United States Patent

Sano et al.

[15] **3,649,276**

[45] **Mar. 14, 1972**

[54] **COLOR PHOTOGRAPHIC SILVER HALIDE LIGHT-SENSITIVE MATERIALS CONTAINING P-AMINDIENZOYL ACETANILIDE COLOR COUPLERS**

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[73] Assignee: **Fuji Photo Film Co., Ltd.,** Kanagawa, Japan

[22] Filed: **Aug. 8, 1969**

[21] Appl. No.: **848,601**

[30] **Foreign Application Priority Data**

Aug. 10, 1968 Japan.....43/56965

[52] **U.S. Cl.**.....**96/55,** 96/84, 96/100

[51] **Int. Cl.**.....**G03c 7/00**

[58] **Field of Search**.....96/100, 84, 55

[56] **References Cited**

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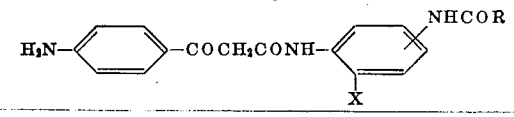
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Primary Examiner—J. Travis Brown

Attorney—Sughrue, Rothwell, Mion, Zinn & Macpeak

[57] **ABSTRACT**

A light-sensitive material for producing a colored image comprising a support and a silver halide emulsion layer thereon containing a yellow-forming coupler having a formula



wherein X represents a halogen atom, —COR represents an acyl group containing 9 to 28 carbon atoms, and said —NHCOR group is located at the 4- or 5-position of the anilide ring.

23 Claims, 2 Drawing Figures

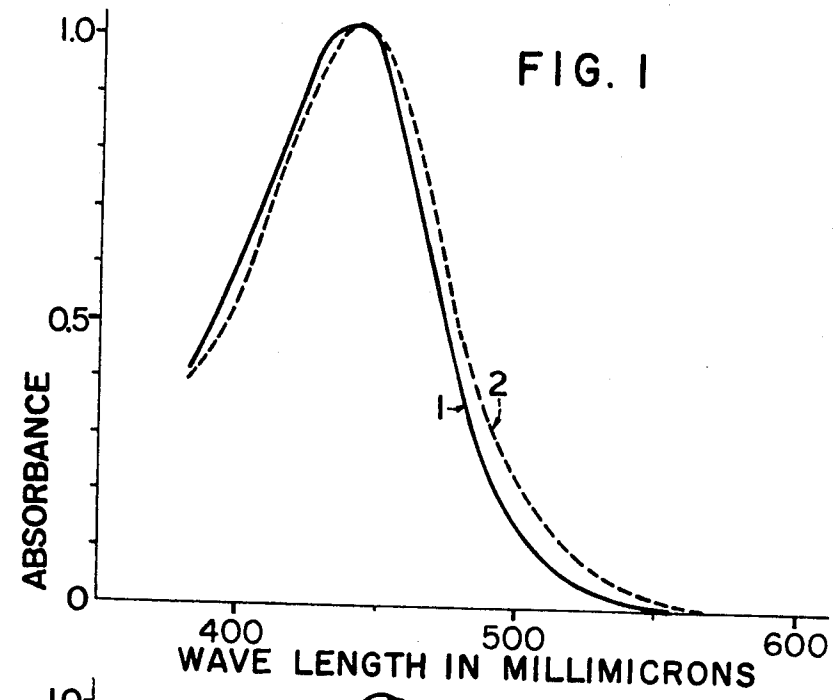

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ABSORBANCE
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WAVE LENGTH IN MILLIMICRONS

FIG. 1

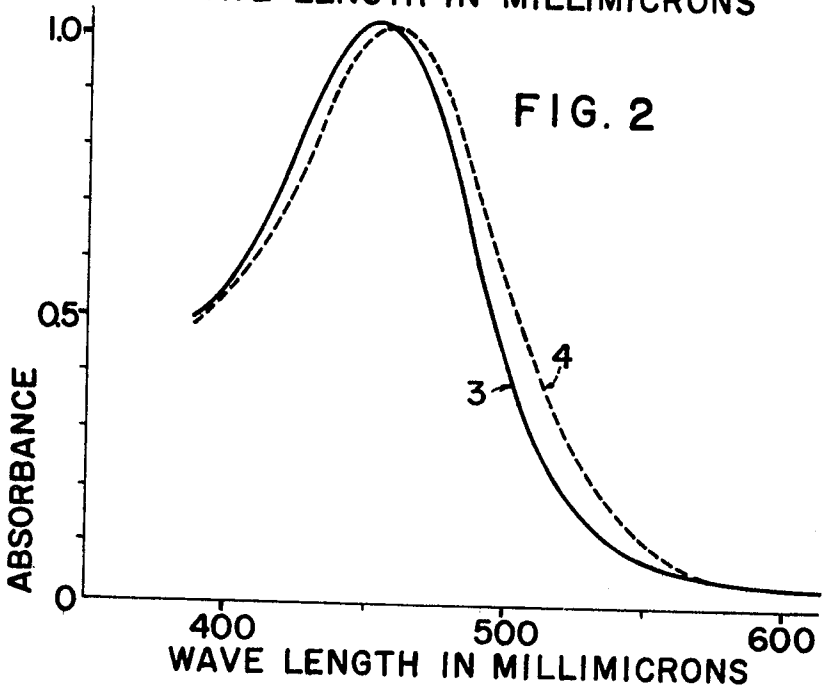

1.0
0.5
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ABSORBANCE
3
4
400
500
600
WAVE LENGTH IN MILLIMICRONS

FIG. 2

COLOR PHOTOGRAPHIC SILVER HALIDE LIGHT-SENSITIVE MATERIALS CONTAINING P-AMINDIENZOYL ACETANILIDE COLOR COUPLERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to color photography and particularly to a color photographic light-sensitive material having a silver halide emulsion layer containing a novel yellow-forming coupler.

