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Sugizaki et al.

[11] **3,926,634**

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[54] **COLOR SILVER HALIDE PHOTOGRAPHIC MATERIALS CONTAINING COUPLERS HAVING AN OLEOPHILIC GROUP**

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[52] **U.S. Cl.** **96/100;** 96/55; 96/56.5; 96/74

[51] **Int. Cl.²** **G03C 1/40**

[58] **Field of Search** 96/100, 74

[56] **References Cited**

UNITED STATES PATENTS

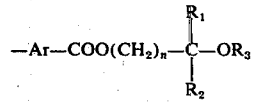
2,808,329	10/1957	Whitmore	96/100
3,551,155	12/1970	Yoshida et al.	96/100
3,658,545	4/1972	Iwama et al.	96/100
3,664,841	5/1972	Iwama et al.	96/100

Primary Examiner—J. Travis Brown

Attorney, Agent, or Firm—Sughrue, Rothwell, Mion, Zinn & Macpeak

[57] **ABSTRACT**

A color photographic material comprising a support having thereon a silver halide emulsion layer containing a coupler which can form a dye by the coupling reaction with the oxidation product of an aromatic primary amino developing agent and which contains a alkoxycarbonylarylene group represented by the formula



wherein R_1 and R_2 represent a hydrogen atom or an alkyl group, R_3 represents an aryl group, Ar represents an arylene group, and n represents an integer of from 1 to 7.

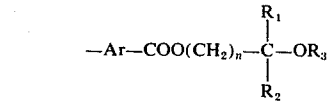
7 Claims, No Drawings

COLOR SILVER HALIDE PHOTOGRAPHIC MATERIALS CONTAINING COUPLERS HAVING AN OLEOPHILIC GROUP

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to color photographic materials. More particularly, the invention relates to a color photographic material having a silver halide emulsion layer containing a coupler having as an oleophilic group the alkoxycarbonylarylene group represented by the following general formula (I)



$$-Ar-COO(CH_2)_n-\underset{\displaystyle R_2}{\overset{\displaystyle R_1}{\overset{|}{\underset{|}{C}}}}-OR_3 \qquad (I)$$

wherein R_1 and R_2 represent a hydrogen atom or an alkyl group, R_3 represents aryl group, Ar represents an arylene group, and n represents an integer of from 1 to 7, the alkoxycarbonylarylene group having from 15 to 50 carbon atoms.

2. Description of the Prior Art

Many investigations have hitherto been made on oleophilic groups for facilitating the dissolution of couplers in organic solvents. For instance, various attempts of combining coupler molecules with alkoxycarbonylarylene groups have been reported since the initial proposal in U.S. Pat. No. 3,043,710. As the alkyl group of such an alkoxycarbonylarylene group, straight chain and branched chain alkyl groups are described. For instance, yellow dye-forming couplers having the aforesaid oleophilic group are described specifically in U.S. Pat. Nos. 3,409,439 and 3,551,155, magenta dye-forming couplers having such an oleophilic group are described in U.S. Pat. application Ser. No. 415,853, filed November 14, 1973, and cyan dye-forming couplers are described in French Pat. No. 1,534,600.

A coupler having the straight chain alkyl group-containing alkoxycarbonylarylene group has a melting point of from about 60°C to about 110°C and may be quite soluble in organic solvents at comparatively high temperatures but the solubility of such a coupler depends greatly on the temperature and the coupler is difficult to dissolve in organic solvents. On the other hand, a coupler having a branched chain alkyl group-containing alkoxycarbonylarylene group generally has a greatly improved solubility as compared to the straight chain alkyl type coupler due to the lower melting point and less temperature dependence of the solubility thereof. However, there is a difficulty in a coupler having a branched chain alkyl type alkoxycarbonylarylene group in that a branched chain alcohol which is a raw material used in producing the coupler is not readily available industrially in a pure form. Such a raw material is only available industrially as a mixture of branched chain alcohols having different numbers of carbon atom or a mixture of isomers of branched chain alcohol, each isomer having each different branching mode. It is not easy to purify the coupler prepared from such a mixture of alcohols or alcohol isomers using recrystallization, etc., and hence it is not advantageous from the standpoints of operation and cost to purify such a coupler as produced from such a raw material to an extent sufficient for use in photographic emulsions.

On the other hand, an attempt of improving the solubility of a coupler by introducing a substituent into the alkyl group of the alkoxycarbonyl group has been made. For instance, the introduction of an alkoxyl group is described in U.S. Pat. Nos. 3,409,439 and 3,551,155 and the introduction of an α-alkoxycarbonyl group is described in U.S. Pat. No. 3,664,841. By the introduction of the alkoxyl group as disclosed in the aforesaid patents, the melting point of the coupler can be greatly reduced, which results in improving remarkably the solubility of the coupler at low temperatures. However, the introduction of the alkoxyl group is accompanied by the disadvantages that the selectivity of the solvent is reduced and thus the purification of the coupler by recrystallization becomes quite difficult. The introduction of an α-alkoxycarbonyl group as disclosed in the above-described patent is accompanied by such a disadvantage that the process of preparing the coupler having such a group is complicated and by the introduction of the group, the melting point and the temperature dependence of the solubility of the coupler are slightly improved as compared with a coupler having a straight chain alkyl type alkoxycarbonylarylene group. That is to say, the improvement obtained by the introduction of an α-alkoxycarbonyl group is insufficient.

On the other hand, it is known that a silver halide emulsion layer containing a coupler having an alkoxycarbonylarylene group has the feature that is exhibits a high development speed, provides a high maximum density, and gives color images having good light absorption characteristics in color development. Also, it is known that a silver halide emulsion layer containing a coupler having an alkoxycarbonylarylene group, in particular a yellow dye-forming coupler of this type, has sufficiently high development speed and coupling density without the need for the use of a conventional high boiling solvent for coupler, such as dibutyl phthalate, tricresyl phosphate, etc.

Furthermore, it is known that when a yellow dye-forming coupler is exposed to formaldehyde vapor, its coupling density at color development generally tends to be reduced (for instance, when a color photographic material is stored in wooden furniture which has been subjected to mothproofing with formaldehyde is subjected to color development, a sufficient yellow density is not obtained), while a yellow dye-forming coupler having an alkoxycarbonylarylene group has a coupling density less reduced by formaldehyde vapor.

It is also known that a phenol type or naphthol type colored cyan coupler having at the coupling position an arylazo group having an alkoxycarbonyl group at the ortho-position to the azo group has good hue as a masking coupler.

However, a coupler having the straight chain alkyl-containing alkoxycarbonylarylene group and a coupler having the alkoxycarbonylarylene group which has an alkyl group substituted with an alkoxyl group or an α-alkoxycarbonyl group have a disadvantage, in addition to the above-described disadvantages in solubility and production difficulties, in that a photographic emulsion layer containing such a coupler has a low film strength. Also, such a coupler as described above has a low affinity for a high boiling solvent for a coupler and it sometimes happens that when a color photographic material having a silver halide emulsion layer containing such a coupler is placed under conditions in which the silver halide emulsions of the color photographic

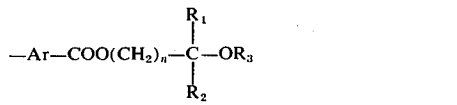
material are greatly deformed (for instance, the color photographic material is mechanically strained when the film is rolled up), the coupler diffuses from the silver halide emulsion to another silver halide emulsion to cause color mixing in the formation of color images on color development.

Examples of couplers having aryloxyalkylamide group are described in British Pat. No. 562,505, U.S. Pat. No. 2,589,004, U.S. Pat. No. 2,908,573, German Pat. No. 1,075,431,and U.S. Pat. No. 3,558,700 and additional examples of couplers having an aryloxyalkylacylamide group are described in German Pat. Offenlegungsschrift Nos. 2,039,970, U.S. Pat. No. 3,761,274, U.S. Pat. No. 2,908,573, and U.S. Pat. No. 3,652,286. Furthermore, examples of couplers having an aryloxyalkoxycarbonylamino group are described in U.S. Pat. No. 3,677,764. These couplers have less temperature dependence of the solubility in organic solvents as compared with a coupler having a straight chain-alkyl group-containing alkoxycarbonylarylene group and a coupler having an alkoxycarbonyl group which has an alkyl group substituted with an alkoxyl group or an α-alkoxycarbonyl group. Also, it is known that a silver halide emulsion layer containing such a coupler has a high film strength and there is less movement of the coupler in a silver halide emulsion layer containing such a coupler.

On the other hand, however, th excellent properties of a coupler having the alkoxycarbonylarylene group as described above cannot be obtained from a coupler having an aryloxyalkylamide group, an aryloxyalkylacylamide group, or an aryloxyalkoxycarbonylamino group.

SUMMARY OF THE INVENTION

As the results of various investigations on discovering couplers having the above-described excellent properties of an alkoxycarbonylarylene group but having less disadvantages as described above, the inventors have discovered that a coupler having an alkoxycarbonylarylene group represented by general formula I shown below;



(I)

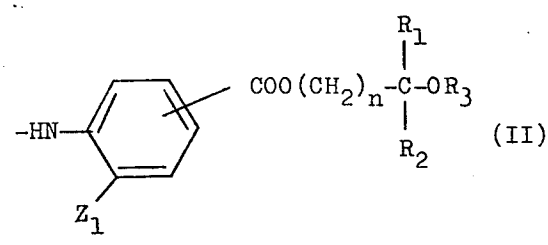
wherein R_1 and R_2 represents a hydrogen atom or an alkyl group, R_3 represents an aryl group, Ar represents an arylene group such as a divalent aromatic group, e.g., a phenylene group and a naphthylene group, and n is an integer of from 1 to 7, in which the aromatic ring Ar may have, further, as substituents at least one of an alkyl group, an alkoxyl group, an aryloxy group, an amino group, and a halogen atom has properties satisfying the above purposes and have succeeded in, based on this discovery, attaining the present invention.

