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COLOR PHOTOGRAPHIC LIGHT-SENSITIVE MATERIALS CONTAINING A NOVEL YELLOW-FORMING COUPLER

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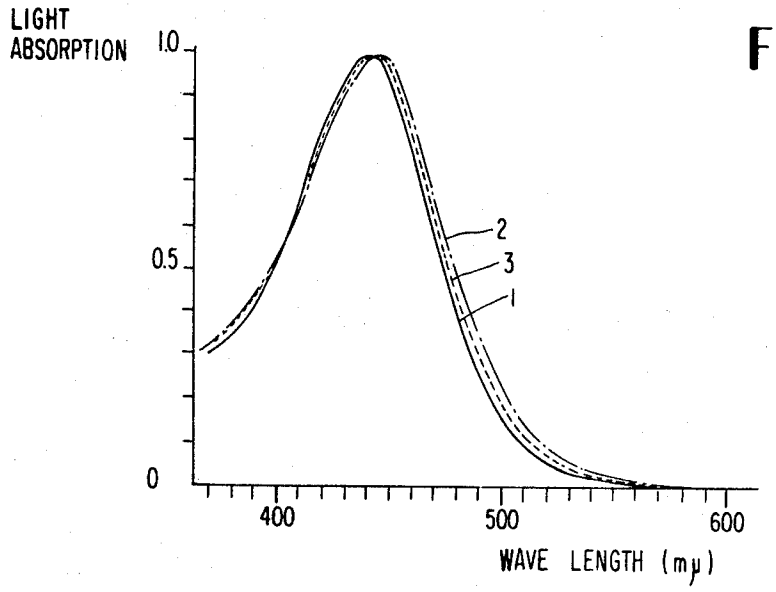



FIG. 1

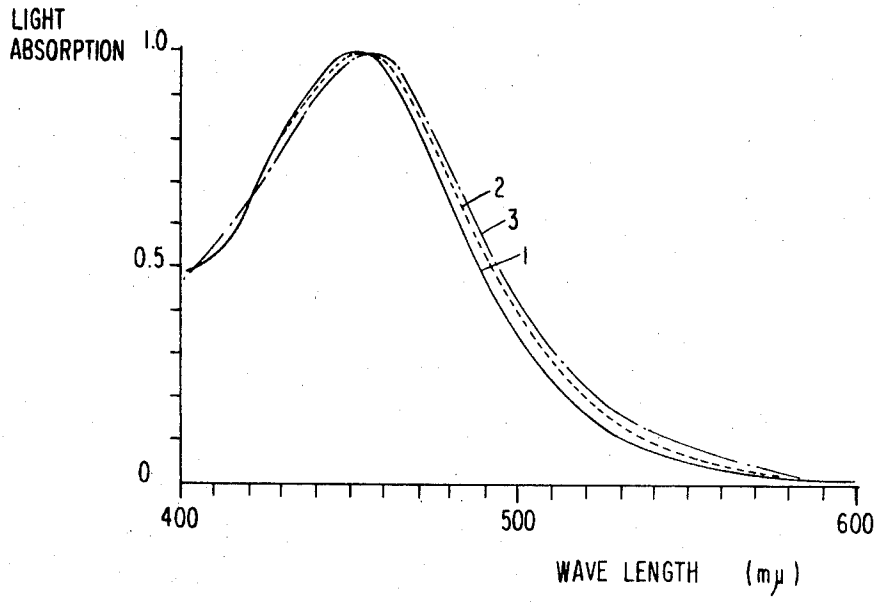



FIG. 2

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ATTORNEYS

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3,725,072

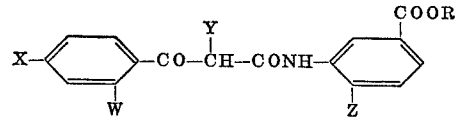
# COLOR PHOTOGRAPHIC LIGHT-SENSITIVE MATERIALS CONTAINING A NOVEL YELLOW-FORMING COUPLER

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Int. Cl. G03c 7/60
U.S. Cl. 96—55 44 Claims

## ABSTRACT OF THE DISCLOSURE

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



wherein R represents an aliphatic radical containing from 8 to 20 carbon atoms, W and X each represents a member selected from the group consisting of a hydrogen atom and a lower alkoxy group, wherein at least one of W and X represents an alkoxy group, Y represents a member selected from the group consisting of a hydrogen atom and a halogen atom, and Z represents a halogen atom, and process for preparing same is disclosed.

## BACKGROUND OF THE INVENTION

The present invention relates to silver halide color photographic light sensitive-materials containing a novel yellow forming coupler.

In a color photographic process based on a subtractive color process, there are employed couplers that form yellow, magenta, and cyan dyes respectively. This results from their coupling reactions with the oxidation product of an aromatic primary amino developing agent formed when exposed silver halide emulsion grains are reduced by an N,N-di-substituted p-phenylenediamine compounds acting as the primary developing agent. In this photographic process, the yellow dye image contributes to absorb blue light having wave lengths from about 400 to 500 millimicrons. In order to obtain color photographic images exhibiting brilliant colors, it is necessary for the yellow image to possess strong absorption in the above-mentioned wave length region and yet weak absorption outside of the wave length region mentioned, i.e., in a green region having wave lengths larger than 500 millimicrons.

In the case of incorporating couplers in silver halide emulsion layers each having different spectral sensivity in the production step of the light sensitive material, the couplers must be non-diffusible or be ballasted in order to prevent the couplers from diffusing into the other emulsion layers to deteriorate the color production. For this purpose, there have been made attempts to introduce a ballasting group having more than 9 carbon atoms into the coupler molecule.

As a means for incorporating ballasting couplers into photographic emulsion layers, two methods have been generally known. They are an aqueous solution-addition system and an oil solution-addition system. In the former system, the coupler has a water-solutilizing group and is added to a photographic emulsion mainly in a neutral or alkaline aqueous solution. In the latter system, a solution of a coupler in an organic solvent or a molten coupler liquid is finely dispersed in an aqueous medium to form an



emulsion and is subsequently added to a photographic emulsion. It is known that the yellow-forming coupler incorporated into a photographic emulsion layer by the oil solution addition system yields a color image having excellent spectral absorption characteristics, high humidity resistance and excellent acid resistance as compared with a coupler incorporated by the aqueous solution addition system.

Of the various yellow forming couplers known to be incorporated by the oil solution addition system, various acylacetanilide derivatives have been proposed.

However, when color images obtained by using many of the conventionally known acylacetanilide type yellow forming couplers are exposed to intense light for a long period of time, they tend to fade and hence present difficulties when one wants to exhibit the color photographs under very bright illumination and preserve them as records over long periods of time.

In addition, color images obtained by using many of the conventionally known acylacetanilide type yellow forming couplers have considerably strong absorptions in the green region of wave lengths which is greater than 500 millimicrons. For the reproduction of brilliant yellow and green colors, the absorption of the yellow image at the greater wave length side is an extreme hindrance.

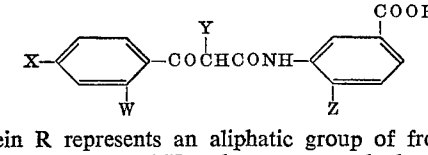
## SUMMARY OF THE INVENTION

Therefore, it is an object of the present invention to provide a color photographic light sensitive material forming a yellow image having excellent light fastness and spectral absorption characteristics suitable for color reproduction by a subtractive color process.