2. Description of the Prior Art

Formation of a color photographic image by a subtractive color process generally requires a developing agent of the N,N-disubstituted paraphenylenediamine series and couplers capable of forming cyan, magenta and yellow dyes respectively, by coupling with the oxidation product of the developing agent formed on development of the silver halide particles.

In the conventional color photographic light-sensitive material of the subtractive color process, an acylacetanilide derivative is employed as a coupler for a yellow image dye. The yellow image thus obtained absorbs blue light of wavelengths between about 400 to about 500 millimicrons. The preferred spectral absorption characteristics of the yellow image are that it absorbs strongly within the aforesaid wavelength region but very weakly outside this region. The technique of incorporating couplers in silver halide emulsions having different spectral sensitivities requires that the couplers quickly diffuse into other emulsion layers which reduces the color reproducibility. To correct this drawback, a ballasting group having more than eight carbon atoms has to be introduced into the coupler to reduce its diffusing tendency.

In general, couplers are incorporated in the photographic emulsion layers by either an aqueous solution method or an oil solution method. In the former system, the coupler has a water solubilizing group and is added to the silver halide emulsion as an aqueous alkaline solution thereof; while in the latter system, the coupler is dissolved in an organic solvent, the solution is emulsified into fine colloidal particles in an aqueous medium, and then added to the photographic emulsion.

A yellow-forming coupler incorporated in a silver halide emulsion layer by the oil solution method provides a color image of better spectral absorption characteristics and higher resistance against humidity than when the aqueous solution method is employed. The oil solution system requires the couplers to be readily soluble in the organic solvent employed and, at the same time, to be less subject to crystallization in this solvent.

On the other hand, in order for the photographic emulsion layer to have a high sensitivity, a desirable gradation and a high developability, it is necessary that the coupler has enough coupling activity toward the oxidation product of the N,N-disubstituted paraphenylenediamine-type developing agent.

This is also desired from the viewpoint of a high conversion yield of the coupler to the dye, which makes a thinner emulsion layer available.

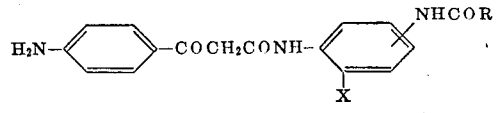
Many of the conventional yellow-forming couplers for the oil solution system capable of providing comparatively good hue do not show a sufficiently high coupling activity toward the oxidation product of the developing agent in the photographic emulsion layer. Attempts have been made to improve the chemical structure of a benzoylacetanilide-type compound to increase its coupling activity but such attempts were always accompanied with the blue shift of the absorption of the formed yellow image, increasing green absorption, and thus reducing color reproducibility. There seems to be a general relationship between the coupling activity of a yellow-forming coupler and the spectral absorption characteristics of the derived yellow image.

Another problem is that the yellow images derived from many of the conventional yellow-forming couplers tend to fade when they are exposed to intense light for a long time, thus shortening the life of the preserved color pictures.

For this reason, the color photographic industry has long searched for a yellow-forming coupler of the oil solution technique exhibiting a sufficiently high coupling reactivity, and, at the same time, leading to a dye of less green absorption and more light fastness.

SUMMARY OF THE INVENTION

After extensive investigation, the present inventors have found that the azomethine dyes derived from α-(p-aminobenzoyl)2'-halogeno-acetoanilides are particularly suitable for color reproduction and also that, among these, the coupler of the following structure has properties particularly suited for the oil solution technique.



I

wherein X represents F, Cl, or Br, and COR represents an acyl group having nine to 28 carbon atoms.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows spectral absorption curves derived from the novel coupler compound of the present invention (1) and from a conventional coupler compound (2).

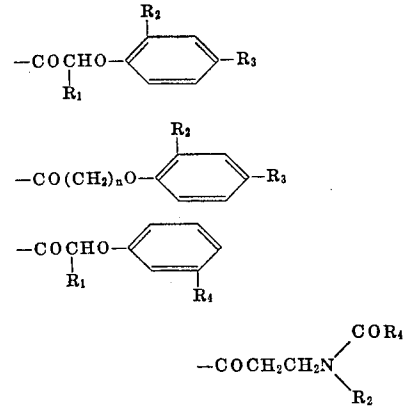
FIG. II shows spectral absorption curves for color images produced employing the coupler compound of this invention (3) and a conventional coupler compound (4).

DETAILED DESCRIPTION OF THE INVENTION

The acyl group represented by —COR in the above formula should not have such water-solubilizing groups as $—SO_3M$, $—OSO_3M$, and —COOM (wherein M represents a hydrogen atom or an alkali metal). If the number of carbon atoms is below nine, the oil-solubility and the ballasting property of the coupler are insufficient and hence the coupler incorporated in a silver halide emulsion layer is partly dissolved in the developer solution and diffuses from one emulsion layer to adjacent layers, thereby reducing the color reproducibility of the color photographic material. On the other hand, if the number of carbon atoms exceeds 28, the increased molecular weight of the coupler decreases the blue absorption per unit area and the solubility of the coupler is lowered due to the dispersion force increment based on this part of the coupler molecule which requires a larger amount of the organic solvent. This results in an increased thickness of the emulsion layer, of which is expected enough blue absorption.

