro-5-(2,4-di-tert-amylphenoxy butylamide) acetanilide.

Procedures for synthesis of the above-mentioned couplers are set forth below.

i. p-t-Butylbenzoic acid was treated with thionyl chloride to form p-t-butylbenzoic acid chloride. This was then reacted with acetoacetic acid ethyl ester which has been converted into its Na-salt by treatment with metallic sodium in benzene. Thereafter, the reaction product was deacetylated by boiling in sodium alcoholate, poured into water, and then acidified with hydrochloric acid to deposit an oily substance. This oily substance was extracted with ether, and the ether layer was concentrated and subjected to distillation to obtain a fraction of 142°–145°C/3 mm in a yield of 63 percent.

ii. The thus obtained 4-t-butylbenzoylacetic acid ethyl ester was condensed in xylene with an amine component. That is, 12.4 g. of the keto-acid ester obtained in the above step (i), 22.8 g. of 2-methoxy-5-octadecyl succinimide aniline (m.p. 87°–88°C.) and 70 ml. of xylene were mixed together, and the resulting mixture was boiled. After removing the formed alcohol by distillation, the mixture was refluxed for 3 hours. Thereafter, the xylene was removed by distillation, and the residue was thoroughly stirred with hexane to deposit a precipitate. Subsequently, the precipitate was recovered by filtration, dried and then recrystallized from methanol to obtain 25 g. of a white powder, m.p. 70°–71°C., yield 74 percent. This powder was the exemplified coupler 1.

In the same manner as above, the exemplified coupler 2 was obtained from 2-chloro-5-(α-dodecyloxycarbonyl ethoxycarbonyl) aniline; the exemplified coupler 3 from 2-phenoxy-5-dodecyloxycarbonyl aniline; the exemplified coupler 4 from 2-methyl-5-myristamidoaniline; the exemplified coupler 5 from 2-chloro-5-(2,4-di-tert-amylphenoxyacetamide) aniline; the exemplified coupler 6 from 3-(2,4,6-tri-sec-butylphenoxyacetamide) aniline; the exemplified coupler 7 from 2-ethoxy-5-(α-di-tert-amylphenoxybutylamide) aniline; the exemplified coupler 8 from 2-chloro-5-(α-3-dodecyloxyphenoxy butylamide) aniline; the exemplified coupler 9 from 2-bromo-5-(2-dodecyloxyphenoxy acetamide) aniline; the exemplified coupler 10 from 2-methoxy-5-(α-2,4,6-trichlorophenoxy lauramide) aniline; the exemplified coupler 11 from 2-fluoro-5-(α-methyl-β-dodecylthiopropionamide) aniline; the exemplified coupler 12 from 2-phenoxy-5-(β-dodecyloxycarbonyl propionamide) aniline; and the exemplified coupler 13 from 2-chloro-5-(2,4-di-tert-aminophenoxy butylamide) aniline.

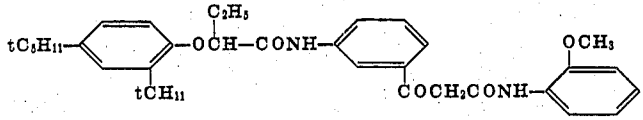
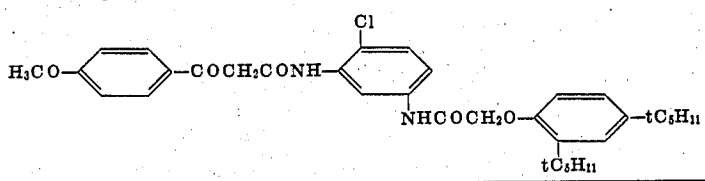
The melting points and nitrogen analysis values of the thus obtained couplers are set forth in Table 1.