Another object of the present invention is to provide a color photographic light sensitive material containing a coupler forming a yellow image having sufficiently high optical density when the light sensitive material is processed by a developing solution containing an N,N-substituted p-phenylene-diamine type primary developing agent.

Still a further object of the present invention is to provide a color photographic light sensitive material containing a yellow forming coupler having sufficient solubility in an organic solvent for the oil-solution system and yet exhibit in a photographic emulsion layer for a long period of time.

Surprisingly, the inventors have discovered that these objects may be attained by employing as the yellow forming coupler a compound of the formula:



(I)

wherein R represents an aliphatic group of from 8–20 carbon atoms, W and X each represents a hydrogen atom or a lower alkoxy group, wherein at least one of said W and X is a lower alkoxy group, Y represent a hydrogen atom or a halogen atom, and Z represents a halogen atom.

## DETAILED DESCRIPTION OF THE INVENTION

Examples of the aliphatic groups shown by R in the above formula are alkyl groups or alkoxyalkyl groups. It has been found that when R is a 2-ethylhexyl or 2-hexyldecyl, high solubility of the coupler is attained. If the carbon atoms of the aliphatic group are less than 8, the cohesive force between the coupler molecules or between the coupler molecule and the solvent molecule is insufficient and leads to coupler dissociation and a dissolving of the coupler in the alkaline developing solution. The result is coupler diffusion to other emulsion layers and deterioration of the color reproduction of the color photographic light sensitive material. On the other hand, if the carbon atom number is larger than 20, the blue absorption co-

efficient per volume of the yellow dye formed becomes less and in order to maintain a determined optical density in the emulsion layer, the thickness of the emulsion layer must be increased.

The examples of the groups W and X in the above-mentioned formula are a methoxy group, an ethoxy group, a propoxy group, a butoxy group, and the like.

Among the halogen atoms of Y in the above-mentioned formula, are the fluorine atom and the chlorine atom, which are preferred since they provide the proper coupling properties necessary.

Also, among the halogen atoms of group Z, a fluorine atom and a chlorine atom are preferred since they furnish a color image having particularly excellent absorption characteristics.

The coupler of the general Formula I wherein an alkoxy group or an allyloxyl group is at the Z position may give a color image having excellent spectral absorption but exhibits insufficient coupling activity.

In the present invention, the coupler represented by general Formula I is employed in an oil-solution addition system. That is to say, the coupler is melted and then dispersed by emulsification in an aqueous medium without the presence of a solvent. Alternatively, the coupler is dissolved in an organic solvent and the solution is dispersed in an aqueous medium to provide finely divided colloidal particles. The dispersion is then incorporated in a photographic emulsion. As the organic solvent used for dissolving the coupler of this invention, those preferred are (i) a non-volatile solvent substantially insoluble in water and having a boiling point of higher than 190° C. at ordinary pressure, (ii) a high boiling solvent miscible with water, and (iii) a low boiling solvent miscible with water or partially soluble in water. Regarding the solvents of type (ii), those that can be removed from the photographic emulsion by water washing are preferred. The organic solvent of type (i) not only facilitates the emulsification of the coupler but also contributes to prevent the crystallization of the coupler in the emulsion layer improves the spectral absorption characteristics of the color image and improves the humidity resistance as well as acid resistance of the color image when it remains in the emulsion layer together with the coupler. On the other hand, the organic solvents of type (ii) and type (iii) assist dispersion of the coupler in an aqueous medium. It is preferred that they do not remain in the emulsion layers of the finished color photographic light sensitive material. Selection of a particular organic solvent or combination of same may be made according to the nature of couplers as well as the light sensitive materials employed.

## PREFERRED EMBODIMENT OF THE PRESENT INVENTION

The organic solvents of type (i) may be suitably selected from carboxylic acid esters, phosphoric acid esters, carboxylic acid amides, ethers, and substituted hydrocarbons. Illustrative of the organic solvents employed are di-n-butylphthalate, diisooctylazelate, dibutyl sebacate, tricresyl phosphate, N,N-diethyl caprylamide, butyl-m-pentadecylphenyl ether, and chlorinated paraffin.

Illustrative of the solvents of type (ii) employed are dimethylsulfoxide, dimethylformamide, and ethyleneglycol monomethyl ether. Similarly, examples of the solvents of type (iii) are propylene carbonate, ethyl acetate, cyclohexanol, tetrahydrofuran, and cyclohexanone.

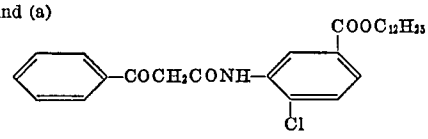
Of the primary color developing agents capable of converting the couplers of this invention into an azomethine dye in the presence of an exposed silver halide are the N,N-di-substituted-p-phenylene diamine derivatives. Suitable compounds which may be employed are N,N-dimethyl-p-phenylenediamine, N,N-diethyl-p-phenylenediamine, N-ethyl-N-(β-hydroxyethyl)-p-phenylenediamine, 4-amino-3-methyl-N,N-diethylaniline, 4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline, 4-amino-3-methyl-N-(β-methanesulfonamidoethyl)-aniline, 4-amino-3-(β-methanesulfonamidoethyl)-N,N-diethylaniline and the salts of same.

For forming a blue-sensitive photographic emulsion layer having good properties, the coupler represented by general Formula I may be employed alone or as a combination of two or more such couplers or together with another yellow forming coupler other than those of general Formula I.

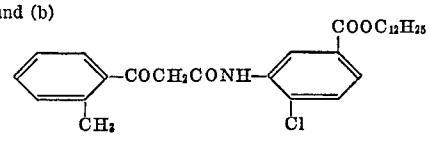
The yellow-forming coupler of general Formula I may be used in the present invention to give a yellow image having excellent light fastness and suitable spectral absorption characteristics for color reproduction by a subtractive color process.

These features are explained below by comparing the compounds of Formula I with other couplers having a similar chemical structure such as coupler (a) having the following formula and disclosed in Japanese patent publication No. 5582/1967 and the couplers (b) and (c) having the following formulas and described in French Pat. No. 1,513,642;

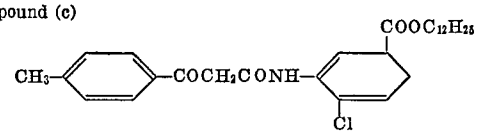
Compound (a)



Compound (b)

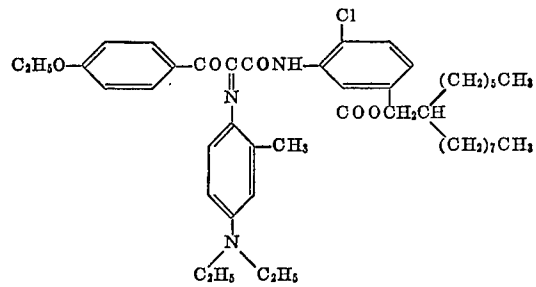


Compound (c)



α-(4-ethoxybenzoyl)-aceto[2'-chloro-5'-(2''-hexyl-decyloxycarbonyl)anilide] (shown as structural Formula F later) of this invention was oxidatively coupled with 4-amino-3-methyl-N,N-diethyl-aniline in the presence of ammoniacal silver nitrate as the oxidant and subsequently recrystallized from methanol. A yellow needle-like crystalled product having the following structural formula (d) and a melting point of 72° C., was prepared.