The acyl group represented by —COR can be positioned at either the 4- or 5-position of the anilide ring, the latter giving a higher solubility to the coupler in organic solvents.

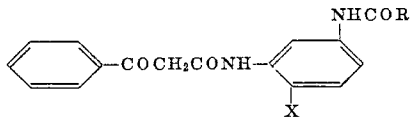
The —COR group may include optionally substituted aliphatic acyl groups, and the following are particularly suitable:



wherein R_1 represents a hydrogen atom or an alkyl group having less than three carbon atoms and N represents an integer from 2 to 5. R_2 and R_3 each represents an alkyl group having less than nine carbon atoms and R_4 represents an alkyl group having five to 18 carbon atoms.

The coupler of the present invention has a high coupling reactivity and sufficient solubility in organic solvents, and the yellow dye derived from this coupler has excellent fastness and particularly suitable spectral absorption characteristics for color reproduction. Color photographic material using the novel coupler of this invention has a high sensitivity and easily provides a good gradation and good image quality, while the resulting photographic image can be preserved for a long time even under severe conditions.

The coupler represented by formula I has almost the same coupling reactivity as that of a conventional coupler represented by the general formula II (shown below), which is known to have the highest level of coupling reactivity. The novel couplers of the present invention also have the same properties of color density, sensitivity, gradation, etc., as those of conventional couplers. On the other hand, the dyes derived from the couplers of general formula I have spectral absorption characteristics more suitable for color reproduction in a subtractive color process than those derived from the couplers of formula II.



II

wherein X and —COR have the same meanings as those of formula I.

FIG. 1 of the accompanying drawings shows the spectral absorption curve (curve 1), in ethyl acetate, of a yellow dye obtained by coupling of the novel coupler α-(p-aminobenzoyl)-[2'-chloro-5'-(2,4-di-tert-amylphenoxyacetamido)] acetanilide and 4-amino-3-methyl-N,N-diethylaniline; in comparison with that (curve 2) of the dye derived from a conventional coupler of formula II, i.e., α-benzoyl-[2'-chloro-5'-(2,4-di-tert-amylacetophenoxyacetamide)]-acetanilide.

FIG. 1 illustrates how sharply the longer wave side absorption of the dye derived from the coupler of this invention cuts itself down in comparison with that of the dye obtained from a conventional coupler.

Obviously, the coupler of this invention provides a yellow image having less green absorption in the region above 500 millimicrons.

The yellow image obtained from the coupler of formula I is not only resistant to heat and humidity but also fades at an extremely slow rate even under intense irradiation.

The light fastness of this dye can further be increased by superposition of a layer that exclusively absorbs below 400 millimicrons. Suitable ultraviolet absorbing layers have been disclosed in, e.g., Japanese Pat. No. 19299/68.

In general, the presence of a small amount of a primary amine in a photographic emulsion gives rise to undesired effects, such as fogging, in its photographic properties. However, a large amount of the coupler can be incorporated in a highly sensitive emulsion without affecting its photographic properties even after a long time of preservation in spite of the primary amino structure of the novel coupler. This result is thought to be due to the protection given to the coupler, by the organic solvent, from emulsion particles.

The organic solvent used to dissolve the coupler of this invention must be substantially insoluble in water and have a boiling point preferably exceeding 190° C. at normal pressure. Such a water-insoluble and high-boiling organic solvent not only facilitates the dispersion of the coupler but also contributes, by remaining together with the coupler in the processed emulsion layer, in preventing the crystallization of the coupler to thereby improve the spectral absorption characteristics of the color image and to protect the resulting dye from outside actions. Such organic solvents may be suitably selected from carboxylic acid esters, phosphoric acid esters, carboxylic acid amides, ethers, and substituted hydrocarbons. Practical examples of the solvent are di-n-butyl phthalate, di-n-octyl phthalate, di-methoxyethyl phthalate, dibutyl adipate, diisooctyl azelate, tri-n-butyl citrate, butyl laurate, dibutyl sebacate, tricresyl phosphate, tributyl phosphate, tris-(2-ethyl-hexyl) phosphate, N,N-diethyl-caprylamide, N,N-di-methylpalmitylamide, butyl m-pentadecyl phenyl ether, ethyl-2,4-di-tert-butylphenyl ether, and chlorinated paraffins.

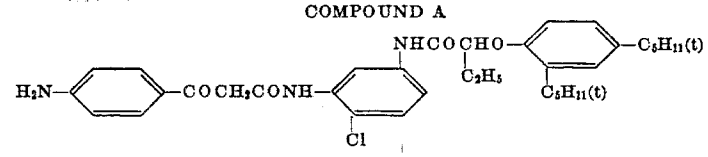
To assist the fine dispersion of the organic solvent solution of the coupler of the present invention into an aqueous medium, it is profitable to use a low boiling solvent or an ether water-soluble high boiling solvent together with the aforesaid water-insoluble high boiling solvent.

Examples of such assistant solvents are propylene carbonate, ethyl acetate, butyl acetate, ethyl propionate, sec-butyl alcohol, tetra-hydrofuran, cyclohexanone, dimethylformamide, dimethylsulfoxide, and ethyleneglycol monomethyl ether. The coupler of general formula I may be used alone or in combination with two or more such couplers, or further may be used together with other types of yellow-forming coupler including water-soluble types, whenever necessary to give desirable properties to the blue-sensitive emulsion. The coupler of this invention is also subject to improvement in color reproduction by adding a small amount of the cyan forming coupler described in Japanese Pat. No. 391/65.