Table 1

| Exemplified coupler | Melting point (°C) | Nitrogen analysis (%) Cal'd | Found |
|---|---|---|---|
| 1 | 70 – 71 | 4.01 | 3.92 |
| 2 | 79 – 80 | 4.46 | 4.50 |
| 3 | 75 – 77 | 4.56 | 4.38 |
| 4 | 120 – 125 | 5.24 | 5.16 |
| 5 | 138 – 140 | 4.52 | 4.39 |
| 6 | 145 – 147 | 4.57 | 4.43 |
| 7 | 116 – 117 | 4.27 | 4.16 |
| 8 | 95 – 97 | 4.05 | 4.10 |
| 9 | 78 – 79 | 3.54 | 3.65 |
| 10 | 110 – 112 | 3.93 | 3.88 |
| 11 | 132 – 134 | 4.57 | 4.53 |
| 12 | 85 – 88 | 4.62 | 4.58 |
| 13 | 149 – 151 | 4.32 | 4.31 |

Test results showing the fact that the color images of color photographic materials containing the couplers 1, 2 and 5 of the present invention are excellent in spectral absorption characteristic are set forth in Table 2. In the table, the present invention couplers are compared in spectral absorption characteristic of the resulting color images with known couplers, and the value $\lambda_1(m\mu)$ is the absorption wave length at an optical density (D) of 0.2, the value of $\lambda max(m\mu)$ is the absorption maximum wave length at an optical density of 1.0, and the value of $\Delta\lambda(m\mu)$ is the difference between the said two values. $\Delta\lambda(m) = \lambda_1 - \lambda max$

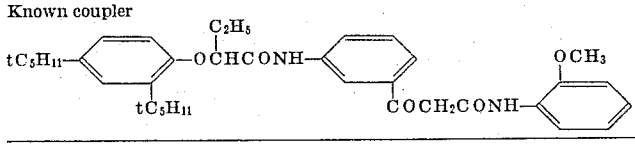
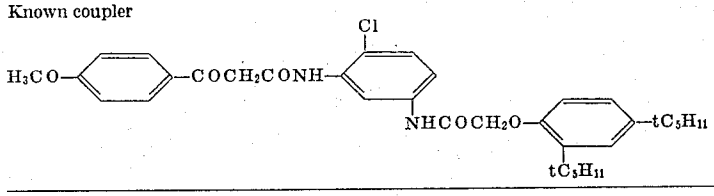
TABLE 2

| Coupler | λmax(D=1.0) (mμ) | λ1(D=0.2) (mμ) | Δλ (mμ) |
|---|---|---|---|
| Known coupler  | 447 | 530 | 83 |
| Known coupler  | 452 | 534 | 82 |
| Exemplified coupler 1 | 445 | 514 | 69 |
| Exemplified coupler 2 | 452 | 520 | 68 |
| Exemplified coupler 3 | 452 | 521 | 69 |

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

In the next place, test results showing the fact that the color images of photographic materials containing the couplers 1, 2 and 3 of the present invention are excellent in stability are set forth in Table 3, in which the numerals percentages of residual color density.

TABLE 3

| Coupler | Fading resistance (irradiation with arc lamp for 16 hours) | Moisture resistance (allowing to stand at 50° C. 80% RH for 14 days) |
|---|---|---|
| Known coupler  | 83 | 96 |
| Known coupler  | 83 | 97 |
| Exemplified coupler 1 | 86 | 98 |
| Exemplified coupler 2 | 85 | 98 |
| Exemplified coupler 5 | 87 | 99 |

The test results set forth in Tables 2 and 3 are measured values of color images formed by developing the individual photographic materials with N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aniline according to Example 1 shown later.

As is clear from Tables 2 and 3, it is understood that the couplers of the present invention are excellent in spectral absorption characteristic and stability of color images as compared with the case of the known couplers, and hence are quite excellent as protect type couplers.

For the incorporation of the couplers of the present invention into a light-sensitive color photographic material, there may be adopted any of the known procedures. For example, the coupler, or a mixture of the couplers, of the present invention is dissolved in a high boiling solvent (b.p. 175°C. or more) such as tricresyl phosphate or dibutyl phthalate, or in a low boiling solvent such as butyl acetate or butyl propionate, or a mixture of said solvents. This solution is mixed with an aqueous gelatine solution containing a surface active agent, and then emulsified by means of a high speed rotary mixer of a colloid mill to form a dispersion. The thus formed dispersion is directly added to a silver halide photographic emulsion, which is then coated on a support such as glass plate, synthetic resin sheet, resin film base, baryta paper or laminated paper, followed by drying, to prepare a light-sensitive color photographic material. Alternatively, the above-mentioned dispersion is once set, finely cut, freed from the low boiling solvent by water-washing or the like means and added to a photographic emulsion, which is then coated on the above-mentioned support and dried to obtain a light-sensitive color photographic material.