Compound (d)



Similarly, by the oxidative condensations of compound (a) and compound (b) with 4-amino-3-methyl-N-, N-diethylaniline, the corresponding orange crystals of azomethine dyes [compound (e) and compound (f)] having melting points 88° C. and 94–96° C., were respectively obtained.

## BRIEF DESCRIPTION OF THE DRAWINGS

By dissolving these three dyes in butyl acetate and measuring the spectral absorptions of the solutions, the results shown in FIG. 1 of the accompanying drawings and the following table were obtained. In FIG. 1, curve 1 is a spectral absorption curve when compound F of this invention is used, and curve 2 and curve 3 are spectral

absorption curves when compound (a) and compound (b) are used respectively.

TABLE 1.—SPECTRAL ABSORPTION CHARACTERISTICS OF SOLUTION OF YELLOW AZOMETHINE DYE (SOLVENT: BUTYL ACETATE)

| Dye | Coupler | Molecular extinction coefficient (1 cm./mole) | Maximum absorption wave length (mμ) | Long wave length absorption (S) | Relative absorbance at 520 mμ |
|---|---|---|---|---|---|
| d | F | $2.15\times10^4$ | 440 | 0.154 | 0.051 |
| e | (a) | $2.35\times10^4$ | 440 | 0.171 | 0.070 |
| f | (b) | $2.18\times10^4$ | 441.5 | 0.164 | 0.061 |

The value of S in the above table is a relative value to the maximum absorption at a wave length of 60 millimicrons greater than the maximum absorption wave length. If the value of S is small, the absorption is cut sharply at the greater wave length side and unnecessary absorption in green region is less.

As shown in the above table, the novel coupler F of this invention exhibits absorption characteristics which are sharply diminished at the greater wave length side as compared with the known compounds (a) or (b) having similar structure. Also, the absorption maximum is positioned at a slightly greater wave length. Therefore, the couplers of the present invention are capable of providing a dye of brilliant yellow having less red tone. This is shown by the small numerical value of the relative absorbance at 520 millimicrons. Also, as shown by the numerical value of the molecular extinction coefficient, coupler F gives as high an absorption power as the acylacet anilides. Compound (c) provides a dye having absorption characteristics very similar to those of compound (b).

The excellent spectral absorption characteristics of the dyes obtained by the couplers of this invention influence greatly the absorption of photographic images obtained by using such couplers. That is to say, the yellow image obtained in the color photographic light-sensitive material of this invention containing such coupler possesses less reddish sharp yellow having a high visible density. This feature is well illustrated in Example 1 which serves as a comparison against known compounds.

The novel yellow forming couplers used in this invention can give a color image showing less fading upon light exposure. Furthermore, if the coupler is left in an emulsion layer without being consumed at the color development stage the coupler is neither discolored nor colored when it is exposed to light. Thus, the color photograph obtained from the color photographic light-sensitive material of this invention can be stored for a longer period of time under the influence of light as compared with conventional color sensitive materials.

Light fastness can be further improved by removing active ultraviolet rays from exposure light. Illustrative of the ultraviolet absorbents useful for this purpose are compounds which do not substantially absorb visible light having wave lengths greater than 400 millimicrons but absorb in great quantities only ultraviolet rays. Illustrative of their compounds are stilbene derivatives (see, e.g., Japanese patent application Nos. 81,695/65 and 81,695/65), 2-arylimino-3-alkyl-5-arylmethylenethiazolidones or 2 - arylimino - 3 - alkyl-5-hetero-methylenethiazolidones (Japanese patent application No. 55,636/65), and 2-benztriazolyl-4-alkylphenols (Japanese patent application No. 19,229/68). These ultraviolet absorbents may be incorporated into silver halide photographic emulsion layers or subsidiary layers of light sensitive materials or may optionally be added to the support. They may also be applied from the outside to the light sensitive material following development. Preferably, the ultraviolet absorbents contemplated for use herein have an aliphatic radical of from 4 to 30 carbon atoms.

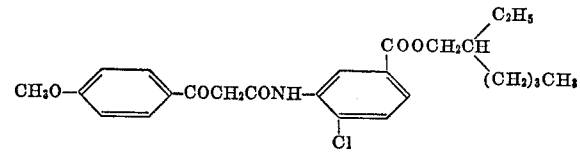
The improved light fastness of the yellow images obtained from the color photographic light sensitive materials of this invention is illustrated in Examples 2, 3, 5 and 6 which follow later.



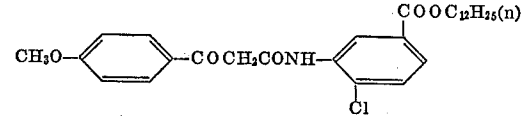
The typical structures of the novel couplers of this invention represented by general Formula I and the examples of synthesizing the couplers are illustrated below:

Examples of couplers

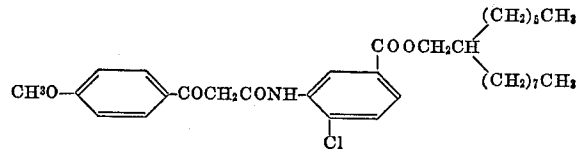
Coupler A:



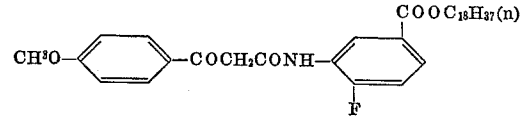
Coupler B



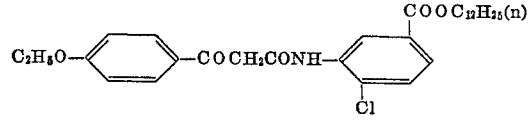
Coupler C



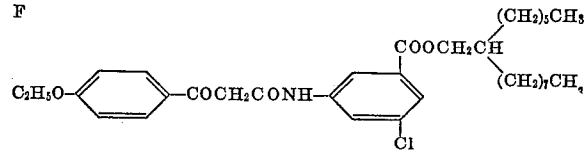
Coupler D



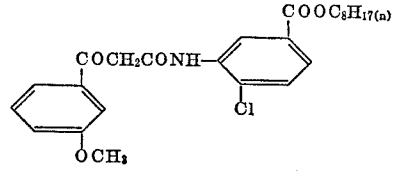
Coupler E



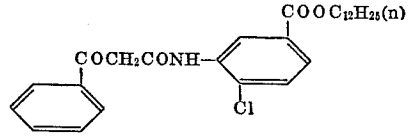
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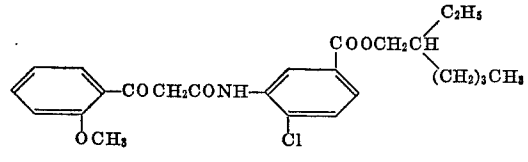
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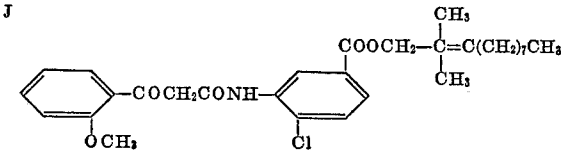
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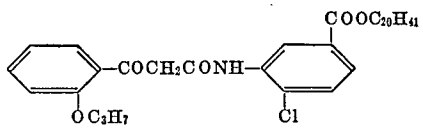
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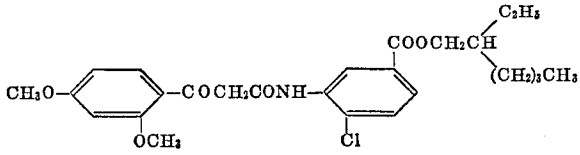
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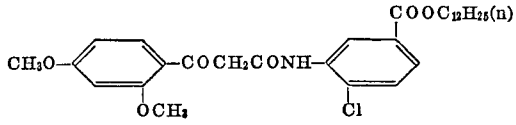
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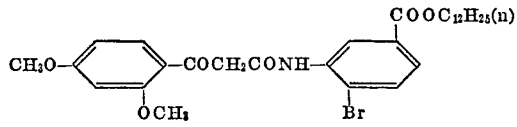
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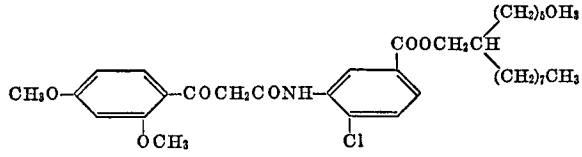
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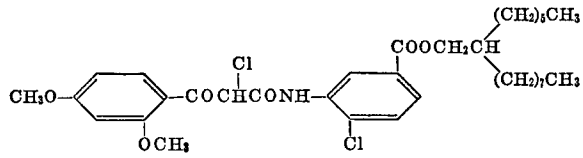
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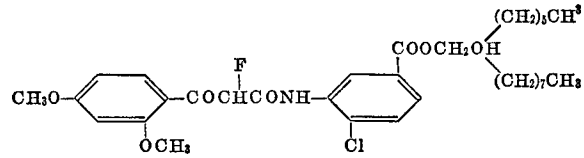
O



P



Q



Di-n-butylphthalate was employed as the solvent for the couplers and 4-amino-3-methyl-N,N-diethyl aniline as the primary color developing agent. The yellow images formed from the compounds illustrated above have the following absorption maximum wave lengths:

| Compound: | Maximum absorption wave length (mμ) |
|---|---|
| A | 452 |
| B | 452 |
| C | 452 |
| D | 449 |
| E | 451 |
| F | 451 |
| G | 444 |
| H | 444 |
| I | 444 |
| J | 445 |
| K | 445 |
| L | 439 |
| M | 439 |
| N | 437 |
| O | 439 |
| P | 452 |
| Q | 437 |

Examples of synthesizing the couplers used in this invention are illustrated below. All parts are by weight unless otherwise stated.

Synthesis 1

(1–a) 2-ethylhexyl-(3-amino-4-chloro)benzoate: Into a 2 liter four necked flask equipped with an agitator, a thermometer, a nitrogen gas inlet, and a distilling pipe for by-produced methanol were charged 380 parts (2.05 mols) of methyl-3-amino-4-chloro-benzoate and 390 parts (3.0 mols) of 2-ethyl-hexyl alcohol. The benzoate was then dissolved in the alcohol by heating to 80° C. 10 parts (by volume) of titanium butoxide were added to the solution and nitrogen gas was introduced in the flask to assist the distillation of methanol by-produced. Thereafter, while maintaining the system at 130–140° C., the methanol was distilled away. After stopping the heating and cooling slowly to 50–60° C., 1 liter of the reaction product was poured into a Claisen flask and an excess of 2-ethylhexyl alcohol was quantitatively distilled away at 60–65° C./2 mm. Hg. The amount of the oil remaining totaled 582 parts (100% in yield).

(1–b) 4 - methoxybenzoylaceto-[2-chloro-5-(2'-ethylhexyloxycarbonyl)]anilide (Compound A): Into a 1 liter three-necked flask equipped with an agitator, a thermometer, a conduit for distilling by-produced ethanol were charged 111 parts (0.5 mol) of ethyl-4-methoxybenzoyl acetate and 142 parts (0.5 mol) of the 2-ethylhexyl-(3-amino-4-chloro)benzoate obtained in (1–a). While heating and stirring, the temperature of the system was maintained at 140–150° C. After about 4 hours 60% by weight of the theoretical amount of ethanol was distilled away.

The agitator was withdrawn, the ethanol was further distilled away for 30 minutes under a reduced pressure. After stopping the heating and cooling slowly, the reaction product was added to 1500 parts (by volume) of petroleum ether. The mixture was allowed to cool overnight, whereby a yellowish white crystal was precipitated. The crystal was recovered by filtration under suction, washed with 300 parts of petroleum ether, and recrystallized from 600 parts of acetonitrile. The amount of the product obtained was 115 parts (50% in yield). The melting point of the produce was 102–104° C.

Synthesis 2

(2–a) Dodecyl-(3-amino-4-chlorobenzoate: The same procedure as synthesis (1–a) was followed using 558 parts of dodecyl alcohol instead of 2-ethylhexyl alcohol. After the reaction was over, the product was poured into a 5 liter beaker and after adding 3000 parts (by volume) of methanol, the mixture was allowed to cool overnight, whereby white crystals were precipitated. The crystal was recovered by filtration and recrystallized from 3000 parts (by volume) of methanol to provide 620 parts of the pure product having a melting point of 58° C. with a yield of 89%.

(2–b) 4-methoxybenzoylaceto-(2-chloro-5-dodecyloxycarbonyl)anilide (Compound B): The same procedure as synthesis (1–b) was followed using 170 parts of dodecyl-3-amino-4-chlorobenzoate obtained in synthesis (2–a) instead of 2-ethylhexyl (3-amino-4-chloro)benzoate obtained in synthesis (1–b). 155 parts of the above product having a melting point of 139–140° C. was obtained with a yield of 60%.

Synthesis 3

(3–a) 2-hexyldecyl-(3-amino-4-chloro)benzoate: The same procedure as synthesis (1–a) was followed by using 725 parts of 2-hexyldecyl alcohol instead of 2-ethylhexyl alcohol produced by synthesis (1–2). 800 parts of the above product was obtained with a yield of 99%.

(3–b) 4-methoxybenzoylaceto-[2-chloro-5-(2'-hexyldecyloxycarbonyl)]anilide (Compound C): The same procedure as synthesis (1–b) was followed by using 198

parts of (2-hexyldecyl)-3-amino-4-chlorobenzoate produced in synthesis (3–a) instead of 2-ethylhexyl(3-amino-4-chloro)benzoate produced in synthesis (1–b). Then, the reaction product liquid was recovered, added to 1000 parts of methanol, and the mixture was allowed to cool overnight. Thereafter, the crystal thus precipitated was recovered by filtration and recrystallized from 500 parts of ethanol to provide 122 parts of the above objective compound having a melting point of 97° C. with a yield of 43%.

Synthesis 4

4 - ethoxybenzoylaceto - (2 - chloro-5-dodecyloxycarbonyl)anilide (Compound E): The same procedure as synthesis (1–b) was followed by using 170 parts of dodecyl-3-amino-4-chlorobenzoate produced in synthesis (2–a) and 118 parts of ethyl-4-ethoxybenzoyl acetate instead of 2-ethylhexyl(3-amino-4-chloro)benzoate and ethyl-4-methoxybenzoyl acetate in synthesis (1–b) and 159 parts of the above-described compound having a melting point of 136° C. was obtained with a yield of 68%.