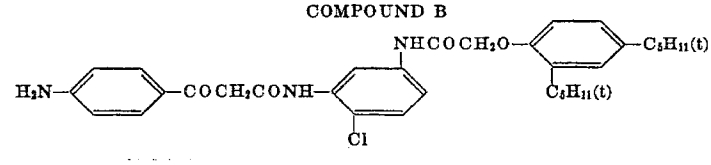
The present invention can be effectively applied to various kinds of photographic light-sensitive materials. For example, it can be applied to color photographic printing papers, positive color films, negative color films, and reversal color films. It can be applied not only to multilayer color photographic materials in which two or more silver halide emulsion layers having different spectral sensitivities and containing different corresponding spectral couplers are superposed on a support, but also to a so-called mixed-grain-type color photographic material in which a mixture of two or more silver halide emulsions of different spectral sensitivities is applied on a support in one layer.

Examples of the compound represented by formula I which may be preferably employed in the practice of the present invention are shown below.

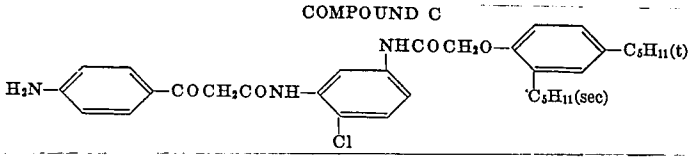
COMPOUND A



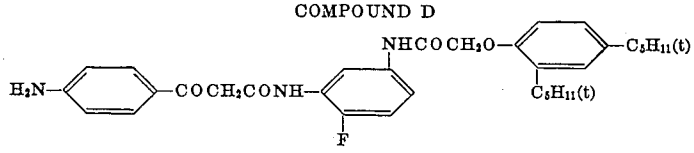
COMPOUND B



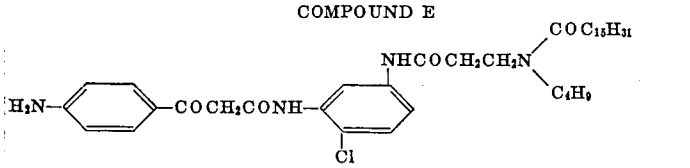
COMPOUND C



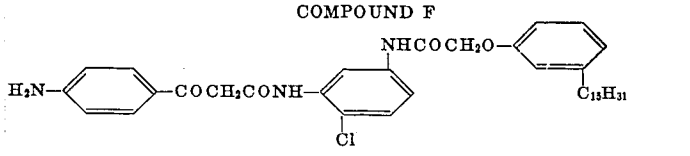
COMPOUND D



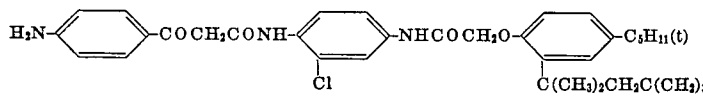
COMPOUND E



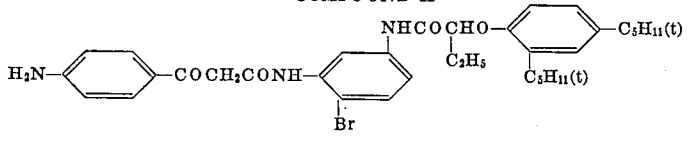
COMPOUND F



COMPOUND G



COMPOUND H



The following examples illustrate the procedures by which the compounds of this invention are prepared.

Preparation 1. (Preparation of Compound A)

In 500 ml. of warm acetonitrile was dissolved 58 g. of 4-chloro-3-nitroaniline and to the resulting solution was added dropwise sufficiently degassed acid chloride prepared from 350 g. of α-(2,4-di-t-amylphenoxy) butyric acid and 180 g. of thionyl chloride. The mixture was then boiled for 90 minutes with stirring to remove about one-third of the solvent through a distillation head.

The residue was added to ice-cooled water and allowed to stand overnight to crystallize the precipitates. The crystals were filtered and dried, recrystallized from 800 ml. of methanol, and were washed with 500 ml. of methanol to provide 60 g. of the anilide melting at 110°–111° C. The whole amount of the product was reduced in ethanol at 65°–70° C. with 50 atms. of hydrogen using a Raney nickel catalyst. After two-thirds of the ethanol was distilled off, the residue was poured into ice-cooled water. The organic components were extracted with 0.5 liter of ether, washed with water and dried. After distilling the ether off, the residue was applied to the subsequent steps as such.

A mixture of 26 g. of ethyl p-nitrobenzoylacetate and 48 g. of the amine thus obtained was heated in 150 ml. of xylene for 3 hours at 135°–140° C. and, after distilling xylene off, the reaction product was allowed to stand in 200 ml. of petroleum ether to form crystals, which were recrystallized from methanol to yield 27 g. of α-(4-nitrobenzoyl)-2′-chloro-5′-[α-(2″,4″-di-t-amylphenoxy)butyramido]-acetanilide melting at 112° C.

The whole amount of this product was dissolved in a mixture of 200 ml. of methanol, 200 ml. of acetic acid, and 27 ml. of water. While stirring and warming the solution, 27 g. of iron powders were added to the solution over a 30 minute period. After the system was stirred and refluxed for 90 minutes the filtered solution was poured in 1 liter of water, the precipitates were collected, dried, and recrystallized twice from ethanol to provide 16 g. of compound A melting at 158° C.

Preparation 2. (Preparation of Compound C)

In the same manner as Preparation 1, 105 g. of 4-chloro-3-nitro-aniline and 124 g. of 2-sec-amyl-4-t-amylphenoxy-acetyl chloride (prepared from sec-amyl-4-t-amylphenol which is the major component of commercial "2,4-di-sec-amylphenol") were treated. The reaction mixture was poured in 300 g. of ice-cooled water and the precipitates thus formed were recovered by filtration, recrystallized from 800 ml. of methanol containing 50 g. of anhydrous sodium acetate, and were washed with 400 ml. of chilled methanol to provide 160 g. of 2-sec-amyl-4-t-amylphenoxyaceto-(2-chloro-5-nitro-anilide) melting at 120°–129° C.

