United States Patent Office

3,737,318

Patented June 5, 1973

3,737,318

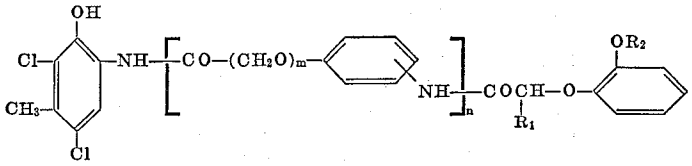
LIGHT-SENSITIVE COLOR PHOTOGRAPHIC MATERIAL

Isaburo Inoue, Teruo Hanzawa, and Takaya Endo, Tokyo, Japan, assignors to Konishiroku Photo Industry Co., Ltd.

No Drawing. Filed May 13, 1971, Ser. No. 143,240
Claims priority, application Japan, May 14, 1970, 45/40,491
Int. Cl. G03c 1/40
U.S. Cl. 96—100 11 Claims

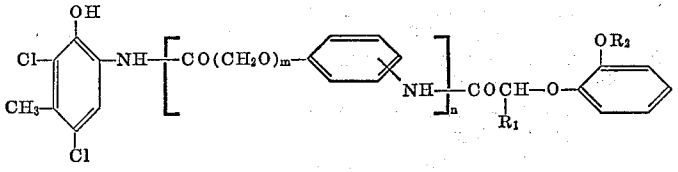
ABSTRACT OF THE DISCLOSURE

A light-sensitive silver halide color photographic material containing as a coupler a compound of the general formula,



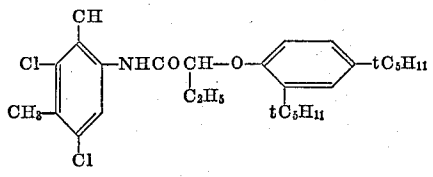
wherein R_1 is a hydrogen atom or a lower alkyl group; R_2 is an aliphatic hydrocarbon residue having 8 to 18 carbon atoms; n is zero or 1; and m is zero or 1.

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



wherein R_1 is a hydrogen atom or a lower alkyl group, R_2 is an aliphatic hydrocarbon residue having 8 to 18 carbon atoms, m is zero or 1, and n is zero or 1.

Although many compounds have heretofore been proposed as protect type couplers, they have various drawbacks, and those which can be prepared at low cost and with high purity have scarcely been known. For example, the coupler of the formula,



which is disclosed in U.S. Pat. No. 2,801,171, has excellent solubility in high boiling solvents but has such drawbacks that it should be prepared by use of expensive starting materials and can be difficultly purified.

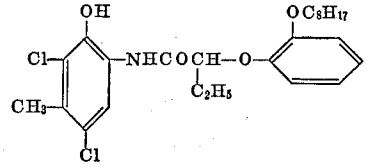
In contrast to this, the coupler of the aforesaid general formula which is used in the present invention can be prepared simply and economically by use of such starting materials as catechol and alkyl bromide which can be obtained with ease and at low cost on the market. Moreover,

it is easily soluble in a high boiling solvent such as dibutyl phthalate, tricresyl phosphate or the like, so that the amount of the solvent for the coupler can be decreased to make it possible to obtain a high concentration coupler dispersion. Further, the coupler is low in melting point and hence is difficultly crystallizable in an emulsion or in a film formed by coating and drying. Due to such characteristics as mentioned above, the coupler of the present invention is quite useful as a protect type coupler, and has greatly overcome the drawbacks of known couplers. Accordingly, the light-sesitive color photographic material according to the present invention, which has been incorporated with the said coupler, is excellent in spectral absorption characteristic and can give a high density color image excellent in transparency.

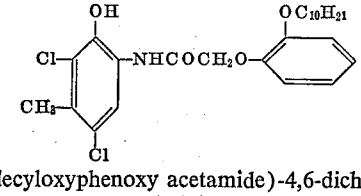
The coupler used in the present invention is synthesized, for example, in the following manner:

A long chain alkyl bromide and catechol are condensed with each other in dimethylformamide in the presence of potassium bicarbonate to form a catechol monoalkyl ether, which is then condensed with a halogenated fatty acid to obtain a long chain alkoxyphenoxy fatty acid. This acid is treated with phosphorus pentachloride to form an acid chloride, which is then condensed with a phenol derivative having an amino group in the o-position to synthesize the desired coupler.

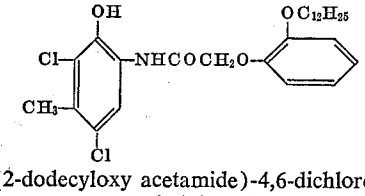
Typical examples of the couplers represented by the general formula are set forth below, but couplers usable in the present invention are not limited only to these.