Synthesis 5

4 - ethoxybenzoylaceto-[2-chloro-5-(2'-hexyldecyloxycarbonyl)]anilide (Compound F): The same procedure as synthesis (1–b) was followed by using 198 parts of 2-hexyldecyl - (3 - amino-4-chloro)benzoate produced in synthesis (3–a) and 118 parts of ethyl-4-ethoxybenzoyl acetate instead of 2-ethylhexyl(3-amino-4-chloro)benzoate and ethyl-4-methoxybenzoyl acetate in synthesis (1–b). Then, by recrystallizing the reaction product from ethanol, 88 parts of the above-mentioned objective compound having a melting point of 108–109° C. A yield of 30% was obtained.

Synthesis 6

2-methoxybenzoylaceto(2-chloro - 5 - dodecyloxycarbonyl)anilide (Compound H): The same synthesis as synthesis (1–b) was followed by using 170 parts of dodecyl-3-amino-4-chlorobenzoate produced in synthesis (2–a) and 111 parts of ethyl-2-methoxybenzoyl acetate instead of 2-ethylhexyl-(3-amino-4-chloro)benzoate and ethyl-4-methoxybenzoyl acetate in synthesis (1–b). The above-mentioned compound was obtained. The yield of produce was 77.5 parts (30% in yield) and the melting point thereof was 79–80° C.

Synthesis 7

2-methoxybenzoyl aceto - [2 - chloro-5-(2'-ethylhexyloxycarbonyl)]anilide (Compound I): The same procedure as synthesis (1–b) was followed by using ethyl-2-methoxybenzoyl acetate instead of ethyl-4-methoxybenzoyl acetate in synthesis (1–b). 57.5 parts of the above compound I having a melting point of 93° C. was obtained with a yield of 25%.

Synthesis 8

2,4 - dimethoxybenzoylaceto - [2 - chloro-5-(2'-ethylhexyloxycarbonyl)]anilide (Compound L): The same procedure as synthesis (1–b) was followed by using 126 parts (0.5 mol) of ethyl-2,4-dimethoxybenzoylacetate instead of the ethyl-4-methoxybenzoyl acetate in synthesis (1–b). 89 parts of the above objective compound having a melting point of 83–85° C. was obtained with a yield of 40%.

Synthesis 9

2,4-dimethoxybenzoylaceto - (2 - chloro-5-dodecyloxycarbonyl)anilide (Compound M): The same procedure as synthesis (1–b) was followed by using 126 parts (0.5 mole) of ethyl-2,4-dimethoxybenzoyl acetate and dodecyl-3-amino-4-chlorobenzoate produced in synthesis (2–a) instead of ethyl-4-methoxybenzoyl acetate and 2-ethylhexyl(3-amino-4-chloro)benzoate in synthesis (1–b). 136 parts of the above mentioned compound having a melting point of 123° C. was obtained with a yield of 50%.

Synthesis 10

2,4-dimethoxybenzoylaceto[2-chloro - 5 - (2' - hexyldecyloxycarbonyl)]anilide (Compound O): The same procedure as synthesis (1–b) was followed by using 126 parts (0.5 mol) of ethyl-2,4-dimethoxybenzoyl acetate and 200 parts (0.5 mol) of 2-hexyldecyl-(3-amino-4-chloro)benzoate obtained in synthesis (3–a) instead of ethyl - 4 - methoxybenzoyl acetate and 2-ethylhexyl(3-amino-4-chloro)benzoate in synthesis (1–b). 75 parts of the above compound having a melting point of 57° C. was obtained with a yield of 25%.

The present invention can be applied to various types of color photographic light sensitive materials and can give color images exhibiting superior properties over those of the prior art. For example, the invention can be applied to color photographic printing papers, color photographic positive films, color photographic negative films, and color photographic reversal films.

The invention may be applied to a so-called multiple layer type color photographic light sensitive material prepared by applying to a support, silver halide emulsions having different color sensitivities and containing the corresponding ballasted couplers as well as to other types of color photographic light sensitive materials such as mixed grain type.

EXAMPLE 1

A better understanding of the present invention will be attained from the following examples which are merely intended to be illustrative and not limitation of the present invention. All parts are by weight unless otherwise stated.

A solution prepared by refluxing a mixture of 20 parts of Compound F shown above, 30 parts (by volume) of di-n-butyl phthalate, and 50 parts (by volume) of ethyl acetate was added to 300 parts (by volume) of an aqueous solution containing 30 parts of gelatin and 2.0 parts of sodium dodecylbenzene sulfonate. The mixture was stirred and passed five times through a preheated, colloid mill, whereby the coupler was finely dispersed by emulsification together with the solvents.

The emulsified dispersion was added to 1000 parts of a photographic emulsion containing 54 parts of silver iodo-bromide and 60 parts of gelatin. After adding 30 parts (by volume) of a 3% acetone solution of triethylene phosphamide as a hardening agent and adjusting the pH of the mixture to 6.0, the mixture was applied to a triacetyl cellulose film in a dry thickness of 7.0 microns. The light sensitive film thus produced was called "film U–1." It was confirmed that the film contained the coupler in an amount of $2.05 \times 10^{-3}$ mole per 1 square meter.

For the sake of comparison, the above procedure was followed using the known coupler (a) instead of the Compound F to provide a light sensitive film, which is called "film U–2."

Similarly, by the same procedure as above using the known couplers (b) and (c), light sensitive films were prepared. They are called "film U–3" and "film U–4" respectively. In the above procedure, however, cyclohexanone was employed for dissolving the compound (c) instead of ethyl acetate. The comparative coupler (a) was synthesized according to the synthesis 2 in Japanese patent publication No. 5,582/67 and the comparable couplers (b) and (c) were prepared according to the synthesis 1 and synthesis 6 respectively of Japanese patent application No. 3,236/66.

These light sensitive films were subjected to stepwise

exposure by means of a sensitometer and processed according to the following procedures:

| | ° C. | Minute |
|---|---|---|
| 1. Color development | 20 | 15 |
| 2. Water washing | 18 | 1 |
| 3. First fixing | 20 | 4 |
| 4. Water washing | 18 | 3 |
| 5. Silver bleaching | 20 | 5 |
| 6. Water washing | 18 | 3 |
| 7. Second fixing | 20 | 3 |
| 8. Water washing | 18 | 15 |

The color development was conducted with a color developing solution having the following composition A.

Color developing solution A:

| | | |
|---|---|---|
| Water | liter | 1 |
| 4 - amino - 3 - methyl - N,N - diethyl aniline hydrochloride | parts | 2.5 |
| Sodium sulfite (anhydrous) | do | 3.0 |
| Sodium carbonate (monohydrate) | do | 47.0 |
| Potassium bromide | do | 2.0 |

The fixing solution used above is an acidic aqueous solution mainly containing sodium thiosulfate. The bleaching solution is a natural aqueous solution mainly containing a ferricyanide.

After the above procedures, the sample films were measured for the density to blue light and the following photographic properties were determined.

PHOTOGRAPHIC PROPERTIES

| Sample | Coupler | Fog | Sensitivity (relative) | Gamma | Maximum density |
|---|---|---|---|---|---|
| U-1 | F | 0.08 | 100 | 2.3 | 3.50 |
| U-2 | a | 0.11 | 103 | 2.5 | 3.45 |
| U-3 | b | 0.09 | 100 | 2.4 | 3.40 |
| U-4 | c | 0.09 | 100 | 2.4 | 3.45 |

The spectral absorption curves of the color images obtained from the light sensitive films are shown in FIG. 2 of the accompanying drawings. As is clear from the results, the spectral absorption curve (curve 1) of the color image of film U–1 had an absorption maximum at 452 millimicrons and had less absorption at the wave length region greater than 500 millimicrons when compared with the absorption curves (curve 2 and curve 3) of the color images obtained from the film U–3 and film U–4. Thus, film U–1 yields brillant yellow with less reddish hue images as compared with other films.