That is to say, the present invention provides a color photographic material comprising a support having thereon at least one silver halide emulsion layer containing a coupler represented by general formula I.

DETAILED DESCRIPTION OF THE INVENTION

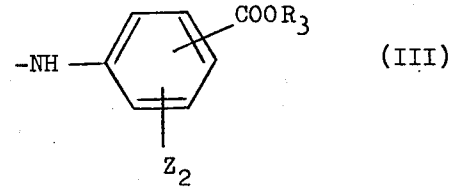
In greater detail R_1 and R_2 represent a hydrogen atom or an alkyl group, e.g., having 1 to 30 carbon atoms, for example an unsubstituted alkyl group such as a methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, t-butyl, sec-butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, stearyl, eicosyl, etc., group and a substituted alkyl group containing a substituent such as an alkoxy, alkenyl, aryl, aryloxy, halogen, amino, acylamino, acylureido, alkylthio, arylthio, hydroxy, cyano, etc. group, e.g., β-methoxyethyl, β-phenethyl, α-phenoxybutyl, 2,4-dichlorohexyl, benzyl, 7-hydroxyheptyl, β-cyanoethyl, oleyl, etc. Suitable examples of aryl groups for R_3 include an unsubstituted aryl groups such as a phenyl, naphthyl, anthryl, pyridyl, quinolyl, etc. substituted with one or more substituents such as alkyl, alkoxy, aryl, aryloxy, halogen, amino, acylamino, acylureido, alkylthio, arylthio, hydroxy, cyano, alkyloxycarbonyl, etc. groups, e.g. 2,4-di-tert-amylphenyl, 4-tert-amylphenyl, 4-methylphenyl, 3-n-pentadecylphenyl, 3-tert-butyl-4-hydroxyphenyl, 3-n-dodecyloxyphenyl, biphenyl, 2,4-dichlorophenyl, 4-methylaminophenyl, 2-acetylaminophenyl, 3-dodecylsulfonamidophenyl, 3-t-butyl-4-hydroxyphenyl, 2-ethoxycarbonylnapthyl, etc. Suitable examples of arylene groups for Ar are anthrylene, phenanthrenediyl, pyridinediyl, both unsubstituted and substituted with the hereinbefore described substituents. Suitable examples of these substituents are alkoxy such as methoxy, ethoxy, hydroxyethoxy, methoxyethoxy, hexyloxy, octyloxy, dodecyloxy, allyloxy, benxyloxy, etc. and aryloxy such as phenoxy, chlorophenoxy, tolyloxy, xylyloxy, ethyloxy, ethoxycarbonylphenoxy, N,N-dimethylaminophenoxy, naphthyloxy, biphenyloxy, phenoxyphenoxy. As described above R_3 and Ar are aromatic in nature and include carbocyclic aromatic groups and heterocyclic aromatic groups. The couplers according to the present invention are characterized by having at least one alkoxycarbonylarylene group represented by the general formula (I) which is connected to a photographic color coupler nucleus, such as a 5-pyrazolone coupler nucleus, a phenolic coupler nucleus, a naphtholic coupler nucleus and an open-chained ketomethylene coupler nucleus.

Particularly referred embodiments of the alkoxycarbonylarylene group represented by the general formula (I) are alkoxycarbonyarylene groups represented by the general formula (II)



(II)

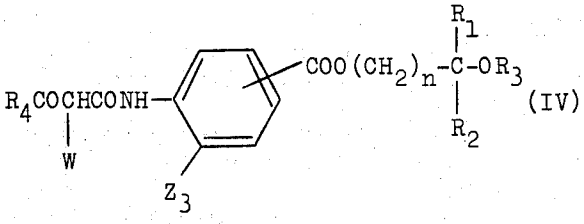
wherein R_1, R_2, and R_3 are as previously defined with respect to the general formula (I) and Z_1 represents a hydrogen atom, a halogen atom, an alkyl residue, an alkoxyl residue, an aryloxy residue, or an amino residue; or an alkoxycarbonylarylene group represented by the general formula (III)



(III)

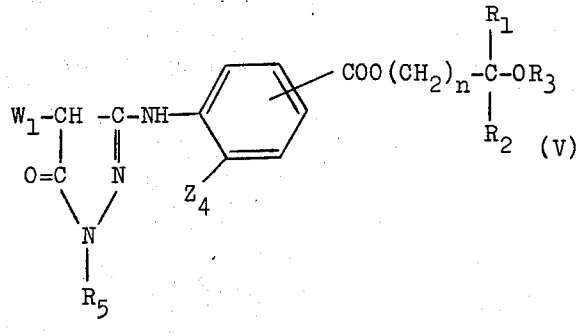
wherein R_3 is as previously defined with respect to the general formula (I) and Z_2 represents a hydrogen atom, a halogen atom, an alkyl residue, an alkoxyl residue, an aryloxy residue, an aryloxy residue, an amino residue, a sulfamoyl residue, or an acylamino residue.

Examples of couplers containing the alkoxycarbonylarylene group represented by the general formula (I) are couplers having the general formula (IV) to (VI), i.e., yellow dye-forming couplers of the general formula (IV)



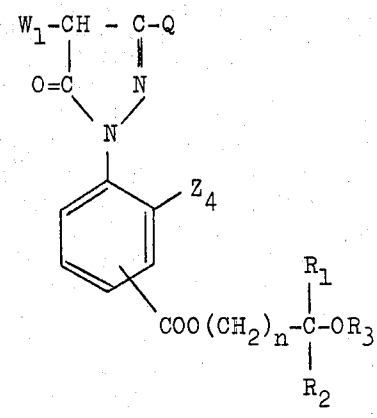
(IV)

wherein R_1, R_2, R_3 and n have the same meaning as described with respect to the general formula (I), R_4 represents an aliphatic residue, an aromatic residue or a heterocyclic residue, W represents a hydrogen atom or a residue capable of being released by the oxidative coupling with the oxidation product of an aromatic primary amino developing agent, and Z_3 represents a hydrogen atom, an alkyl residue, an alkoxyl residue, an aryloxy residue, an amino residue, or a halogen atom, with the alkoxycarbonyl group being at the 4- or 5-position of the anilide ring; magenta dye-forming couplers of the general formula (V)

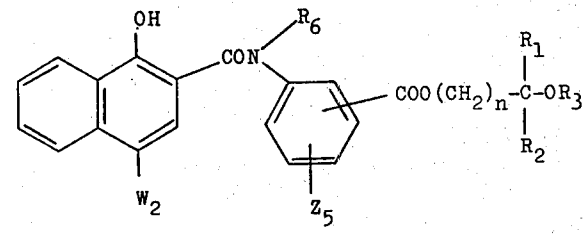


(V)

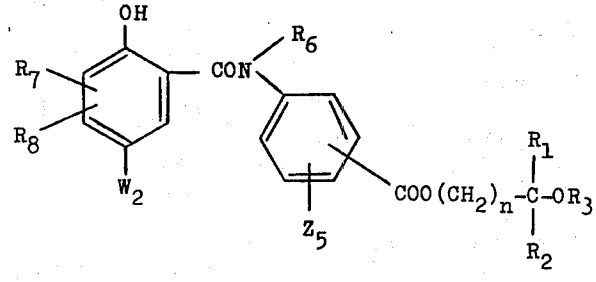
wherein R_1, R_2, R_3 and n have the same meaning as described with respect to the general formula (I), R_5 represents an aromatic residue or a heterocyclic residue, W_1 represents a hydrogen atom or a residue capable of being released by the oxidative coupling with the oxidation product of an aromatic primary amino developing agent, Z_4 represents a hydrogen atom, an alkyl residue, an alkoxyl residue, an aryloxy residue, or a halogen atom, with the alkoxycarbonyl group being at the 4- or 5- position of the anilino ring; and magenta dye-forming couplers of the general formula (Va)



wherein R_1, R_2, R_3, W_1, Z_4 and n have the same meaning as described with respect to the general formula (V), Q represents an alkyl residue, an alkoxy residue, a N-alkyl amino residue, an anilino residue or an acylamino residue, and cyan dye-forming couplers of the general formula (VI)



wherein R_1, R_2, R_3 and n have the same meaning as described with respect to the general formula (I), R_6 represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, W_2 represents a hydrogen atom or a residue capable of being released by the oxidative coupling with the oxidation product of an aromatic primary amino developing agent, Z_5 represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxyl group, an aryl group, an aryloxy group, an amino group, or an acylamino group; and cyan dye-forming couplers of the general formula (VIa)



wherein R_1, R_2, R_3, R_6, W_2, Z_5 and n have the same meaning as described with respect to the general formula (VI), R_7 and R_8 each represents a hydrogen atom, a halogen atom, an alkyl group and an alkoxy group.