The whole amount of the nitro compound thus obtained was reduced in ethanol at 60°–70° C, with about 50 atms. of hydrogen using a Raney nickel catalyst. After removing half of the ethanol by distillation, the residue was poured in ice-cooled water and the precipitates thus formed were dried and recrystallized from hexane to provide 110 g. of the amine melting at 103° C.

A mixture of 44 g. of this amine, 20 g. of ethyl p-nitrobenzoyl acetate, 200 ml. of xylene, and 1 ml. of dimethylaniline was refluxed for 90 minutes. After distilling off the ethanol formed by the reaction, 50 ml. of acetonitrile was added to the system and the mixture was allowed to stand overnight to provide 32 g. of crystals melting at 130° C. The product was used in the subsequent reaction without purification. The whole amount of the product was refluxed with stirring in a three-necked flask together with 150 ml. of methanol, 150 ml. of acetic acid, and 25 ml. of water, while 15 g. of iron powder was added to the system over a ten minute period. The system was refluxed for an additional 1 hour and then poured into 1 liter of ice-cooled water. Two recrystallizations of the precipitates from methanol gave 15 g. of compound C melting at 146° C.

Preparation 3. (Preparation of Compound E)

A mixture of 144 g. of 3-(N-butylhexadecaneamido)-propionic acid (its preparation has been given in Japanese Pat. No. 23902/67) and 55 g. of thionyl chloride was allowed to stand for 90 minutes at 40° C. and then mixed with 190 ml. of acetonitrile. After dropwise addition of 65 g. of 4-chloro-3-nitroaniline dissolved in 320 ml. of acetonitrile to the mixture, the system was refluxed for 2 hours. The product was poured into 1 kg. of ice and the precipitates collected, washed with water, dried, and recrystallized from methanol to give 180 g. of the nitro compound melting at 74°–85° C.

The whole amount of the nitro compound was reduced by the same manner as in preparation 1 and the reduced product was recrystallized from methanol to provide 130 g. of the amine melting at 70° C. A mixture of 40 g. of this amine, 19 g. of ethyl p-nitrobenzoylacetate and 100 ml. of xylene was boiled for 2 hours and the ethanol formed by the reaction was removed through a distillation head. The reaction mixture was cooled to form crystals, which were collected and recrystallized from ethanol to give a compound melting at 80°–81° C. In a mixture of 120 ml. of acetic acid, 120 ml. of methanol and 15 ml. of water was dissolved 15 g. of the compound prepared above and while refluxing the mixture, 15 g. of powdered iron was added thereto over a 30 minute period. The product was refluxed for an additional 2 hours and poured into 1 liter of water. The precipitates were collected, dried and recrystallized from acetonitrile to provide 9 g. of compound E melting at 111° C.

Preparation 4. (Preparation of Compound G)

A mixture of 35 g. of 4-(1,1-dimethylpropyl)-2-(1,1-3,3-tetra-methylbutyl) phenoxyacetyl chloride, 150 ml. of acetonitrile, and 18 g. of 3-chloro-4-nitroanilline, prepared by the process described in the Journal of the Chemical Society, Volume 1928, page 692, was refluxed for 200 minutes. To the product was added 20 ml. of water to form precipitates, which were collected by filtration, dried, and reduced in ethanol at 80° C. with 100 atms. of hydrogen using palladium on carbon as a catalyst. After distilling the solvent off, the formed crystals were recrystallized from acetonitrile. A mixture of 7.5 g. of ethyl p-nitrobenzoylacetate, 50 ml. of xylene and 15 g. of the amine thus prepared was refluxed for 3 hours. After distilling xylene off from the reaction mixture, the residue was cooled and the crystals formed thereby were recrystallized from acetonitrile to provide 14 g. of α-(4-nitrobenzoyl-2'-chloro-4'-[4(1, 1-dimethylpropyl)-2-(1,1,3,3 - tetramethylbutyl)phenoxyacetamido] acetanilide melting at 188°–189° C. The whole amount was reduced as in Preparation 1 and recrystallized from ethanol and then from ethyl acetate to provide 4.5 g. of compound G melting at 195°–196° C.

While stirring a mixture of 65.6 g. of p-t-amylphenol and 45.2 g. of 2,4,4-trimethyl-1-octene at 45° C., a mixture of 40 ml. of methanol and 40 ml. of sulfuric acid was added thereto dropwise during 2 hours. The resulting mixture was washed with water and the organic phase was extracted with ether, dried, and distilled under reduced pressure to provide 88 g. of a fraction boiling at 123° C./1 mm. The fraction was refluxed with stirring for three days together with 70 g. of ethyl bromoacetate, 100 g. of potassium carbonate, and 200 ml. of acetone. The solution filtered from the insoluble materials was subjected to vacuum distillation, whereby 70 g. of a fraction boiling at 180°–200° C./1 mm. was collected, which was refluxed for 30 minutes in 200 ml. of ethanol containing 30 g. of potassium hydroxide. When the product was neutralized with diluted hydrochloric acid, the oily product separated and soon crystallized. The crystals were recrystallized from ligroin to provide 56 g. of the acid. The acid chloride was obtained by boiling the acid together with any excess thionyl chloride according to the conventional method.