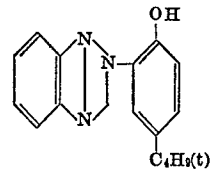
## EXAMPLE 2

A solution prepared by refluxing a mixture of 57.5 parts of compound C shown above, 105 parts (by volume) of tri-o-cresyl phosphate, and 250 parts (by volume) of butyl acetate was added to 700 parts (by volume) of an aqueous solution containing 50 parts of gelatin and 3.0 parts of sodium dodecylsulfate with stirring. Subsequently, the mixture was vigorously stirred mechanically in a high speed agitator for 30 minutes, whereby the coupler was finely dispersed in the aqueous solution together with the solvents.

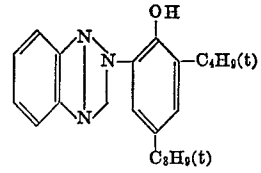
The whole portion of the emulsified dispersion was added to 2000 parts of a photographic emulsion containing $6.03\times10^{-1}$ mols of silver bromide and 167 parts of gelatin. After adding 50 parts by volume of a 3% acetone solution of triethylene phosphamide and adjusting the pH to 7.0, the mixture was applied to a triacetyl cellulose base to a dry thickness of 6.0 microns.

A solution prepared by dissolving under heating 15 parts of each of the ultraviolet absorbents (e), (f) and (g) having the structures shown below, 50 parts (by volume) of di-n-butyl phthalate, and 120 parts (by volume) of ethyl acetate was added to 700 parts (by volume) of an aqueous solution containing 150 parts of gelatin and 3.0 parts of sodium dodecyl sulfate. The mixture was vigorously stirred for 30 minutes in a high speed agitator, whereby the ultraviolet absorbent was finely dispersed together with the solvents.

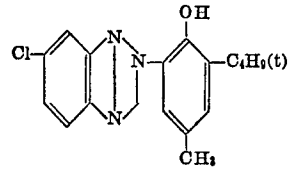
Ultraviolet absorbent (e)




Ultraviolet absorbent (f)




Ultraviolet absorbent (g)




The emulsified dispersion of the ultraviolet absorbent was applied onto the silver halide emulsion layer containing the above-mentioned yellow forming coupler to a dry thickness of 3.0 microns. A further gelatin solution containing triethylene phosphamide was applied onto the layer in a thickness of 1.10 micron to provide film V–1. The light sensitive film contained $1.81\times10^{-5}$ mols of the yellow forming coupler and .0107 part of the ultraviolet absorbent per 100 cm.$^2$ of the film.

By the same procedure, films, V–2 and V–3 having the same layer structure as above were prepared by using the known couplers (a) and (c) respectively instead of coupler C of film V–1.

These light sensitive films were exposed stepwise by means of a sensitometer and the process of Example 1 except that color development was conducted for 15 minutes at 24° C. with the developing solution having the following composition.

Color developing solution B:

| | | |
|---|---|---|
| Water | liter | 1 |
| Benzyl alcohol | parts by volume | 12.0 |
| Sodium hexametaphosphate | parts | 2.0 |
| Sodium sulfite (anhydrous) | do | 2.0 |
| Sodium carbonate (monohydrate) | do | 27.5 |
| Hydroxylamine sulfate | do | 2.5 |
| 4 - amino - 3 - methyl - N - ($\beta$-methanesulfonamidoethyl)aniline sesquisulfate (monohydrate) | do | 4.0 |

The film V–1 of this invention gave a brilliant yellow image with less reddish hue as compared with films V–2 and V–3 containing the known couplers. The absorption maximum wave length of the color image was 453 millimicrons.

The three kinds of the colored films discussed above were exposed to a Xenon Arc lamp of 1.5 kw. equipped with a water filter for 30 hours and reduction in the blue densities of color image was measured. The results are shown in the following table.

From these results, it was confirmed that the color photograph obtained by using the coupler C of this invention was less fading when exposed to intense light as compared with the color images obtained from the known couplers.

FADING OF THE YELLOW IMAGE BY LIGHT (REDUCTION RATIO OF BLUE DENSITY TO INITIAL DENSITY)

| Film | Coupler | Initial density 1.0 | 2.0 |
|---|---|---|---|
| V-1 | C | 14 | 14 |
| V-2 | (a) | 36 | 32 |
| V-3 | (c) | 30 | 30 |

Moreover, the above three kinds of colored films were stored under conditions of 65° C. temperature and 75% relative humidity for 20 days. No reduction in blue densities was observed.

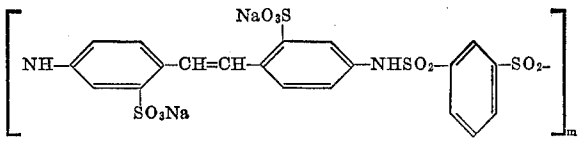
## EXAMPLE 3

A solution prepared by refluxing at 60° C. a mixture of 24 parts of the compound P shown above, 12 parts (by volume) or di-n-butyl sebacate, 0.5 part of sorbitan monolaurate, and 24 parts (by volume) of ethyl acetate was added to 400 parts (by volume) of an aqueous solution containing 5.0 parts of sodium di-isooctyl-sulfosuccinate and 36 parts of gelatin. The mixture was vigorously stirred by means of an homogenizer, whereby the coupler was finely dispersed in the aqueous solution together with the solvents.

The whole portion of the emulsified dispersion was added to 500 parts of a photographic emulsion containing 45 parts of silver iodobromide and 50 parts of gelatin. After adding 30 parts (by volume) of a 3% acetone solution of triethylene phosphoamide as a hardening agent and adjusting the pH to 6.5, the mixture was applied to a polyethylene terephthalate base to a dry thickness of 6.0 microns.

1000 parts of an aqueous solution containing 4 parts of the high-molecular ultraviolet absorbent (h) shown below and 40 parts of gelatin was applied onto the silver halide emulsion layer to a dry thickness of 2.5 microns. The high-molecular ultraviolet absorbent was synthesized according to the method disclosed in the specification of French Pat. No. 1,505,736.

The high-molecular ultraviolet absorbent used above has the following formula:




wherein *m* represents a large positive integer depending upon the value of the compound viscosity.

The light sensitive film thus prepared is called "film W–1." For comparison, a film W–2 was prepared by the same procedure as above using the known coupler (b) as the yellow forming coupler.

These light sensitive films were exposed stepwise by means of sensitometer and then color-developed using the color developing solution B shown in Example 2.

The film W–1 of this invention gave a brilliant yellow image with less reddish hue as compared with that of the film W–2. The film W–1 had the absorption maximum at 435 millimicrons, whereas the film W–2 had the absorption maximum at 449 millimicrons.

After exposing the above two kinds of the colored films to intense light from carbon arc for 24 hours, the reduction in blue densities of the color images were measured. The results are shown in the following table:

FADING OF YELLOW IMAGE BY LIGHT (REDUCTION RATIO OF BLUE DENSITY TO THE INITIAL DENSITY)

| Film | Coupler | Initial density 1.0 | 2.0 |
|---|---|---|---|
| W-1 | P | 10 | 7 |
| W-2 | (b) | 25 | 22 |

From these results, it was confirmed that the coupler P of this invention gave a color image which faded less upon exposure to intense light.