Suitable examples of alkyl residues for Z_1 to Z_5 in the above described formulas (II) to (VI) are alkyl groups such as methyl, ethyl, n-propyl, iso-propyl, n-butyl,

t-butyl, sec-butyl, amyl, dodecyl, benzyl, groups, etc., alkoxy groups such as methoxy, ethoxy, propoxy, butoxy, dodecyloxy, pentadecyloxy groups, etc., aryloxy groups such as phenoxy, 4-t-butylphenoxy, 2,5-dichlorophenoxy groups, etc., amino groups such as dibutylamino, methylamino, dibenzyl amino groups etc. For R_4 suitable examples of aliphatic residues are t-butyl, α',α'-dimethylpropyl, 2-phenoxypropyl groups, etc., of aromatic residues are phenyl, 3-methylphenyl, 3-octadecylphenyl, 2-methoxyphenyl, 4-methoxyphenyl, 2-chloro-5{α-(2,4-di-t-amylphenoxy) butylamido}phenyl, 2-chloro-5-dodecylsulfonamidophenyl groups, etc. and of heterocyclic residues are furyl groups, etc. For R_5 illustrative groups for the aromatic residue are 2,4,6-trichlorophenyl, 2-chloro-4,6-dimethylphenyl, 2,6-dichloro-4-methoxyphenyl, phenyl, 4-methylphenyl, 4-acylaminophenyl groups, etc., and for the heterocyclic residue are benzofuranyl, napthoxazolyl, quinolyl groups, etc. Suitable alkyl groups having 1 to 5 carbon atoms for R_6 include alkyl groups such as methyl, ethyl, n-butyl, n-amyl, β-cyanoethyl groups, etc. Illustrative sulfamoyl groups for Z_2 in general formula (III) are sulfamoyl, N-methylsulfamoyl, N,N-diethylsulfamoyl, N-phenylsulfamoyl groups, etc., illustrative aryl groups for Z_5 in general formula (VI) are phenyl, tolyl, chlorophenyl, methoxyphenyl groups, etc. and suitable acylamino groups for Z_2 in general formula (II) and for Z_5 in general formula (VI) are acetylamino, butoxycarbonylamino, benzoylamino groups, etc.

For W, W_1, W_2 in the above general formulas (IV) to (VI) are halogen atoms (F, Cl, Br, I), aryloxy groups (e.g., phenoxy, 4-chlorophenoxy, 4-carbophenoxy, 4-(4-hydroxy phenylsulfonyl) phenoxy), acyloxy groups (acetoxy, benzoxy), alkylthio groups (ethylthio, dodecylthio), arylthio groups (phenylthio, 2-carbophenylthio), imido groups (phthalimido, oxazoldinylimido), azo groups (phenylazo, 2-ethoxycarbonylnaphthylazo, 3-methoxyphenylazo), etc..

Couplers which can be used containing the group of the general formula (I) in this invention are specifically illustrated below but the couplers of this invention are intended to be limited to these couplers specifically and include any other couplers containing the group represented by general formula I:

1. 5'-[β-(2,4-Di-tert-amylphenoxy)ethoxycarbonyl]-(2'-chloro)benzoylacetanilide,
2. 5'-[β-(2,4-Di-tert-amylphenoxy)ethoxycarbonyl]-(2'-methoxy)2-methylbenzoylacetanilide,
3. 5'-[β-(2,4-Di-tert-amylphenoxy)ethoxycarbonyl]-(2'-chloro)2-methylbenzoylacetanilide,
4. 5'-[β-(2,4-Di-tert-amylphenoxy)ethoxycarbonyl]-(2'-methoxyl)benzoylacetanilide,
5. 5'-[γ-(2,4-Di-tert-amylphenoxy)propoxycarbonyl]-2'-chloro-2-methylbenzoylacetanilide,
6. 5'-[-(4-tert-Amylphenoxy)octyloxycarbonyl]-(2'-chloro)-4-methoxybenzoylacetanilide,
7. 2'-Chloro-5'-[β-(4-methylphenoxy)tetradecyloxycarbonyl]-benzoylacetanilide,
8. 5'-[β-(2,4-Di-tert-amylphenoxy)-butoxycarbonyl]-2'-chloro-2-methylbenzoylacetanilide,
9. 5'-[β-(2,4-Di-tert-amylphenoxy)-butoxycarbonyl]-(2'-chloro)benzoylacetanilide,
10. 2'-Chloro-5'-[β-(3-n-pentadecylphenoxy)-ethoxycarbonyl]-2-methylbenzoylacetanilide,
11. 5'-[β-(3-tert-Butyl-4-hydroxyphenoxy)-tetradecyloxycarbonyl]-2'-chloro-4-methoxybenzoylacetanilide,
12. 2'-Methoxy-5'-{[β-methyl-β-(3-m-pentadecylphenoxyl]-propoxycarbonyl}-benzoylacetanilide,
13. 5-[β-(2,4-Di-tert-amylphenoxy)ethoxycarbonyl]-2-chloro-α-pivaloylacetanilide,
14. 4-[β-(2,4-Di-tert-amylphenoxy)butoxycarbonyl]-2-chloro-α-pivaloylacetanilide,
15. 5'-[β-(2,4-Di-tert-amylphenoxy)ethoxycarbonyl]-2'-chloro-α-(5,5-dimethyl-3-hydantoinyl)-α-(4-methoxybenzoyl)-acetanilide,
16. 5'-β-(2,4-Di-tert-amylphenoxy)ethoxycarbonyl-2'-methoxy-α-phthalimido-α-(2-methylbenzoyl-)acetanilide,
17. 5'-β-(2,4-Di-tert-amylphenoxyl)ethoxycarbonyl-2'-methoxy-α-(5,5-dimethyl-3-hydantoinlyl)-α-(2-methylbenzoyl)-acetanilide,
18. 5'-[β-(2,4-Di-tert-amylphenoxy)butoxycarbonyl]-2'-chloro-α-succinimido-α-(2,4-Dimethoxybenzoyl)-acetanilide,
19. 5-[β-(2,4-Di-tert-amylphenoxy)propoxycarbonyl]-2-chloro-α-(4-chlorophenoxy)-α-pivaloylacetanilide,
20. 5-[β-(2,4-Di-tert-amylphenoxy)ethoxycarbonyl]-2-chloro-α-(5,5-dimethyl-3-hydantoinyl)-α-pivaloylacetanilide,
21. 5'-[β-(2,4-Di-tert-amylphenoxy)-ethoxycarbonyl]-2'-chloro-α-phthalimido-α-(2-methylbenzoyl-)acetanilide,
22. 5'-[β-(2,4-Di-tert-amylphenoxy)ethoxycarbonyl]-2'-chloro-α-(5,5-dimethyl-3-hydantoinyl)-α-(2-methylbenzoyl)-acetanilide,
23. 5'-[β-(2,4-Di-tert-amylphenoxy)ethoxycarbonyl]-2'-chloro-4-methoxybenzoylacetanilide,
24. 1-(2,4,6-Trichlorophenyl)-3-{2-chloro-5-[β-(2,4-di-tert-amylphenoxy)ethoxycarbonyl]anilino}-2-pyrazole-5-on,
25. 1-(2,4,6-Trichlorphenyl)-3-{2-chloro-5-[β-2,4-di-tert-amylphenoxy)butoxycarbonyl]anilino}-2-pyrazole-5-on,
26. 1-(2,4,6-Trichlorophenyl)-3-{2-chloro-5-[β-(3-tert-butyl-4-hydroxyphenoxy)tetradecyloxycarbonyl]-anilino}-2-pyrazole-5-on,
27. 1-(2,4,6-Trichlorophenyl)-3-{2-methoxy-5-[β-(3-n-pentadecylphenoxy)butoxycarbonyl]anilino}-2-pyrazole-5-on,
28. 1-(2,6-Di-chloro-4-methoxyphenyl)-3-{2-chloro-5-[β-(2,4-di-tert-amylphenoxy)butoxycarbonyl-]anilino}-4-(4-methoxyphenyl)azo-2-pyrazole-5-on,
29. 1-(2,46-Dichloro-4-methoxyphenyl)-3-[N'-{3-[β-(2,4-di-tert-amylphenoxy)butoxycarbonyl]-phenylureido}]-2-pyrazole-5-on,
30. 1-(2,4-Dichloro-6-methylphenyl)-3-{3-[β-(3-n-dodecyloxyphenoxy)ethoxycarbonyl]benzamido}-2-pyrazole-5-on,
31. 1-Hydroxy-2-5'-[β-(2,4-di-tert-amylphenoxy)-ethoxycarbonyl] -2'-chloro -naphthanilide,
32. 1-Hydroxy-4-chloro-2-{3-[β-(2,4-di-tert-amylphenoxy)butoxycarbonyl]-N-ethyl}-naphthanilide,
33. 1-hydroxy-4-{2-[β-(2,4-di-tert-amylphenoxy)-ethoxycarbonyl]phenyl}-azo-2-[N-(1-naphthyl)]-naphthamide,
34. 1-Hydroxy-4-chloro-2-{5'-[β-(2,4-di-tert-amylphenoxy)ethoxycarbonyl]-2'-chloro}-naphthanilide,
35. 5-[β-(2,4-Di-tert-amylphenoxy)-ethoxycarbonyl]-2-chloro-α-(5,5-dimethyl-2,4-dioxo-3-oxazolidinyl)pivaloylacetanilide,
36. 5'-[β-(2,4-Di-tert-amylphenoxy)ethoxycarbonyl]-2'-chloro-(5,5-dimethyl-2,4-dioxo-3-oxazolidinyl)-α-(2-methylbenzoyl)acetanilide.

The production of several couplers having groups represented by general formula I are illustrated by the following examples. Unless otherwise indicated, all parts, percents, ratios and the like are by weight.