2-[α-(2-octyloxyphenoxy)butylamide]-4,6-dichloro-5-methylphenol

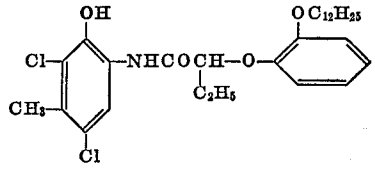
2. 

2-(2-decyloxyphenoxy acetamide)-4,6-dichloro-5-methylphenol

3. 

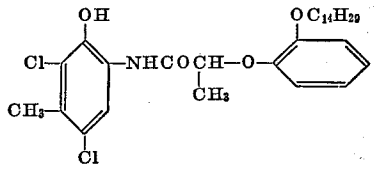
2-(2-dodecyloxy acetamide)-4,6-dichloro-5-methylphenol

4.



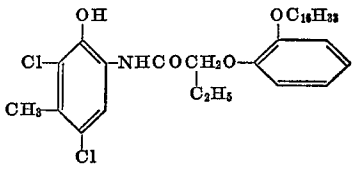
2-[α-(2-dodecyloxyphenoxy)butylamide]-4,6-dichloro-5-methylphenol

5.



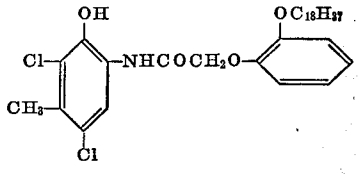
2-[α-(2-tetradecyloxyphenoxy)propionamide]-4,6-dichloro-5-methylphenol

6.



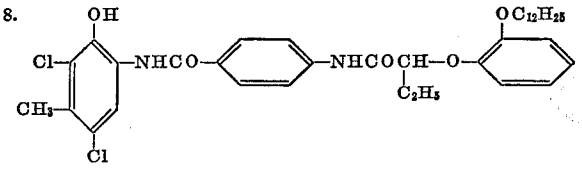
2-[α-(2-hexadecyloxyphenoxy)butylamide]-4,6-dichloro-5-methylphenol

7.



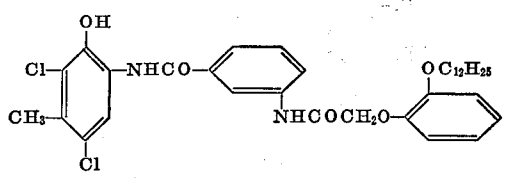
2-(2-octadecyloxyphenoxy acetamide)-4,6-dichloro-5-methylphenol

8.



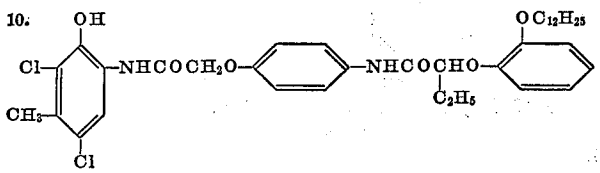
2-[4-(α-dodecyloxyphenoxy)butylamide]benzamide-4,6-dichloro-5-methylphenol

9.



2-[3-(2-dodecyloxyphenoxy acetamide)benzamide]-4,6-dichloro-5-methylphenol

10.



2-[4-(α-2-dodecyloxyphenoxy butylamide) phenoxy acetamide]-4,6-dichloro-5-methylphenol

Concrete procedures for synthesis of typical couplers among those represented by the aforesaid general formula are set forth below with reference to the synthesis example.

Synthesis example

(a) A mixture comprising 110 g. of catechol, 500 ml. of dimethylformamide, 140 g. of potassium carbonate and 280 g. of dodecyl bromide was stirred at 110° to 120° C. for 3 hours. Subsequently, the mixture was poured into water, and the oil layer was extracted with ether, washed with water and dried with Glauber's salt. Thereafter, the ether was removed by distillation, and then the residue was subjected to distillation to obtain a fraction of catechol monododecyl ether, B.P. 203–205° C./4 mm. Hg, yield 65%.

In the same manner as above, there were obtained catechol monooctyl ether, B.P. 180–183° C./4 mm. Hg; catechol decyl ether, B.P. 192–195° C./4 mm. Hg; catechol tetradecyl ether, B.P. 220–225° C./4 mm. Hg; catechol hexadecyl ether, B.P. 225–228° C./4 mm. Hg; and catechol octadecyl ether, B.P. 230–235° C./3 mm. Hg.