## EXAMPLE 4

A solution prepared by dissolving under heating 24 parts of the compound P of this invention shown above in 70 parts (by volume) of butyl acetate was added to 700 parts (by volume) of a gelatin solution containing 1.5 parts of sodium dodecylsulfate and 50 parts of gelatin with stirring. The mixture was passed five times through a preheated colloid mill, whereby the coupler was finely emulsified together with the solvent.

The whole portion of the emulsified dispersion was mixed with 500 parts of a photographic emulsion containing 45 parts of silver iodobromide, 50 parts of gelatin and 2 parts of polyvinyl pyrrolidone. After adding 30 parts (by volume) of a 3% acetone solution of triethylene phosphamide as a hardening agent and adjusting the pH to 6.5, the mixture was applied to a polyethylene terephthalate film base in a dry thickness of 8.0 microns. An aqueous gelatin solution was further applied to the emulsion layer to a dry thickness of 1.0 micron to provide a light sensitive film.

When the film was color-developed by using the color developing solution A described in Example 1, a brilliant yellow image having the absorption maximum at 439 millimicrons was obtained.

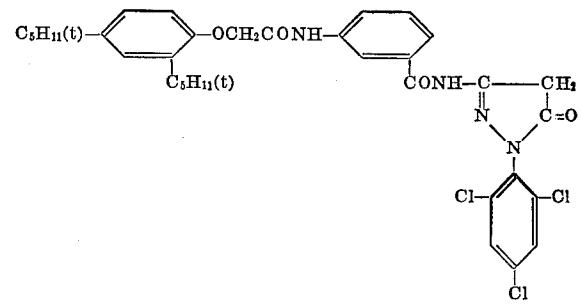
## EXAMPLE 5

A solution was prepared by refluxing a mixture of 10.5 parts of compound F shown above, 15 parts (by volume) of diisooctyl phthalate and 1 part of sodium di-isooctyl-sulfosuccinate. 40 ml. of ethyl acetate was added to an aqueous solution at 50° C. containing 20 parts of gelatin. The mixture was vigorously stirred in a homogenizer to finely disperse the coupler in the aqueous solution together with the solvents.

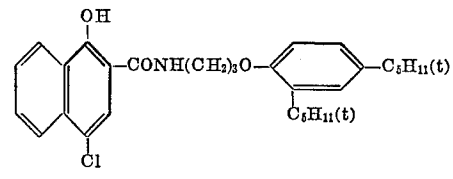
The whole portion of the emulsified dispersion prepared above was added to 540 parts of a blue-sensitive photographic emulsion containing 30 parts of silver chlorobromide and 35 parts of gelatin. After adding 30 parts (by volume) of a 3% acetone solution of triethylene phosphamide as a hardening agent, the mixture was applied to baryta-coated paper to a dry thickness of 4.5 microns.

Onto the emulsion layer was further applied a green-sensitive emulsion containing a magenta forming coupler having the following Formula i as the second layer. Onto the green-sensitive emulsion layer was applied a red-sensitive emulsion of a cyan forming coupler having the following Formula j as the third layer:

Magenta forming coupler (i)




Cyan forming coupler (j)

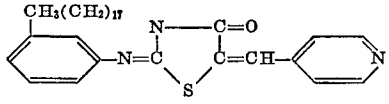



Subsequently, onto the red-sensitive emulsion layer was applied an ultraviolet absorption layer of 2.5 microns in

thickness and containing an ultraviolet absorbent having the structural Formula k as shown below in a proportion of 2.0 parts/m.$^2$ in area density. Finally, a protective layer of 1.0 micron in thickness was applied onto the ultraviolet absorption layer to provide a color photographic paper.

The ultraviolet absorbent (k) used above was produced according to the method disclosed in the specification of U.S. Pat. No. 3,352,681.

Ultraviolet absorbent (k)



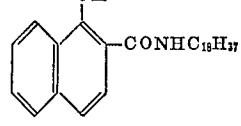
A color negative was printed on the color photographic light sensitive paper prepared above and this color paper was processed by the color developing solution B of Example 2. The color print obtained, exhibited excellent color reproducibility having brilliant color and particularly, yellow with less reddish tone. The yellow image had the absorption maximum at 447 millimicrons.

When the color print was exposed directly to sunlight for 5 days, fading was scarcely noted. Also, no coloring appeared at the highlight regions.

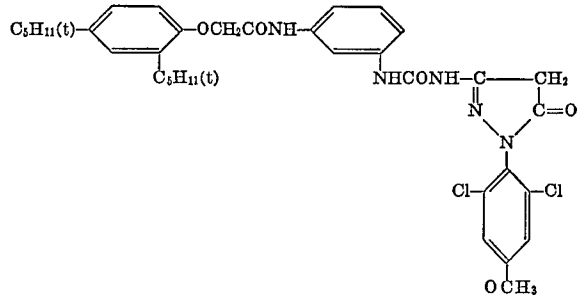
## EXAMPLE 6

A red-sensitive emulsion layer containing a cyan forming coupler (1) having the structure shown below was applied to a transparent triacetyl cellulose film base containing the ultraviolet absorbent (e) shown above in an area density of 2.0 parts/m.$^2$ as the first layer. Onto the first layer was applied a green-sensitive emulsion layer containing a magenta forming coupler (m) having the structure shown below as the second layer. Subsequently, an aqueous gelatin solution containing yellow colloidal silver was applied as the third layer.

Cyan forming coupler (1)



Magenta forming coupler (m)



A solution prepared by heating a mixture of 21.2 parts of the compound E shown above, 50 parts (by volume) of tri-n-hexyl phosphate, 55 parts (by volume) of cyclohexanone and 2.0 parts of sodium dinonylnaphthalene sulfonate was added to 500 parts (by volume) of an aqueous solution containing 30 parts of gelatin with stirring. The mixture was passed five times through a preheated colloid mill to finely disperse the coupler.

The whole portion of the emulsified dispersion was added to 1000 parts of a photographic emulsion containing 54 parts of silver iodobromide and 60 parts of gelatin. After adding 30 parts (by volume) of a 3% acetone solution of triethylene phosphamide as a hardening agent and adjusting the pH of the mixture to 6.0, the blue-sensitive emulsion thus prepared was applied onto the third layer to a dry thickness of 6.5 microns as the fourth layer. Finally, a gelatin protective layer was applied thereto as the uppermost layer.

A color negative was printed to the photographic film thus prepared and the film was processed with the color developing solution B as described in Example 2, whereby a color print having brilliant colors was obtained.

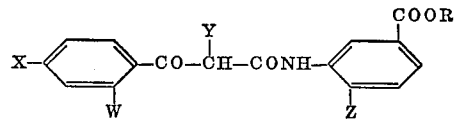
When the color print was exposed to a number of fluorescent lamps equipped with scattering plates for 40 days so that the side of film base faced the light sources, the fading of the yellow image was extremely minute.

The yellow image of the color print had an absorption maximum at 444 millimicrons.

Though the present invention has been adequately set forth in the foregoing specification and examples included therein, it is readily apparent that various modifications and changes may be made, without departing from the scope thereof.