EXAMPLE 1

Preparation of 5'-[β-(2,4-Di-tert-amylphenoxy)Ethoxycarbonyl]-'2'-chloro)benzoylacetanilide (Coupler 1):

(1-a): Preparation of β-(2,4-di-tert-amylphenoxy)-ethanol:

2,4-Di-tert-amylphenoxy acetic acid chloride was dissolved in anhydrous diethyl ether and then the reaction was conducted using lithium aluminum hydride as a reducing agent. After adding acetic acid to the reaction system to stop the reaction, the reaction product was poured into water and then the organic layer formed was extracted with ethyl acetate. After distilling off the ethyl acetate from the mixture, under reduced pressure the high boiling residue thus formed was further distilled under reduced pressure, whereby the desired product was obtained. The boiling point thereof was 128°–130°C/1.5 mm Hg.

(1-b): Preparation of 5-[β-(2,4-di-tert-amylphenoxy)-ethoxycarbonyl]-2-chloroaniline:

A mixture of methyl-3-amino-4-chlorobenzoate (93 g) and 2,4-di-tert-amylphenoxy ethanol (183 g) was heated to 130°–140°C using tetrabutyl titanate as an ester exchange catalyst.

After the reaction was completed, n-hexane was added to the reaction system and the crystals thus precipitated were recovered by filtration. By recrystallizing the crystals using n-hexane, the desired product was obtained. The amount thereof was 155 g and the melting point was 85.5°–86.5°C.

(1-c): Preparation of 5'-[β-(2,4-di-tert-amylphenoxy)-ethoxycarbonyl]-(2'-chloro)benzoylacetanilide:

A mixture of ethylbenzoyl acetate (23 g) and 5-[β-(2,4-di-tert-amylphenoxy)ethoxycarbonyl]-2-chloroaniline (43 g) was heated to about 120°–130°c for about 3 hours at reduced pressure. Then, methanol was added to the reaction system and the crystals precipitated were recovered by filtration. By recrystallizing the crystals thus recovered using ethanol, the desired product (coupler) was obtained. The amount thereof was 48 g and the melting point was 121°–122°C.

EXAMPLES 2

Preparation of 5'-[β-(2,4-Di-tert-amylphenoxy)ethoxycarbonyl]-(2'-chloro)-2-methylbenzoylacetanilide (Coupler 3):

The same procedure as described in Example 1 (1-c) was conducted except that ethyl-2-methylbenzoyl acetate (25 g) was used instead of ethylbenzoyl acetate. By recrystallizing the crystals thus recovered using n-hexane, the desired product (Coupler 3) was obtained. The amount of the coupler was 41 g and the melting point was 80.5°–81.0°C.

EXAMPLE 3

Preparation of 5'-[β-(2,4-Di-tert-amylphenoxy)-butoxycarbonyl]-(2'-chloro)benzoylacetanilide (Coupler 9):

(3-a): Preparation of β-2,4-di-tert-amylphenoxyl butanol:

By reducing β-2,4-di-tert-amylphenoxy butyric acid chloride with lithium aluminum hydride in anhydrous diethyl ether as described in Example 1 (1-a), the desired product was obtained. The melting point of the product was 125°–126°C/0.5 mm Hg and the yield thereof was 77 percent.

(3-b): Preparation of 5-[β-(2,4-di-tert-amylphenoxy)-butoxycarbonyl]-2-chloroaniline:

The same procedure as described in Example 1 (1-b) was conducted except that the β-2,4-di-tert-amylphenoxyl butanol (159 g) prepared in (3-a) was used instead of 2,4-di-tert-amylphenoxy ethanol. By recrystallizing the crystals recovered using n-hexane, the desired product was obtained. The amount thereof was 116 g and the melting point was 88°–89°C.

(3-c): Preparation of 5'-[β-(2,4-di-tert-amylphenoxy)-butoxycarbonyl]-(2'-chloro)benzoylacetanilide:

The same procedure as described in Example 1 (1-c) was conducted except that the 5-[β-(2,4-di-tert-amylphenoxy)-butoxycarbonyl]-2-chloroaniline (44 g) prepared in (3-b) was used instead of 5-[β-(2,4-di-tert-amylphenoxy)ethoxycarbonyl]-2-chloroaniline. Then, by recrystallizing the crystals thus recovered using ethanol, the desired product (Coupler 9) was obtained, the amount thereof 40 g and the melting point was 132°–133°C.

EXAMPLE 4

Preparation of 5'-[β-(2,4-Di-tert-amylphenoxy)-butoxycarbonyl]-2'-chloro-2-methylbenzoylacetanilide: (Coupler 8):

The same procedure as described in Example 3(3-c) was conducted using ethyl-3-methylbenzoyl acetate (25 g) instead of ethylbenzoyl acetate and by recrystallizing the crystals thus recovered using methanol, the desired coupler was contained. The amount thereof was 39 g and the melting point was 110°–110.5°C.

EXAMPLE 5

Preparation of 5'-[β-(2,4-Di-tert-amylphenoxy)ethoxy carbonyl]2'-chloro-α-phthalimide-α-(2-methylbenzoyl)acetanilide (Coupler 21):

(5-a): Preparation of 5'-[β-(2,4-di-tert-amylphenoxy)-ethoxycarbonyl]-2'-chlor-α-bromo-benzoylacetanilide:

5'-[β-(2,4-Di-tert-amylphenoxy)ethoxycarbonyl]-2'-chloro-α-(2-methylbenzoyl)acetanilide (59 g) was dissolved in chloroform (300 ml) and then bromine (16 g) was added dropwise to the solution under ice cooling. After distilling off of the chloroform, the residue formed was crystallized using methanol, whereby the desired product was obtained. The amount of the product was 44 g and the melting point was 94°–95°C.

(5-b): Preparation of 5'-[β-(2,4-di-tert-amylphenoxy)-ethoxycarbonyl]-2'-chloro-α-phthalimido-α-(2-methylbenzoyl)-acetanilide (Coupler 21):

5'-[β-(2,4-Di-tert-amylphenoxy)ethyloxycarbonyl]-2'-chloro-α-bromo-α-(2-methylbenzoyl)acetanilide (67 g) and potassium phthalimide (50 g) were stirred in dimethylformamide (500 ml) for about 5 hours at 23°C. Thereafter, water was added to the reaction product and the organic layer formed was extracted with ethyl acetate. The ethyl acetate solution layer was washed with a 5 percent aqueous hydrochloric acid solution and then with water, and dried. After distilling off the ethyl acetate under reduced pressure from the reaction product, the residue was recrystallized from a mixture (1:1 by volume) of ethyl acetate and n-hexane to provide the desired coupler. The amount of the coupler was 55 g and the melting point was

177.5°–179°C.

EXAMPLE 6

Preparation of 5'-[β-(2,4-Di-tert-amylphenoxy)ethoxycarbonyl-]-2'-chloro-α-(5,5-dimethyl-3-hydantoinyl)-α-(2-methylbenzoyl)acetanilide (Coupler 22):

5'-[β-(2,4-Di-tert-amylphenoxy)ethoxycarbonyl]-2'-chloro-α-bromo-α-(2-methylbenzoyl)acetanilide (67 g) was dissolved in dimethylformamide (500 ml). 5,5-dimethylhydantoin (40 g) and potassium hydroxide (16 g) were dissolved in methanol (40 ml) and the solution was added to the solution prepared above. The mixture was stirred for about 4 hours.

By treating the reaction product as described in Example 5 (5-b), the desired coupler was obtained. The amount thereof was 52 g and the melting point was 167°–167.5°C.

EXAMPLE 7

Preparation of 1-(2,4,6-Trichlorophenyl)-3-{2-chloro-5-[β-(2,4-di-tert-amylphenoxy)ethoxycarbonyl]anilino}-2-pyrazole-5-on (Coupler 20):

(7-a): Preparation of 1-(2,4,6-trichlorophenyl)-3-(2-chloro-5-methoxycarbonylanilino)-2-pyrazole-5-on:

A mixture of β,β-diethoxyacrylic acid ethyl ester (52 g) prepared as described in S. A. Glickman et al, Journal of Americal Chemical Society, 67, 1017(1945) and 2-chloro-5-methoxycarbonylaniline (55 g) was stirred for about 5 hours at 130°–140°C to provide β-ethoxy-β-(2-chloro-5-methoxycarbonylanilino)acrylic acid ethyl ester. Without isolating the ester, the reaction product was mixed with 2,4,6-trichlorophenylhydrazine (60 g) and glacial acetic acid (400 ml) and then the mixture was refluxed under heating for 2 hours.

After allowing the reaction product to cool, methanol (400 ml) was added to the product and the mixture was allowed to stand, whereby the desired product (98 g) was obtained.

(7-b): Preparation of 1-(2,4,6-trichlorophenyl)-3-{2-chloro-5-[β-(2,4-di-tert-amylphenoxy)ethoxycarbonyl]anilino}-2-pyrazole-5-on:

The 1-(2,4,6-trichlorophenyl)-3-(2-chloro-5-methoxycarbonyl-anilino-2-pyrazole-5-on (44.7 g) prepared in (7-a) above-described was caused to react with β-2,4-di-tert-amylphenoxy ethanol (33.4g) prepared using tetrabutyl titanate (3.0 g) as an ester exchange catalyst using the method described in U.S. Pat. No. 3,409,439. By recrystallizing the reaction product from ethanol, 21.8g of the colorless crystals of the desired coupler was obtained. The melting point thereof was 180°–183°C.