The above-mentioned procedures for incorporation of the couplers of the present invention are illustrative and are not limitative.

In the above case, the amount of coupler to be added to the photographic emulsion is preferably in the range of 10 to 100 g. per mole of silver halide, but may be varied so as to be in conformity to application purposes, without being limited to the above-mentioned range. Further, it is not objectionable to add the coupler of the present invention to 2 or more of emulsion layers of a multi-layered color photographic material.

The emulsion used in the present invention may be prepared by use of any of such silver halides as silver chloride, silver iodobromide and silver chlorobromide, and may contain a chemical sensitizer, e.g., sulfur sensitizer, a natural sensitizer present in gelatine, a reducing sensitizer or a noble metal salt. Further, the emulsion may have been incorporated with any of ordinary photographic additives such as, for example, antifoggant, stabilizers, anti-stain agents, anti-irradiation agents, physical property-improving high molecular additives, hardeners and coating aids. Still further, the emulsion may contain a known carbocyanine or merocyanine dye as an optical sensitizer therefor.

The thus obtained light-sensitive color photographic material of the present invention is exposed to radioactive rays such as α-rays or β-rays, visible rays or infrared rays, developed with a developer containing a p-phenylenediamine type developing agent as a main ingredient, and then bleached, desilvered and fixed to obtain a high density color image which is excellent in spectral absorption characteristic and durability and high in transparency. Further, a color photographic material containing the coupler of the present invention is incorporated with an UV-absorber of the benzophenone type (e.g. 2-hydroxy-4-dodecyloxybenzophenone) or the triazole type [e.g., 2-(2'-hydroxy-3',5'-di-tert-butylphenyl) benzotriazole], whereby the resulting color image can further be increased in durability.

Typical examples of the main ingredient of the developer used for development of the present color photographic material are sulfates, sulfites and hydrochlorides of 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, N,N-diethyl-2-methyl-p-phenylenediamine and N,N-diethyl-2-methyl-p-phenylenediamine. Further, the developer may contain a development-controlling agent such as citrazinic acid, in addition to the above-mentioned main ingredient.

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

Example 1

20.0 Grams of the exemplified coupler (1) was added to a mixed solution comprising 20 ml. of dibutyl phthalate and 60 ml. of butyl acetate, and the resulting mixture was heated to 60°C., whereby the coupler was completely dissolved. The thus formed solution was mixed with 10 ml. of a 10 percent aqueous solution of Alkanol B (alkylnaphthalenesulfonate, produced by Du Pont and 200 ml. of a 5 percent aqueous gelatine solution, and the mixture was subjected to a colloid mill to form a dispersion. This coupler dispersion was added to 1 kg. of a high sensitivity gelatine silver iodobromide emulsion, which was then coated on a cellulose triacetate film base and dried to obtain a light-sensitive color photographic material having a stable coating film. This light-sensitive material was exposed according to an ordinary procedure and then developed at 20°C. for 10 minutes with a developer of the following composition:

| | |
|---|---|
| N-Ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate | 5.0 g. |
| Anhydrous sodium sulfite | 2.0 g. |
| Benzyl alcohol | 3.8 g. |
| Sodium carbonate (monohydrate) | 50.0 g. |
| Potassium bromide | 1.0 g. |
| Caustic soda | 0.55 g. |
| Water to make | 1,000 ml. |

Thereafter, the developed material 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:

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

Subsequently, the material was washed with water for 5 minutes and then fixed for 5 minutes in a fixing bath of the following composition:

| | |
|---|---|
| Sodium thiosulfate | 250 g. |
| Water to make | 1,000 ml. |

Thereafter, the thus treated material was washed with water for 20 to 25 minutes and then dried to obtain a clear yellow color image having an absorption maximum at 445 mμ.