(b) 86.5 grams (0.3 mole) of the thus obtained catechol monododecyl ether was added to a solution of 13.8 g. of metallic sodium in 300 ml. of alcohol, and the resulting mixture was boiled for 30 minutes. Thereafter, the mixture was charged with 50.5 g. (0.3 mole) of α-bromobutyric acid, stirred with boiling for 3 hours, poured into ice water and then acidified with hydrochloric acid to deposit a precipitate. The precipitate was recovered by filtration and then recrystallized from n-hexane to obtain α-(2-dodecyloxyphenoxy) butyric acid, M.P. 74–76° C., yield 75%.

In the same manner as above, there were obtained various long chain alkoxyphenoxy fatty acids, i.e. 2-dodecycloxyphenoxy acetic acid (M.P. 68–70° C.) from catechol monododecyl ether and monochloroacetic acid; 2-decycloxyphenoxy acetic acid (M.P. 75–78° C.) from catechol monodecyl ether and monochloroacetic acid; α-(2-octyloxyphenoxy) butyric acid (M.P. 78–80° C.) from catechol monooctyl ether and α-bromobutyric acid; α-(2-tetradecyloxyphenoxy) propionic acid, M.P. 79–81° C.) from catechol monotetradecyl ether and α-bromopropionic acid; α-(2-hexadecyloxyphenoxy) butyric acid (M.P. 85–88° C.) from catechol monohexadecyl ether and α-bromobutyric acid; and 2-octadecyloxyphenoxy acetic acid (M.P. 95–98° C.) from catechol monooctadecyl ether and monochloroacetic acid.

(c) The thus obtained long chain alkoxyphenoxy fatty acid was treated with phosphorus pentachloride to form an acid chloride. For example, a suspension of 36.4 g. of 2-dodecyloxyphenoxy acetic acid in 100 ml. of chloroform was charged with 23 g. of phosphorus pentachloride, and the resulting mixture was allowed to stand for 30 minutes and then heated for 30 minutes in a water bath at 60° C. Thereafter, the formed phosphorus oxychloride and chloroform were removed by distillation under reduced pressure, and the residual chloride was used in the subsequent acylation step.

(d) 40.0 grams of the thus obtained chloride was added to a mixture comprising 22.9 g. of 2-amino-4,6-dichloro-5-methylphenol hydrochloride, 550 ml. of acetone and 25.0 g. of diethyl aniline, and the resulting mixture was stirred for 1 hour, boiled for an additional 1 hour and then filtered. Subsequently, the filtrate was concentrated, and the concentrate was poured into a mixed liquid of concentrated hydrochloric acid and water, whereby a solid mass separated from the oil. The thus formed solid was recovered by filtration, washed with water, dried and then recrystallized from hexane to obtain 36.0 g. (64.5%) of a white powder having a melting point of 73 to 75° C. This powder was the exemplified coupler (3) of the present invention.

In the same manner as above, the exemplified couplers (1), (2), (4), (5), (6), (7), (8), (9) and (10) could be synthesized by the condensation of acid chlorides having different alkyl chains.

Exemplified coupler	M.P. (° C.)	Nitrogen analysis (percent) Calculated	Found
1	82–84	3.20	3.11
2	88–90	3.20	3.08
3	73–75	2.74	2.63
4	69–71	2.60	2.51
5	74–76	2.53	2.40
6	77–79	2.35	2.25
7	90–93	2.35	2.18
8	115–117	4.26	4.07
9	112–114	4.45	4.32
10	123–125	4.07	4.01

Tables 1 and 2 show the fact that the couplers used in the present invention have a low melting point and have excellent solubility in a high boiling solvent as compared with known couplers.

In Table 2, the comparison in solubility in a high boiling solvent was carried out by measuring the amount of dibutyl phthalate necessary to dissolve 1 g. of coupler at 60° C.

In order to substantiate the fact that the couplers of the present invention are excellent in durability, particularly heat resistance, of the resulting color images as compared with known couplers, the exemplified coupler (4) and know couplers were individually treated in the same manner as in Example 2 mentioned later, and the resulting color images were subjected to heat resistance test (at 77° C. for 2 days) and light resistance test (irradiation with an arc-lamp for 32 hours) to obtain such results as set forth in Table 3, in which the heat and light resistance values are residual color ratios at a density of 1.0.