EXAMPLE 8

Preparation of 1-Hydroxy-2-{5-[β-(2,4-di-tert-amylphenoxy)ethoxycarbonyl]-2-chloro}-naphthanilide (Coupler 31):

1-Hydroxy-2-anphthoic acid phenyl ester (20 g) was caused to react with 3-amino-1-[β-(2,4-di-tert-amylphenoxy)-ethoxycarbonyl]-4-chlorobenzene (32 g) for about 1 hour at 150°–160°C. Then, while maintaining the reaction system at reduced pressure at the same temperature and distilling off the phenol formed from the reaction system, the reaction was further continued for about 2 hours. Then, by recrystallizing the reaction product from ethyl acetate, the desired product was obtained. The amount thereof was 35 g and the melting point was 167°–168°C.

EXAMPLE 9

Preparation of 5'-[β-(2,4-Di-tert-amylphenoxy)ethoxycarbonyl]-2'-chloro-α-(5,5-dimethyl-2,4-dioxo-3-oxazolinyl)-α-(2-methylbenzoyl)acetanilide (Coupler 36):

The same procedure as described in Example 6 was conducted for about 2 hours using 5,5-dimethyl-2,4-oxazolidinedione (40 g) instead of 5,5-dimethylhydantoin. By treating the reaction product as described in Example 5 (5-b), the desired coupler was obtained. The amount thereof was 54 g and the melting point was 150°–151°C.

The above-described excellent properties of a coupler having an alkoxycarbonylarylene group, such as the excellent color development characteristics, good color image hue, and high resistance to formaldehyde are the general properties of the alkoxycarbonylarylene group and such excellent properties are not lost by the introduction of the alkoxyl group thereto.

Also, the excellent properties of a coupler having an aryloxyalkylamide group or an aryloxyalkylacrylamide group, such as the solubility, film strength, and reduced mobility in the silver halide emulsion layer are not the characteristics of an amide group or an acylamide group but are the characteristics of an aryloxyalkyl group.

It is clear as shown by Hildebrand's Regular Solution Theory that the important factors on the solubility of a solid material in a solvent are the melting point of the solid, the fusion enthalpy of the solid, and the solution enthalpy of the solid in the solvent. Of these factors the fusion enthalpy and the solution enthalpy relate to the temperature dependence of the solubility and since one or both of these enthalpies are lower, the temperature dependence is reduced. The solubility of a solid in a solvent at a definite temperature becomes higher as the melting point of the solid is lower and the temperature dependence of the solubility is lower.

In general, a coupler having a straight chain alkyl group has a high fusion enthalpy and solution enthalpy and hence a high temperature dependence of solubility is shown. Therefore, a coupler having a straight chain alkyl group must have a low melting point if it is to have sufficient solubility. On the other hand, a coupler having an aryloxyalkyl group has a comparatively high melting point but has a high solubility. Also, even when a coupler having a straight chain alkyl group has a same solubility as the coupler having an aryloxyalkyl group at a certain temperature (for instance at the temperature of dissolving the coupler), a coupler having a straight chain alkyl group shows a low solubility at low temperatures due to the high temperature dependence of solubility and hence tends to be precipitated at low temperatures as compared with a coupler having an aryloxyalkyl group.

Furthermore, a solution of a coupler having an aryloxyalkyl group in a high boiling oil or dispersion has a higher viscosity than that of a solution of the coupler having a straight chain alkyl group of the same concentration as above, which results in reducing the mobility of the coupler in the emulsion layer.

Since the coupler of this invention having an aryloxyalkoxycarbonylarylene group has less tendency to precipitate as compared with a coupler having a straight chain alkoxycarbonyl group, the property of the coupler having an alkoxycarbonylarylene group in which the reduction in the color development charac-

teristics is less when the amount of the high boiling oil for dispersion is reduced is more enhanced in the coupler of this invention.

Also, a coupler having an alkoxycarbonylarylene group substituted with an α-alkoxycarbonyl group as described in U.S. Pat. No. 3,664,841 is positioned between a coupler having a straight chain alkoxycarbonyl group and a coupler having an aryloxycarbonylarylene group in solution characteristics but is, in fact, near the coupler having a straight chain alkoxycarbonyl arylene group and hence the improvement in the coupler in this respect is small as described above.

The coupler of this invention can be added to a photographic hydrophilic colloid using any known technique. For instance, the coupler can be dissolved in a high boiling solvent (e.g., above 200°C) such as dibutyl phthalate, tricresyl phosphate, and trihexyl phosphate as described in, e.g., U.S. Pat. No. 2,322,027 using, if desired, a subsidiary solvent such as ethyl acetate, tetrahydrofuran, acetophenone, isopropyl acetate, ethyl propionate, β-ethoxyethyl acetate, n-butylcarbitol acetate, etc., as described in U.S. Pat. Nos. 3,253,921 and 3,574,627 and then the solution is dispersed in a hydrophilic colloid. A suitable coupler amount in the solvent ranges from about 0.01 to 100 percent by weight.

Also, a coupler solution can be prepared using only the aforesaid subsidiary solvent without using the high boiling solvent and the solution can be dispersed in a hydrophilic colloid.

The coupler dispersion prepared in the manner as illustrated above is mixed with a silver halide emulsion such as a silver bromide emulsion, a silver iodobromide emulsion, a silver chloroiodobromide emulsion, a silver chloride emulsion, and a silver chlorobromide emulsion or a silver halide emulsion of the socalled conversion halide type as described in, e.g., U.S. Pat. Nos. 2,592,250 and 3,622,318 and British Pat. No. 635,841 and then the mixture is applied to a support together with, if desired, a hydrophilic colloid can be added to the mixture before coating.

The dispersion of at least one coupler of this invention in a hydrophilic colloid containing, if desired, at least one known coupler which is not included within the scope of the couplers of this invention can constitute at least one photographic emulsion layer of a multilayer silver halide color photographic material comprising a support having thereon a blue-sensitive silver halide emulsion layer containing a yellow dye-forming coupler, a green-sensitive emulsion layer containing a magenta dye-forming coupler, and a red-sensitive emulsion layer containing a cyan dye-forming coupler. As the silver halide emulsions for the multilayer type color photographic material, the aforesaid silver halide emulsions can be appropriately used. Examples of these multilayer materials are disclosed in U.S. Pat. Nos. 3,582,322; 3,622,318; 3,547,640; 3,672,898; 3,516,831; 3,705,799~3,715,208; 3,737,312; 3,703,375; 3,379,529; 3,402,046; 3,620,747; and 3,450,536; British Pat. No. 923,045; U.S. Pat. applications Ser. No. 206,060 filed Dec. 8, 1971 and Ser. No. 29,666, filed Apr. 17, 1970.

As the support for the silver halide emulsion containing the coupler of this invention, there are a cellulose ester film such as cellulose nitrate film, a cellulose acetate film, etc.; a polyester film such as a polyethylene terephthalate film, etc., a polyvinyl chloride film, a polystyrene film, a polycarbonate film, a paper, a so-called baryta-coated paper prepared by coating barium sulfate on a paper support, a laminate film prepared by coating a cellulose ester, a polyester, a polyvinyl chloride, a polystyrene, or a polycarbonate on a paper or a baryta-coated paper, and a synthetic paper.

Also, examples of the hydrophilic colloid which can be used for the coupler dispersion and the silver halide photographic emulsion are gelatin; a gelatin derivative such as acylated gelatin, graft gelatin, etc.; albumin, gum arabic; agar agar; a cellulose derivative such as acetyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose, etc.; and a synthetic resin such as polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylamide, etc.

The dispersion of the coupler in the aforesaid hydrophilic colloid or a mixture of the dispersion of the coupler and a silver halide emulsion can be subjected to a reduced pressure treatment or washed with water as described in U.S. Pat. Nos. 2,949,360 and 3,396,027 prior to coating as emulsion layers of the color photographic material for removing the subsidiary solvent used for dispersing the coupler.

Furthermore, in the case of dissolving the coupler in a solvent before the coupler solution is dispersed in a hydrophilic colloid, the dissolution of the coupler can be promoted if desired, using heat or ultrasonic waves.

The aforesaid multilayer color photographic material of this invention having at least one silver halide emulsion layer containing the coupler of this invention can have, in addition to the above-described silver halide emulsion layers, other layers conventionally employed for constituting the color photographic material, such as, for instance, a protective layer, a filter layer, an intermediate layer, an anti-halation layer, a subbing layer, a backing layer, a layer containing an ultraviolet absorber, etc. Also, as the binders for these layers, the hydrophilic colloid used for the silver halide emulsion layers can be employed.

Each layer of the color photographic material of this invention can further contain a hardening agent for the hydrophilic colloid. Typical examples of such hardening agents are aldehyde type compounds such as formaldehyde, glyoxal, succinaldehyde, glutaraldehyde, 2,3-dihydroxy-1,4-dioxane, mucohloric acid, dimethylolurea, etc.; active vinylic compounds such as divinylsulfone, methylene bismaleimide, 5-acetyl-1,3-diacryloyl-1,3,5-hexahydrotriazine, N,N′, N′-triacryloyl-1,3,5-hexahydrotriazine, etc.; active halogen compounds such as 2,4-dichloro-6-oxytriazine sodium salt, 2,4-dichloro-6-methoxytriazine, sebacic acid bis-chloromethyl ester, N,N′-bis(α-chloroethylcarbamyl)-piperazine, etc.; epoxy compounds such as bis(2,3-epoxypropyl)methylpropyl ammonium para-toluene sulfonate, 1,4-bis(2′, 3′-epoxypropyloxy)butane, 1,3-diglycidyl-5-(γ-acetoxy-β-oxypropyl)isocyanurate, etc.; ethyleneiminic compounds such as 2,4,6-triethyleneimino-1,3,5-trazine, bis-β-ethylene-iminoethyl thioether, etc.; and methane sulfonate compounds such as 1,2-di(methanesulfonyloxy)ethane, 1,4-di(methanesulfonyloxy)butane, 1,5-di(methanesulfonyloxy)-pentane, etc., as described in U.S. Pat. Nos. 3,232,764, 3,288,775, 2,732,303, 3,635,718, 3,232,763, 2,732,316, 2,586,168, 3,103,437, 3,017,280, 2,783,611, 2,725,294, 2,725,295, 3,100,704, 2,091,537, 3,321,313, etc.