What is claimed is:

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



wherein R represents an aliphatic radical containing from 8 to 20 carbon atoms, W and X each represents a member selected from the group consisting of a hydrogen atom and a lower alkoxy group, wherein at least one of W and X represents an alkoxy group, Y represents a member selected from the group consisting of a hydrogen atom and a halogen atom, and Z represents a halogen atom.

**2.** The light-sensitive material of claim **1**, wherein Y represents a hydrogen atom and R represents a branched alkyl group.

**3.** The light-sensitive material of claim **2**, wherein R is a member selected from the group consisting of 2-ethylhexyl and 2-hexyldecyl.

**4.** The light-sensitive material of claim **1**, wherein said Z represents a chlorine atom.

**5.** The light-sensitive material of claim **1**, wherein said Z represents a fluorine atom.

**6.** The light-sensitive material of claim **1**, wherein said coupler is α-(4-methoxybenzoyl) - aceto-2'-chloro-5'-(2''-hexyldecyloxycarbonyl)-anilide.

**7.** The light-sensitive material of claim **1**, wherein said coupler is α-(4-ethoxybenzoyl) - aceto-2'-chloro-5'-(2''-hexyldecyloxycarbonyl)-anilide.

**8.** The light-sensitive material of claim **1**, wherein said coupler is α-(2-methoxybenzoyl)-aceto-2'-chloro-5'-dodecyloxycarbonylanilide.

**9.** The light-sensitive material of claim **1**, wherein said coupler is α-(2,4-dimethoxybenzoyl) - aceto-2'-chloro-5'-(2''-hexyldecyloxycarbonyl)-anilide.

**10.** The light-sensitive material of claim **1**, wherein further comprising an additional layer containing an ultraviolet absorbing agent.

**11.** The light-sensitive material of claim **10**, wherein the ultra-violet absorbing agent contains an aliphatic radical of from 4 to 30 carbon atoms.

**12.** The light-sensitive material of claim **11**, wherein said ultra-violet absorbing agent is a 2-benztriazolyl-4-alkylphenol derivative.

**13.** The light-sensitive material of claim **11**, wherein said ultra-violet absorbing agent is a member selected from the group consisting of 2-arylimino-3-alkyl-5-arylmethylene-thiazalidones and 2-aryl-amino-3-alkyl-5-hetero methylene-thiazalidones.

**14.** The light-sensitive material of claim **1**, wherein said support contains at least an ultra-violet absorbing agent.

**15.** The light-sensitive material of claim **14**, wherein

the ultra-violet absorbing agent contains an aliphatic radical of from 4 to 30 carbon atoms.

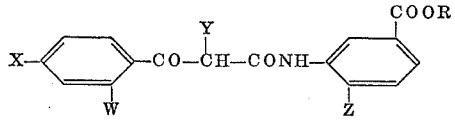
16. The light-sensitive material of claim 15, wherein said ultra-violet absorbing agent is a member of selected from the group consisting of 2-arylimino-3-alkyl-5-aryl-methylene thiazolidones, 2-arylimino-3-alkyl - 5 - hetero-methylene thiazolidones and 2-benz triazolyl - 4 - alkyl-phenols.

17. The light-sensitive material of claim 1 containing an α-[2-(lower alkoxy)-benzoyl]-aceto - 2' - chloro-5'-alkoxycarbonylanilide.

18. A light-sensitive material of claim 1, containing an α-[4-(lower alkoxy)-benzoyl]-aceto-2'-chloro - 5' - alkoxycarbonylanilide.

19. A light-sensitive material of claim 1, containing an α-[2,4-bis-(lower alkoxy)-benzoyl]-aceto - 2' - chloro-5'-alkoxycarbonylanilide.

20. A method for 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 incorporated therein, said coupler having the formula:




wherein R represents an aliphatic radical containing from 8 to 20 carbon atoms, W and X each represents a member selected from the group consisting of a hydrogen atom and a lower alkoxy group wherein at least one of W and X represents an alkoxy group, Y represents a member selected from the group consisting of a hydrogen atom and a halogen atom, and Z represents a halogen atom.

21. The method of claim 20, wherein said Y represents a hydrogen atom and said R represents a branched alkyl group.

22. The method of claim 21, wherein R is a member selected from the group consisting of 2-ethylhexyl and 2-hexyldecyl.

23. The method of claim 21, wherein said Z represents a chlorine atom.

24. The method of claim 21, wherein Z is a fluorine atom.

25. The method of claim 14, wherein said coupler is α-(4-methoxybenzoyl)-aceto-2'-chloro - 5' - (2'-hexyldecyloxycarbonyl)-anilide.

26. The method of claim 14, wherein said coupler is α-(4-ethoxybenzoyl)-aceto - 2' - chloro-5'-(2'-hexyldecyloxycarbonyl)-anilide.

27. The method of claim 14, wherein said coupler is α-(2-methoxybenzoyl)-aceto - 2' - chloro-5'-dodecyloxycarbonylanilide.

28. The method of claim 14, wherein said coupler is α-(2,4-dimethoxybenzoyl)-aceto-2'-chloro - 5' - (2'-hexyldecyloxycarbonyl)-anilide.

29. The method of claim 20, wherein an ultra-violet absorbing agent is present in the silver halide emulsion.

30. The method of claim 29, wherein the ultra-violet absorbing agent is a member selected from the group consisting of 2-arylimino-3-alkyl-5-aryl - methylene thiazalidones and 2-aryl-amino-3-alkyl-5-hetero methylene-thiazalidones.

31. The method of claim 21, wherein the aromatic pimay amino developing agent is an N,N-disubstituted-p-phenylenediamine and salts thereof.

32. The method of claim 31, wherein the N,N-disubstituted-p-phenylenediamine is a member selected from the group consisting of N,N-dimethyl-p-phenylene diamine, N,N-diethyl-p-phenylene diamine, N-ethyl-N(β-hydroxyethyl)-p-phenylene diamine, 4-amino-3-methyl-N,N - diethylaniline, 4-amino-3-ethyl-N-ethyl-N(β-hydroxyethyl)-aniline, 4-amino-3-ethyl-N-ethyl-N-(β - methonesulfonamidoethyl)-aniline, and 4-amino-3-(β - methanesulfonamidoethyl)-N,N-diethylaniline and salts thereof.

33. The method of claim 21, wherein the coupler is an α-[2-(lower alkoxy)-benzoyl] - aceto-2'-chloro-5'-alkoxycarbonyl-anilide.

34. The method of claim 21, wherein the coupler is an α-[4-(lower alkoxy)-benzoyl] - aceto-2'-chloro-5'-alkoxycarbonylanilide.

35. The method of claim 21, wherein the coupler is an α-[2,4-bis-(lower alkoxy)-benzoyl] - aceto-2'-chloro-5'-alkoxycarbonylanilide.

36. The developed product of claim 21.

37. The light-sensitive material of claim 1 wherein X is alkoxy and W is hydrogen.

38. The light-sensitive material of claim 1 wherein X is hydrogen and W is alkoxy.

39. The light-sensitive material of claim 1 wherein X and W are alkoxy.

40. The method of claim 20 wherein X is alkoxy and W is hydrogen.

41. The method of claim 20 wherein X is hydrogen and W is alkoxy.

42. The method of claim 20 wherein X and W are alkoxy.

43. The light-sensitive material of claim 1 wherein X and/or W is alkoxy, the alkoxy group has 1–4 carbon atoms.

44. The method of claim 20 wherein X and/or W is alkoxy, the alkoxy group has 1–4 carbon atoms.

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