The couplers of this invention can be prepared by condensing ethyl p-nitrobenzoyl acetate, which is highly reactive, with aniline derivative and reducing the nitro group of the produce, and, as is shown by the above examples, they are obtained with obvious ease and at a low cost.

The present invention will now be further illustrated by the following nonlimiting examples.

EXAMPLE 1

A solution prepared by heating a mixture of 20 g. of compound A, shown above, 12 ml. of di-n-butylphthalate, and 50 ml. of butyl acetate was added to 500 ml. of an aqueous solution containing 40 g. of gelatin and 2.0 g. of sodium dodecylbenzene-sulfonate, followed by stirring, and then the mixture was passed through a colloid mill five times, whereby the coupler solution was finely dispersed.

The whole amount of the dispersion was added to 1.0 kg. of a photographic emulsion containing 54 g. of silver iodobromide and 60 g. of gelatin. After the addition of 30 ml. of a 3 percent acetone solution of tri-ethylenephosphoramide as a hardening agent and adjusting the pH to 6.0, the emulsion was applied to a triacetyl cellulose film to a dry thickness of 7.0 microns (film L).

The light-sensitive film thus prepared was exposed through an optical wedge using a sensitometer and was produced as follows:

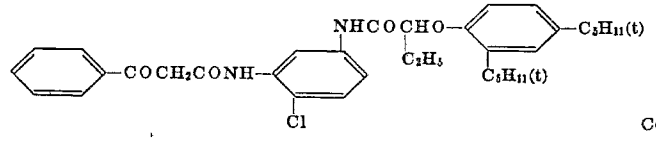
	Process	Temperature	Time
1.	Color development	20° C.	15 min.
2.	Washing	18° C.	1 min.
3.	First fixing	20° C.	4 min.
4.	Washing	18° C.	3 min.
5.	Bleaching	20° C.	5 min.
6.	Washing	18° C.	3 min.
7.	Second fixing	20° C.	3 min.
8.	Washing	18° C.	15 min.

The composition of the color developer used above was as follows:

Color Developer A	
Water	1,000 ml.
4-Amino-3-methyl-N,N-diethylaniline hydrochloride	2.5 g.
Sodium sulfite (anhydrous)	3.0 g.
Sodium carbonate (monohydrate)	47 g.
Potassium bromide	2.0 g.

The fixing and the bleaching solutions contained mainly sodium thiosulfate and potassium ferricyanide, respectively.

For comparison, the above procedure was repeated to provide a light-sensitive film (film M) using a conventional type coupler (as in Formula II) (a) of the following formula, in place of coupler A:



Coupler (a)

Film M was exposed and developed as shown above. The photographic properties of both films are shown in the following table:

Film	Coupler	Fog	Relative Sensitivity	Gamma	Maximum density
L	A	0.06	100	1.20	2.90
M	(a)	0.07	105	1.35	2.90

After storing film L and film M under various conditions, they were subjected to exposure and development and then to measurement of the photographic properties, the results of which are shown below:

Film	(A) Sensitivity	(A) Fog	(B) Sensitivity	(B) Fog	(C) Sensitivity	(C) Fog
L	100	0.06	100	0.06	95	0.08
M	105	0.07	105	0.07	100	0.10

(A): immediately after coating; (B): stored for 60 days at room temperature and normal humidity; (C): stored for 2 days at 50° C. and at a relative humidity of 75 percent.

The spectral absorption curves of the color images of the two films are shown in FIG. 2 of the accompanying drawings. As is clear from the results, the spectral absorption curve (curve 3) of the color image obtained from film L gave less absorption in the wavelength region above 500 millimicrons than the absorption curve (curve 4) of the color image obtained from film M. Thus, it was observed that film L gave a sharp and less reddish yellow image.

As is clear from the above results, coupler A, corresponding to general formula I, could give a brilliant yellow image having excellent photographic properties. Also, it was confirmed that the emulsion containing the coupler was stable and could be stored for a long time without affecting the photographic properties.

EXAMPLE 2

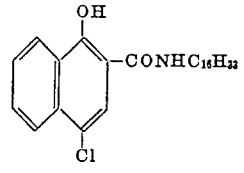
The following three kinds of light-sensitive films were prepared:

(i) Film N:

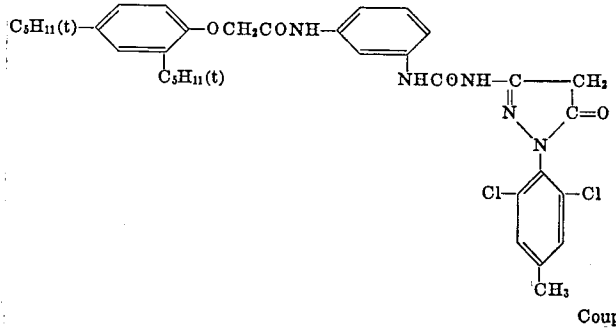
A solution obtained by heating to 60° C. a mixture of 15 g. of coupler C, 20 ml. of di-n-butyl phthalate and 30 ml. of cyclohexanone was added to 300 ml. of an aqueous solution containing 25 g. of gelatin and 1 g. of sodium dodecylbenzenesulfonate at this temperature, and the mixture was mechanically stirred for 30 minutes by means of a homoblender to emulsify the coupler solution.

The whole amount of the emulsion was mixed with 500 g. of a blue-sensitive photographic emulsion containing 45 g. of silver iodobromide and 50 g. of gelatin, and after adding 30 ml. of a 3 percent acetone solution of triethylene phosphoramide as a hardening agent and adjusting the pH to 7.0, applied to a triacetyl cellulose film to a dry thickness of 7.0 microns.