The silver halide emulsion containing the coupler of this invention can be chemically sensitized using active gelatin or a sulfur compound as described in U.S. Pat. Nos. 1,574,944, 1,623,499, 2,410,689, etc. Also, the emulsion can be sensitized using a salt of a noble metal

such as palladium, gold, ruthenium, rhodium platinum, etc., as described in U.S. Pat. Nos. 2,448,060, 2,399,083, 2,642,361, etc. Furthermore, the silver halide emulsion can be sensitized using a reducing agent such as a stannous salt, as described in U.S. Pat. No. 2,487,850, and also can be sensitized using a polyalkylene oxide derivative. Moreover, the silver halide emulsion can be spectrally sensitized with a cyanine dye or a merocyanine dye, as disclosed in U.S. Pat. Nos. 2,519,001, 2,666,761, 2,734,900, 2,739,964, 3,481,742, etc.

The silver halide emulsion containing the coupler of this invention can further contain a stabilizer such as a mercury compound, an azaindene, etc., as described in U.S. Pat. Nos. 2,886,437, 2,444,605, 2,403,927, 3,266,877, 3,397,987, etc., a plasticizer such as glycerine as described in C. E. K. Mees and T. H. James The Theory of Photographic Process pages 53–54, The Macmillan Co. New York. (1966), and U.S. Pat. Nos. 2,904,434, 2,940,854, etc., and a coating aid such as saponin, polyethylene glycol monolauryl ether, etc. as described in U.S. Pat. Nos. 3,415,649, 3,441,413, 3,502,473, 3,514,293, 3,506,449, 3,539,352, 3,545,974, 3,507,660, 3,442,654, 3,475,174, 3,462,520, 3,493,379, 3,516,833, 3,516,835, 3,589,906, 3,617,292, 3,619,199, 3,663,229, 3,666,478, etc. Still further, the silver halide emulsion can contain an antistatic agent as described in U.S. Pat. Nos. 2,739,888, 3,428,456, 3,437,484, 3,457,076, 3,549,375, 3,549,369, 3,551,152, 3,552,972, 3,547,643, 3,564,043, 3,615,531, 3,625,695, 3,655,287, 3,653,906, 3,655,386, 3,686,368, 3,756,828, 3,754,924, etc., a ultraviolet absorber as described in U.S. Pat. Nos. 2,415,624, 3,052,636, 3,074,971, 3,085,097, 3,067,456, 3,215,536, 2,719,086, 2,537,877, 2,784,087, 2,882,150, 2,875,053, 2,739,971, 3,097,100, 3,060,029, 2,632,701, 2,858,346, 2,748,021, etc., a fluorescent whitening agent as described in U.S. Pat. Nos. 3,630,738, 3,615,544, 3,586,673, 3,434,837, British Pat. Nos. 1,332,475, 1,319,763, 1,333,586, etc., an anti-irradiation dye as disclosed in U.S. Pat. No. 3,445,231, etc.

In the color photographic material containing the coupler or couplers of this invention, any couplers other than the coupler of this invention can also used. For instance, as a yellow dye-forming coupler there are open chained type ketomethylenic couplers and typical examples of such couplers are benzoylacetanilide couplers, acylacetanilide couplers, etc. As a magenta dye-forming coupler, there are pyrazolone type couplers, indazolone type couplers, pyrazolobenzimidazole type couplers, cyanoacetyl type couplers, etc. Also, as cyan dye-forming couplers, there are illustrated phenol type couplers, naphthol type couplers, etc. Suitable examples of these couplers which can be used are described in U.S. Pat. Nos. 1,108,028, 2,186,84 2,206,142, 2,343,702, 2,367,531, 2,369,489, 2,483,730, 2,436,130, 2,474,293, 2,600,788, 2,689,793, 2,728,658, 2,742,832, 2,808,329, 2,998,314, 3,046,129, 3,062,653, 3,265,506, 3,311,476, 3,408,194, 3,419,390, 3,419,391, 3,458,315, 3,476,563, 3,516,831, 3,617,291, 3,551,155, 3,511,156, 2,908,573, 3,642,485, 3,062,653, 3,558,319, etc.

Each of these couplers can have at the active carbon of the coupling position a group capable of being released on oxidative coupling with an aromatic primary amine developing agent, such as a halogen, ether, thioether, acyloxy, phthalimide, hydantoin, thiocyano, sulfo, sulfino, saccharin, benzotriazole, etc. group, besides a hydrogen atom. Also, the coupler can be a so-called colored coupler having a chromophore such as a diazo group, a styryl group, etc., as a releasable group. Furthermore, the coupler can have a so-called anti-diffusion group so that the coupler is prevented from diffusing in the emulsion layers. Also, the coupler can have a group such as a sulfo group, a carboxyl group, etc., for dispersing the coupler in a micellar state as an alkali metal salt or an alkaline earth metal salt thereof.

In the case of dispersing the coupler of this invention for preparing the coupler dispersion, a dispersion assistant can be advantageously used and further in the case of coating the silver halide emulsions and other coating compositions for producing the color photographic material of this invention, a coating assistant can also be advantageously used. Examples of such coating assistants are an anionic active agent containing a sulfonic acid, a sulfuric acid, a phosphoric acid, a carboxylic acid group, or a salt thereof; a nonionic surface active agent containing a hydroxyl group; a cationic surface active agent containing an ammonium, phosphonium, anilinium, pyridinium, etc. group; and an amphoteric surface active agent having an anionic group and a cationic group in the same molecule.

The color photographic material of this invention can be processed, after exposure, using known processing methods. For instance, when the photographic material of this invention is a negative-positive type negative or positive color photographic material, the color photographic material can be processed using the following main steps:

1. Color Development
2. Stop or fix
3. Bleach and fix, or blix

Of these steps the second step may be omitted. Also, if necessary, a hardening step for hardening the emulsion layers and an alkaline bath pre-treatment step for removing a resin backing layer can be employed before the first step, or step 1 described above. Furthermore, if desired, a hardening step can be employed between step 1 and step 2 or step 2 and step 3 or further after step 3. Still further, if desired, a stabilization step for improving the stability of images formed can be employed. Moreover, washing steps can also be employed between each steps and after the last step.

After all of the photographic process steps are finished, the color photographic material is dried. That is to say, the color photographic material can be dried by natural drying by exposing to air, heating, hot-air drying, infrared radiation, electron rays, etc.

When the color photographic material is used as a reversal type photographic material, the color photographic material is processed using the following main steps:

1. Black and white development
2. Reversal exposure
3. Color development
4. Stop or fix
5. Bleach and fix or blix.

When the bath for color development step 3 contains a fixing agent, step 2 can be omitted. In the reversal processing, a hardening step, an alkaline bath pre-treatment step, a stabilization step, and washing steps can be, if desired, employed before or after each step described above. Also, after finishing all of the processing

steps, the color photographic material is also dried as described for the aforesaid negative-positive type treatment.

For each step of the aforesaid negative-positive type treatment and the reversal type treatment, processing baths of known compositions can be used.

A useful color developer is an alkaline solution containing a color developing agent. As the color developing agent, any known aromatic primary amine developing agents can be used as disclosed, for example, in U.S. Pat. Nos. 2,592,364, 2,193,015 and C. E. K. Mees, T. H. James, The Theory of the Photographic Process, page 294–295 Macmillan Co. (1966), such as N,N-diethyl-p-phenylene diamine, N-ethyl-N-hydroxyethyl-p-phenylene diamine, N-ethyl-N-hydroxyethyl-2-methyl-p-phenylene diamine, N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline, N,N-diethyl-2-methyl-p-phenylene diamine, and the sulfates, hydrochlorides, sulfites of these compounds.

The color developer used for developing the color photographic material of this invention can further contain conventional additives such as an alkali metal (e.g., sodium or potassium) sulfite, an alkali metal carbonate, an alkali metal bisulfate, an alkali metal bromide, an alkali metal iodide, benzyl alcohol, a water softener (such as sodium hexametaphosphate, an alkali metal hydroxide, hydroxylamine, a sulfate of hydroxylamine, and a hydrochloride of hydroxylamine), a competitive coupler (such as mono-sodium 1-amino-8-naphthol-3,6-disulfonate, citrazinic acid, etc.), and the like.

The stop solution used in the aforesaid processings can contain a known pH-reducing agent (such as acetic acid, phthalic acid, etc.).

The fix solution can contain a known fixing agent such as sodium thiosulfate, ammonium thiosulfate, potassium thiocyanate, etc.

The bleach solution can contain a known bleaching agent such as a ferricyanide (e.g., potassium ferricyanide), a bichromate (e.g., potassium bichromate), a ferric salt of ethylenediamine tetraacetic acid, etc.