Example 2

10 Grams of the exemplified coupler (2) was added to a mixed solution comprising 10 ml. of tricresyl phosphate and 30 ml. of butyl acetate, and the resulting mixture was heated to 50°C., whereby the coupler was completely dissolved. The thus formed solution was mixed with 5 ml. of a 10 percent aqueous Alkanol B solution and 800 ml. of a 5 percent aqueous gelatine solution, and the mixture was subjected to a colloid mill to form a dispersion. This coupler dispersion was added to 500 g. of a gelatine silver iodobromide emulsion, which was then coated on a polyester film base and then dried to prepare a photographic material having a stable coating film.

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

| | |
|---|---|
| p-Methylaminophenyl sulfate | 3.0 g. |
| Anhydrous sodium sulfite | 50.0 g. |
| Hydroquinone | 6.0 g. |
| Anhydrous sodium carbonate | 40.0 g. |
| Potassium bromide | 3.5 g. |
| Potassium rhodanide | 2.0 g. |
| Water to make | 1,000 ml. |

After ordinary stopping, film-hardening and water-washing treatments, the material was subjected to second exposure by use of a white light, and then developed at 21°C. for 3 minutes with a developer of the following composition:

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

Subsequently, the thus treated material was subjected to ordinary stopping, water-washing, bleaching and fixing treatments, washed with running water for 20 minutes and then dried to obtain a yellow positive color image which had an absorption maximum at 455 mμ and was excellent in transparency.

Example 3

10 Grams of the exemplified coupler (3) was added to 20 ml. of dibutyl phthalate, and the resulting mixture was heated to 50°C., whereby the coupler was completely dissolved. The thus formed solution was mixed with 5 ml. of a 10 percent aqueous Alkanol B solution and 200 ml. of a 5 percent aqueous gelatine solution, and the mixture was subjected several times to a colloid mill to form a dispersion. This dispersion was added to 500 g. of a gelatine silver chlorobromide emulsion, which was then coated on a baryta paper, followed by drying, to prepare a light-sensitive material. The thus prepared light-sensitive material was exposed and then developed at 25°C. for 10 minutes in a bath having the following composition:

| | |
|---|---|
| N-Ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate | 8.5 g. |
| Trisodium phosphate, $12H_2O$ | 15.0 g. |
| Sodium metaborate | 10.0 g. |
| Anhydrous sodium sulfite | 7.0 g. |
| Hydroxyamine sulfate | 2.0 g. |
| Potassium bromide | 0.5 g. |
| 6-Nitrobenzimidazole nitrate | 0.04 g. |
| Benzyl alcohol | 10 ml. |
| Diethylene glycol | 20 ml. |
| Caustic soda | 1.2 g. |
| Water to make | 1,000 ml. |

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

| | |
|---|---|
| Ammonium thiosulfate | 120 g. |
| Potassium metabisulfite | 20 g. |
| Glacial acetic acid | 10 cc. |
| Water to make | 1000 ml. |

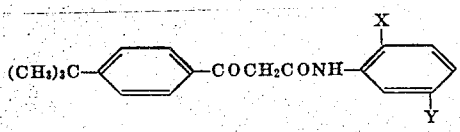
Subsequently, the material was washed with water for 5 minutes and then bleached at 25°C. for 3 minutes in a bath of the following composition:

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

Thereafter, the material was washed with water for 10 minutes, dipped in a stabilization bath for 2 minutes and then dried to obtain a yellow color image which had an absorption maximum at 445 mμ and was excellent in resistance to light and moisture.

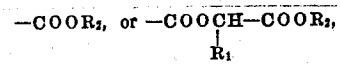
What we claim is:

**1.** A compound selected from the group consisting of



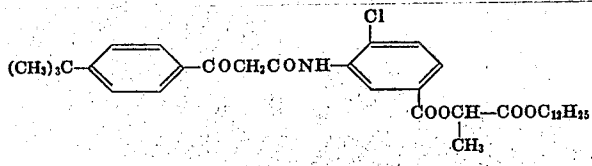


wherein X is hydrogen, halogen, a lower alkoxy group, a lower alkyl group or a phenoxy group; and Y is



where $R_1$ is a lower alkyl group and $R_2$ is a hydrocarbon residue having eight to 18 carbon atoms.

**2.** A compound as claimed in claim **1**, having the formula



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