To the emulsion layer thus formed were applied a red-sensitive emulsion containing a cyan-forming coupler (b), a green-sensitive emulsion containing a magenta-forming coupler (c), both shown below, and then a protective layer comprising gelatin to provide a color photographic positive film.



Coupler (b)



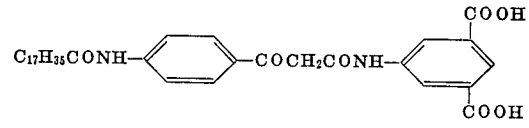
Coupler (c)

(ii) Film O:

The same procedure was repeated using a conventional coupler (a) [shown in Example 1] instead of compound (C) of this invention as the yellow-forming coupler to provide a color photographic positive film.

(iii) Film P:

A solution prepared by dissolving 15 g. of yellow-forming coupler (d), shown below, in a mixture of 15 ml. of methanol, 50 ml. of normal sodium hydroxide, and 100 ml. of distilled water was added to 500 g. of a blue-sensitive photographic emulsion containing 45 g. of silver iodobromide and 50 g. of gelatin, and after adding 90 ml. of an aqueous 3 percent solution of saponine and adjusting its pH to 7.0 by addition of an aqueous 10 percent solution of citric acid, the emulsion was applied to a triacetyl cellulose film to a dry thickness of 6.0 microns and was dried.



Coupler (d)

Onto this layer were superposed a red-sensitive emulsion, a green-sensitive emulsion and a protective layer.

These films (N, O and P) were exposed to blue light and processed as in Example 1 to provide a yellow image. The films thus processed were stored in a chamber kept at a constant temperature of 65° C. and a constant humidity of 75 percent R.H., and the changes of blue densities of the yellow images were measured, the results of which are shown in the following table, in which the fading tendency of the yellow image was shown by the reduction percentage of blue density to the initial blue density.

Film	Yellow-forming Coupler	Duration of storage 0	10 days	20 days
N	Coupler C	0	3%	3%
O	Coupler (a)	0	4%	5%
P	Coupler (d)	0	35%	65%

The three processed films were exposed to an xenone lamp of 1.5 kw. through a water filter for 20 hours and thereafter the density reduction of the yellow image was determined, the results of which are shown in the following table:

Film	Yellow-forming Coupler	Initial Density 1.0	2.0
N	Coupler C	10%	9%
O	Coupler (a)	23%	18%
P	Coupler (d)	65%	45%

From these results, it was confirmed that coupler C of the

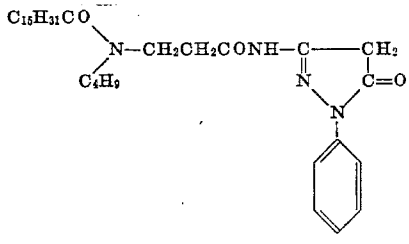
present invention gave yellow images of remarkable fastness to heat, humidity and intense light.

EXAMPLE 3

A solution prepared by heating a mixture of 10 g. of coupler G of this invention, shown above, 20 ml. of tricresyl phosphate, 30 ml. of cyclohexanone, and 10 ml. of dimethyl formamide was added, with vigorous stirring, to 100 ml. of an aqueous solution containing 0.7 g. of sodium dodecyl sulfate and 8 g. of gelatin, and the mixture was further stirred vigorously in a homogenizer, whereby the coupler solution was finely dispersed in an aqueous medium. The emulsion was chilled, finely cut, and washed in a water stream.

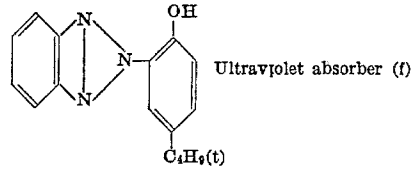
The whole amount of this emulsion was added to 540 g. of a blue-sensitive photographic emulsion containing 30 g. of silver chlorobromide and 35 g. of gelatin and, after addition of 30 ml. of a 3 percent acetone solution of triethylene phosphoramide and 7 g. of polyvinylpyrrolidone, the resulting emulsion was applied to a baryta-coated paper as the bottom layer to a dry thickness of 4.5 microns.

Onto this emulsion layers were superposed, successively, a green-sensitive emulsion layer containing a magenta-forming coupler (e) having the structure shown below and a red-sensitive emulsion containing a cyan forming coupler (b), shown above.

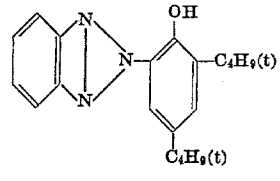


Coupler (e)

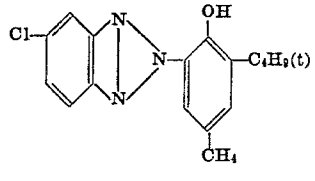
Onto the top thereof was coated a gelatin layer containing a total of 2.0 g./m.^{2} of the same amount of three kinds of the following ultraviolet absorbers:



Ultraviolet absorber (f)



Ultraviolet absorber (g)



Ultraviolet absorber (h)

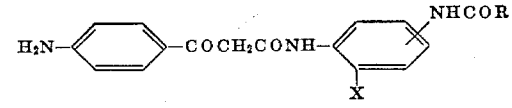
This color photographic printing paper was exposed through a color negative film and subjected to color development for 12 minutes at 24° C. in a color developer of the following composition. The paper was then fixed, bleached and washed according to the procedures as in Example 1, whereby a brilliant color print was obtained.