When the bleach step and the fix step are conducted in one bath, a blix bath containing a known solvent for silver halide and a known silver oxidizing agent can be used. Examples of such a silver halide solvent are a thiosulfate (e.g., ammonium or potassium thiosulfate), a thiocyanate (e.g., ammonium or potassium thiocyanate), an organic diol containing an oxygen or sulfur atom (such as 3-thio-1,5-pentanediol, 3,6-dithio-1,8-octanediol, 9-oxa-3,6,12,15-tetrathia-1,17-heptadecanediol, etc.), a sulfur-containing organic dibasic acid or a salt thereof (such as ethylenebisthioglycolic acid, a sodium salt thereof, etc.), imidazolidinethione, and the like. Also, examples of the oxidizing agent for silver are a ferricyanide (e.g., potassium or ammonium ferricyanide), a quinone (e.g., quinone, p-benzoquinone, o-benzoquinone, p-toluquinone 1,2-naphthoquinone), a ferric salt (e.g., a chloride or sulfate), a cupric salt (e.g., a chloride or sulfate), a cobaltic acid or salt (e.g., a chloride or sulfate), a complex salt of an ammonium ion or alkali metal ion, a ferric ion, a cupric ion, or a cobalt ion, and an organic acid (such as malonic acid, tartaric acid, ethylmalonic acid, malic acid, fumaric acid, diglycolic acid, dithioglycolic acid, ethyliminopropionic acid, nitrilotriacetic acid, ethylenediamine tetraacetic acid, aminotriacetic acid, ethylenedithioglycolic acid, dithioglycolic acid, etc.), and a chelate compound of a ferric ion, a cupric ion, or a cobalt ion (examples of coordination compounds of these chelate compounds are ethylenediamine, diethylenetriamine triethylenetetramine, diaminopropane, diaminocyclohexane, polyethyleneimine, acetylacetone, diethyldithiocarbomate, oxyquinoline, dithizone, dipyridyl, phenanthrenine, etc., ferric ethylenediaminetetraacetic acid sodium salt, cupric malonic acid sodium salt), and the like.

These photographic processing compositions, and the components and proportions contained therein are well known in the art, as disclosed in The Journal of the Society of Motion Picture and Television Engineers, vol. 61 page 667–701; U.S. Pat. Nos. 3,189,452 and 3,582,322; L. F. A. Mason, Photographic Processing Chemistry page 187–188 Focal Press (1966) German Patent 866,605, and 966,410; and the British Journal of Photography, page 122–123, 126 (1966).

The couplers of this invention can be used, in addition to the aforesaid multilayer color photographic materials based on subtractive color process, for other silver halide photographic materials forming color images by color development using aromatic primary amino developing agents, such as color radiographic photographic materials, infrared photographic materials, photographic materials for radar images, color microphotographic materials, and the like.

Now, the invention will further be explained by reference to the following examples. The comparison couplers used in the examples are as follows.

A. 2′-chloro-5′-(hexadecyloxycarbonyl)benzoylacetanilide,

B. 2′-chloro-5′-[β-(dodecyloxycarbonyl)butyloxycarbonyl]-benzoylacetanilide,

C. 2′-chloro-5′-dodecyloxycarbonyl-2-methylbenzoylacetanilide,

D. 2′-chloro-5′-dodecyloxycarbonyl-4-ethoxybenzoylacetanilide,

E. 2′-chloro-5′-(dodecyloxycarbonyl)benzoylacetanilide,

F. 2′-chloro-5′-[α-(2,5-di-tert-amylphenoxy)-butyramido]-4-methoxybenzoylacetanilide,

G. 2′-methoxy-5′-{N-[2-methoxy-5-(N,N-diethylsulfamoyl)-phenyl]carbamoyl}-acetyl-2,4-di-tert-benzoylacetanilide,

H. 2′-chloro-5′-[α-(2,4-di-tert-amylphenoxy)-butyramido]-2-methylbenzoylacetanilide,

I. 2′-chloro-5′-hexadecyloxycarbonyl-1-hydroxy-2-napthanilide,

J. 2′-chloro-5′-hexadecyloxycarbonyl-1-hydroxy-4-chloro-2-napthanilide.

EXAMPLE 10

The melting points, the fusion enthalpies (ΔH fusion), and the solution enthalpies (ΔH solution) in ethyl acetate of the couplers of this invention and the comparison couplers are shown in Table 1.

In the example, the value of the ΔH fusion was measured using a Perkin-Elmer DSC-IB type differential scanning calorimeter. The value of the ΔH solution was measured using a CM-204 type twin heat conductive calorimeter.

Table 1

Coupler of This Invention				Comparison Coupler			
Coupler	Melting Point (°C)	ΔH Fusion Kcal/mol	ΔH Solution Kcal/mol (at °C)	Coupler	Melting Point (°C)	ΔH Fusion Kcal/mol	ΔH Solution Kcal/mol (at °C)
1	121–122	11.48	7.38 (25)	A	96	12.33	13.19 (25)
7	132–133	9.64	6.89 (25)	B	87–84	11.46	10.69 (25)
3	78–78.5	8.49	6.86 (25)	C	68	11.21	33.2 (25)
8	110–110.5	9.29	5.92 (25)	C	68	11.21	33.2 (25)
23	150–152.5	12.19	7.65 (45)	D	139–140	12.49	—
31	167–168	11.56	8.34 (45)	I	82	16.36	16.34 (45)
34	150–151	11.02	6.28 (45)	J	83	16.12	16.98 (45)

From the results shown in Table 1, it can be understood that Couplers 1, 7, 3, 8, 23, 31, and 34 of this invention and a low ΔH fusion and/or a ΔH solution as compared with those of Comparison Couplers A, B, C, D, I, and J having similar skeletons to those of the couplers of this invention and hence have a low temperature dependence of solubility (i.e., show less reduction in solubility at low temperatures) as compared with the latter comparison couplers.

EXAMPLE 11

Each of Coupler 3 of this invention and Comparison Couplers C, F, and G was mixed with dibutyl phthalate in the ratio shown in Table 2 and using such a mixture, coated samples 1 to 12 were prepared in the folllowing manner.

That is to say, 20 ml of ethyl acetate and dibutyl phthalate in the amount shown in Table 2 were added to 10 g of the coupler followed by heating to dissolve the coupler and after adding to the solution 100 g of an aqueous 10 percent gelatin solution and sodium alkylbenzenesulfonate as an emulsifying aid, the mixture was stirred vigorously using a homogenizer to form an emulsified dispersion of the coupler. Then, the emulsion thus prepared in an amount corresponding to a coupler content of 0.0035 mol was mixed with 40 g of a silver iodobromide emulsion (containing 0.029 mol of silver) containing 1.2 mol percent iodine. Then, after adding a hardening agent (4 ml of a 2 percent aqueous solution of 2,6-dichloro-4-oxy-S-triayine sodium salt), the mixture was coated (0.75 g/m^2 as silver) on a transparent cellulose acetate film support and dried. Thus, samples 1–12 were prepared.

Each of samples 1–12 was exposed to white light through a filter having a stepwise density difference and then processed in the following steps (processing temperature 21°C):

Processing Step	
1. Color Development	14 minutes
2. Fix	4 minutes
3. Wash	4 minutes
4. Bleach	8 minutes
5. Wash	4 minutes
6. Fix	4 minutes
7. Wash	20 minutes

The compositions of the processing solutions used in the steps were as follows:

Color Developer A (pH 10.5)	
Water	1000 ml
4-Amino-3-methyl-N,N-diethylaniline Hydrochloride	2.5 g
Sodium Sulfite (anhydrous)	10 g
Sodium Carbonate (mono-hydrate)	47 g
Potassium Bromide	2 g

-continued

Fix Solution (pH 4.5)	
Water	1000 g
Sodium Thiosulfate (hexa-hydrate)	80 g
Sodium Sulfite (anhydrous)	5 g
Borax	6 g
Glacial Acetic Acid	4 ml
Chromium Alum	7 g
Bleach Solution (pH 7.2)	
Water	1000 ml
Potassium Ferricyanide	100 g
Boric Acid	10 g
Borax	5 g

The transmission density of each of the strip samples thus colored stepwise a yellow color was measured using a blue light source. The maximum density (D_{max}) obtained is shown in Table 2.

Table 2

Sample No.	Coupler	Amount (ml) of Dibutyl Phthalate per 10 g of Coupler	D_{max}
1	3	0	2.3
2	3	1	2.6
3	3	5	2.5
4	C	0	2.6
5	C	1	2.6
6	C	5	2.6
7	F	0	0.5
8	F	1	1.8
9	F	5	2.6
10	G	0	0.4
11	G	1	1.5
12	G	5	2.5

As is clear from the results in Table 2, the samples containing Couplers F and G having an aryloxyalkylacylamide group showed a great reduction in D_{max} as the amount of dibutyl phthalate decreased, while the samples containing Coupler 3 of this invention and Comparison Coupler C showed substantially no reduction in D_{max} as the amount of dibutyl phthalate decreased.

EXAMPLE 12

A mixture of 10 g of coupler (as shown in Table 3), 1 ml of dibutyl phthalate and 20 ml of ethyl acetate was heated to dissolve the coupler and then the solution was treated as described in Example 11 to form an emulsified dispersion. Then, the emulsified dispersion thus prepared in an amount corresponding a coupler content 0.0035 mol was mixed with 50 g of a silver iodobromide emulsion (containing 0.028 mol of silver) containing 6.0 mol percent iodine and the mixture was coated on a support as described in Example 11. Thus, coated samples 1 to 8 were prepared. The couplers used in samples 1 to 8 are shown in Table 3.

Each of the samples 1 to 8 was exposed stepwise and developed as described in Example 10 except that the color development was conducted using Developer B having the following composition for 12 minutes at 21°C.

Color Developer B (pH 10.7)	
Water	1000 ml
Benzyl Alcohol	4 ml
Sodium Sulfite (anhydrous)	3 g
Sodium Carbonate (mono-hydrate)	50 g
N-Ethyl-N-(β-methanesulfonamide-ethyl)-p-phenylenediamine sulfate	5 g
Potassium Bromide	1 g

The maximum density of the transmission density of the yellow images thus obtained for blue light is shown in Table 3.

Table 3

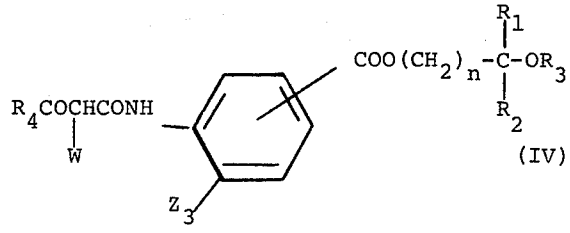
Sample No.	Coupler	D_{max}
1	1	1.93
2	3	1.97
3	8	1.85
4	9	1.86
5	C	1.88
6	E	2.02
7	F	0.61
8	H	1.03

As is clear from the results shown in Table 3, in the case of using a small amount of the high boiling oil as in this example, the samples containing Comparison Couplers F and H having an acylamide group showed a great reduction in D_{max}, while the samples containing Couplers 1, 3, 8, and 9 of this invention having an alkoxycarbonyl group and the samples containing Comparison Couplers C and E showed sufficiently high D_{max}.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

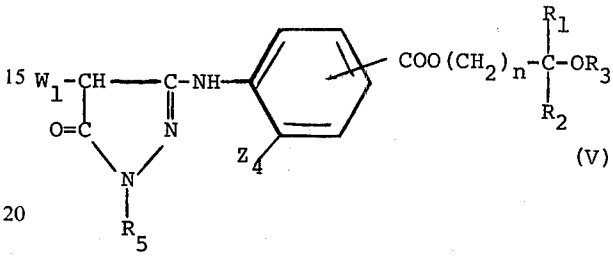
1. A color photographic material comprising a support having thereon at least one silver halide emulsion layer containing at least one coupler capable of forming a dye by an oxidative coupling reaction with the oxidation product of an aromatic primary amino developing agent, wherein said coupler is selected from the group consisting of couplers represented by the general formulae (IV), (V), (Va), (VI) or (VIa) below:



(IV)

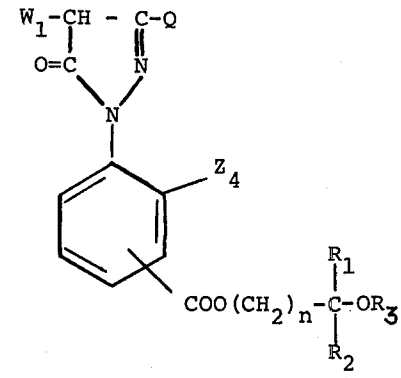
where n represents an integer from 1 to 7,

R_1 and R_2 each represents a hydrogen atom or an alkyl group; R_3 represents an aryl group; R_4 represents an aliphatic residue, an aromatic residue, or a heterocyclic residue, W represents a hydrogen atom or a coupling residue capable of being released by oxidative coupling with the oxidation product of an aromatic primary amino developing agent, and Z_3 represents a hydrogen atom, an alkyl residue, an alkoxyl residue, an aryloxy residue, an amino residue, or a halogen atom, said alkoxycarbonyl group being at the 4- or 5-position of the anilide ring;



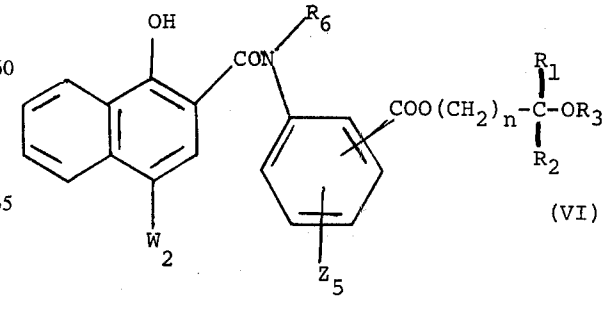
(V)

wherein R_1, R_2, R_3 and n have the same meaning as in general formula (IV); R_5 represents an aromatic residue or a heterocyclic residue, W_1 represents a hydrogen atom or a coupling residue capable of being released by oxidative coupling with the oxidation product of an aromatic primary amino developing agnet, and Z_4 represents a hydrogen atom, an alkyl residue, an alkoxyl residue, an aryloxy residue, or a halogen atom, the alkoxycarbonyl group being at the 4- or 5-position of the anilino ring;



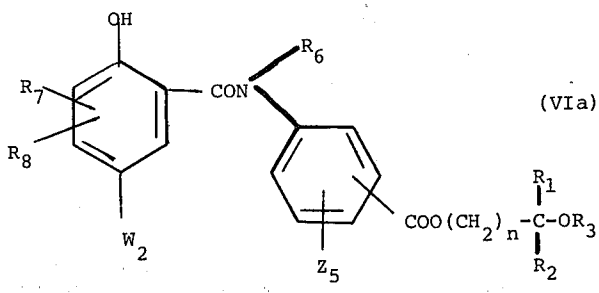
(Va)

wherein R_1, R_2, R_3, W_1, Z_4 and n have the same meaning as described with respect to general formula (V), Q represents an alkyl residue, an alkoxy residue, a N-alkylamino residue, an anilino residue or an acylamino residue;



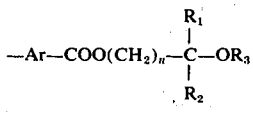
(VI)

wherein R_1, R_2, R_3 and n have the same meaning as in general formula (IV), R_6 represents a hydrogen atom or an alkyl group having less than 5 carbon atoms, W_2 represents a hydrogen atom or a coupling residue capable of being released by oxidative coupling with the oxidation product of an aromatic primary amino developing agent, and Z_5 represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxyl group, and aryl group, an aryloxy group, an amino group, or an acylamino group; or

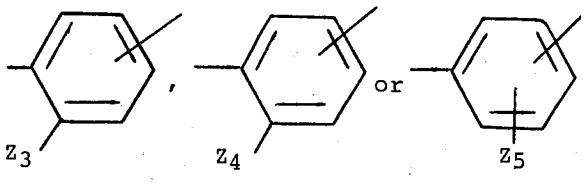


(VIa)

wherein R_1, R_2, R_3, R_6, W_2, Z_5 and n have the same meaning as described with respect to general formula (VI), R_7 and R_8 each represents a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group; wherein the alkoxycarbonylarylene group of said couplers has from about 15 to 50 carbon atoms, said group being representable by the formula:



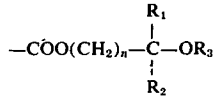
wherein -Ar- is



for couplers of the general formula IV, (V) +(Va) and (VI) + (VIa), respectively.

2. The color photographic material of claim 1, in which R_3 represents a phenyl group substituted with 1 or 2 alkyl groups of alkoxyl groups.

3. The color photographic material of claim 1, in which said alkoxylcarbonyl group represented by



is selected from the group consisting of a β-(2,4-di-tert-butylphenoxy)ethoxycarbonyl group, a β-(2,4-di-tert-amylphenoxy)ethoxycarbonyl group, a γ-(2,4-di-tert-amylphenoxy)propoxycarbonyl group, a δ-(2,4-di-tert-amylphenoxy)butoxycarbonyl group, a β-(2,4-di-tert-amylphenoxy)butoxycarbonyl group, a β-(4-methylphenoxy)tetradecyloxycarbonyl group, a β-(3-tert-butyl-4-hydroxyphenoxy)tetradecyloxycarbonyl group, a β-(3-n-pentanedecylphenoxy)butoxycarbonyl group, β-(3-n-pentadecylphenoxy)-β-methylpropoxycarbonyl group, and β-(3-n-dodecyloxyphenyl)ethoxycarbonyl group.

4. The color photographic material of claim 1 in which said coupling residue is selected from the group consisting of an open chain active methylene group, an open chain active methylene group substituted with a group capable of being released by the oxidative coupling with the oxidation product of an aromatic primary amino developing agent, a cyclic active methylene group, a cyclic active methylene group substituted with a group capable of being released by the oxidative coupling with the oxidation product of an aromatic primary amino developing agent and a phenolic hydroxyl group.

5. The color photographic material of claim 1, in which said coupling residue is selected from the group consisting of an acylacetanilide residue, a 5-pyrazolone residue, a phenol residue, and a naphthol residue.

6. The color photographic material of claim 1, wherein W, W_1 and W_2 are selected from the group consisting of halogen atoms, aryloxy groups, acyloxy groups, alkylthio groups, arylthio groups, imido groups and azo groups.

7. The color photographic material of claim 1, wherein W, W_1 and W_2 are selected from the group consisting of fluorine, chlorine, bromine, iodine, phenoxy, 4-chlorophenoxy, 4-carbophenoxy, 4-(4-hydroxy phenylsulfonyl) phenoxy, acetoxy, benzoxy, ethylthio, dodecylthio, phenylthio, 2-carbophenylthio, phthalimido, oxazoldinylimido, phenylazo, 2-ethoxycarbonylnaphthylazo and 3-methoxyphenylazo.

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