Color Developer B	
Water	1,000 ml.
Sodium hexametaphosphate	2.0 g.
Sodium sulfite (anhydrous)	2.0 g.
Benzyl alcohol	12.0 g.
Sodium carbonate (monohydrate)	27.5 g.
Potassium bromide	0.5 g.
Hydroxylamine sulfate	2.5 g.
4-amino-N-ethyl-N (β-methanesulfonamidoethyl)-m-toluidine sesquisulfate (monohydrate)	4.0 g.

The yellow image of the color print almost entirely survived exposure to direct sunlight for 2 days.

What is claimed is:

1. A light-sensitive material for producing a colored image comprising a support and a silver halide emulsion layer thereon containing a yellow-forming coupler having the formula



wherein X represents a halogen atom, —COR represents an acyl group containing nine to 28 carbon atoms, and said —NHCOR group is located at the 4- or 5-position of the anilide ring.

2. A light-sensitive material as in claim 1, wherein X represents a chlorine atom and said —NHCOR group is located at the 5-position of said anilide ring.

3. A light-sensitive material as in claim 1, wherein R represents a member selected from a group consisting of a 2,4-di-alkylphenoxyalkyl, a 3-alkyl-phenoxyalkyl and an N-alkyl-(aliphatic acyl)-aminoethyl group.

4. A light-sensitive material as in claim 1, wherein said coupler is α-(4-aminobenzoyl)-2'-chloro-5'-[α-(2,4-di-tert-amylphenoxy)-butylamido]-acetanilide.

5. A light-sensitive material as in claim 1, wherein said coupler is α-(4-aminobenzoyl)-2'-chloro-5'-(2-sec-amyl-4-tert-amylphenoxyacetamido)-acetanilide.

6. A light-sensitive material as in claim 1, wherein said coupler is α-(4-aminobenzoyl)-2'-chloro-5'-[3-(N-butylhexadecaneamido)-propionamideo]-acetanilide.

7. A light-sensitive material as in claim 1, wherein said coupler is α-(4-aminobenzoyl)-2'-chloro-5'-[4(1,1-dimethylpropyl)2-(1,1,3,3-tetramethylbutyl)phenoxyacetamido]-acetanilide.

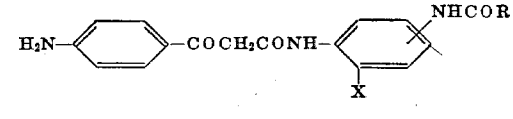
8. A light-sensitive material as in claim 1, wherein said coupler is α-(4-aminobenzoyl)-2'-chloro-5'-(3-n-pentadecylphenoxy-acetamido]-acetanilide.

9. A light-sensitive material as in claim 1, wherein said light-sensitive material comprises at least one additional layer containing an ultraviolet absorbing agent having at least one aliphatic radical containing from four to 20 carbon atoms.

10. A light-sensitive material as in claim 9, wherein said ultraviolet absorbing agent is a 2-benztriazolyl-4-alkylphenol derivative.

11. A light-sensitive material for producing a colored image comprising a support and a silver halide emulsion layer containing α-(4-amino-benzoyl)-2'-chloro-5'-acylaminoacetanilide, said acylamino group containing from nine to 28 carbon atoms.

12. A method of producing a colored photographic image comprising developing an exposed silver halide emulsion layer with an aromatic primary amino developing agent in the presence of a yellow-forming coupler having the formula:



wherein X represents a halogen atom, —COR represents an acyl group containing from nine to 28 carbon atoms, and said

—NHCOR group is located at the 4- or 5-position of the anilide ring.

13. A method of producing a colored photographic image as in claim 12, wherein X represents a chlorine atom and said —NHCOR group is located at the 5-position of said anilide ring.

14. A method of producing a colored photographic image as in claim 12, wherein R represents a member selected from a group consisting of a 2,4-dialkylphenoxy-alkyl, an 3-alkylphenoxyalkyl and an N-alkyl-(aliphatic acyl)-aminoethyl group.

15. A method of producing a colored photographic image as in claim 12, wherein said coupler is α-(4-aminobenzoyl)-2'-chloro-5'- [2-(2,4-di-tert-amylphenoxy)-butylamido] -acetanilide.

16. A method of producing a colored photographic image as in claim 12, wherein said coupler is α-(4-aminobenzoyl)-2'-chloro-5'-(2-secamyl-4-tert-amylphenoxyacetamido)-acetanilide.

17. A method of producing a colored photographic image as in claim 12, wherein said coupler is α-(4-aminobenzoyl) -2'-chloro - 5' - [3-(N-butyl-hexadecaneamido)-propionamido] -acetanilide.

18. a method of producing a colored photographic image as in claim 12, wherein said coupler is α-(4-aminobenzoyl)-2'-chloro-5' - [4-(1,1-dimethylpropyl)-2-(1,1,3,3-tetramethylbutyl)phenoxyacetamido]-acetanilide.

19. a method of producing a colored photographic image as in claim 12, wherein said coupler is α-(4-aminobenzoyl)-2'-chloro-5'-(3-n-pentadecylphenoxyacetamido)-acetanilide.

20. A method of producing a colored photographic image by developing an exposed silver halide emulsion layer with an aromatic primary amino developing agent in the presence of α-(4-aminobenzoyl)-2'-chloro-5'acylaminoacetanilide, said acylamino group containing from nine to 28 carbon atoms.

21. A light-sensitive material as in claim 1 wherein said —NHCOR group is located at the 4-position of said anilide ring.

22. A light-sensitive material as in claim 9 wherein said ultraviolet absorbing agent absorbs below 400 millimicrons.

23. A method of producing a color photographic image as in claim 12, wherein said —NHCOR group is located at the 4-position of said anilide ring.

* * * * *