TABLE 1.—COMPARISON IN MELTING POINT BETWEEN THE PRESENT COMPOUNDS AND KNOWN COUPLERS SIMILAR IN STRUCTURE THERETO

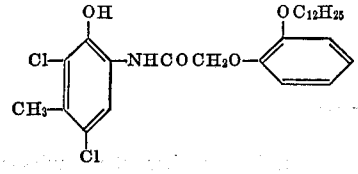
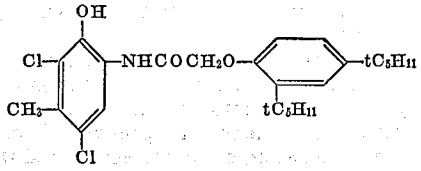
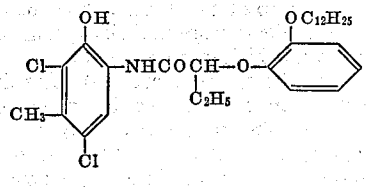
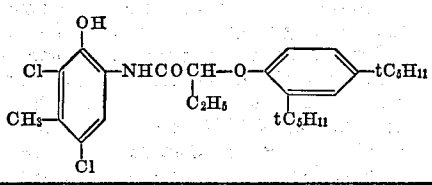
Coupler	Structural formula	M.P. (° C.)
Exemplified coupler (3).		73–75
Known coupler		158–160
Exemplified coupler (4).		69–71
Known coupler		123–124

TABLE 2.—COMPARISON IN SOLUBILITY

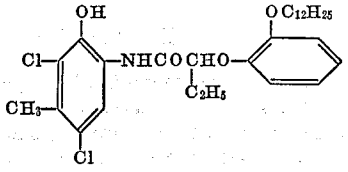
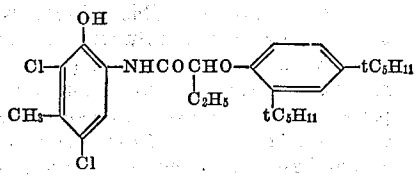
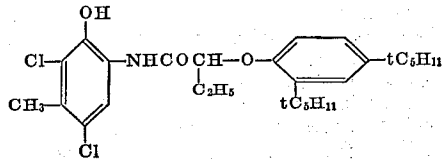
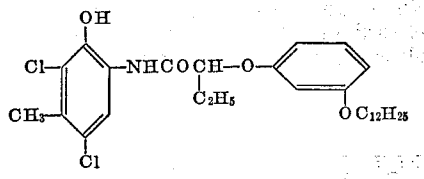
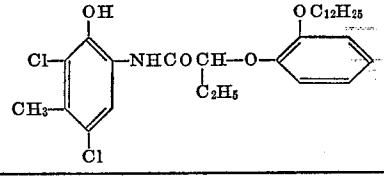
Coupler	Structural formula	Amount of dibutyl phthalate (ml.)
Exemplified coupler (4).		1.5
Known coupler		3.0

TABLE 3.—COMPARISON IN HEAT AND LIGHT RESISTANCE

Coupler	Structural formula	Heat resistance	Light resistance
Known coupler		83	97
Do		70	92
Exemplified coupler (4).		84	98

As is clear from Tables 1, 2 and 3, it is understood that the couplers used in the present invention are not only low in melting point but also excellent in solubility in high boiling solvents and particularly high in durability of resulting color images as compared with known couplers, and hence are extremely useful as protect type couplers.

In order to incorporate the couplers used in the present invention into a light-sensitive color photographic material, there may be adopted any of the known procedures. For example, the couplers are dissolved either singly or in combination of 2 or more in a high boiling solvent (B.P. 175° C. or more) such as tricresyl phosphate or dibutyl phthalate, or a low boiling solvent such as butyl acetate or butyl propionate, or a mixture of said solvents. This solution is mixed with an aqueous gelatin solution containing a surface active agent and then emulsified by means of a high speed rotary mixer or a colloid mill. Subsequently, the emulsified liquid is added directly to a silver halide photographic emulsion, which is then coated on a support such as a glass plate, synthetic resin sheet, film base, baryta paper or laminated paper, followed by drying, to prepare a light-sensitive color photographic material. Alternatively, the above-mentioned emulsified liquid is once set, finely cut, freed from the low boiling solvent by water-washing or the like means and added to a photographic emulsion, which is then coated on a support such as mentioned above, followed by drying, to prepare a light-sensitive color photographic material.

The above-mentioned procedures are illustrative and are not limitative.

In the above case, the amount of couplers to be added to the photographic emulsion is preferably in the range of 10 to 100 g. per mole of silver halide but may be varied as occasion demands without being limited to said range. Further, the coupler may be incorporated into 2 or more different emulsion layers of a multi-layered color photographic material.

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

The thus obtained light-sensitive color photographic material is exposed to radioactive rays such as α-rays or β-rays, visible rays or infrared rays, developed with a developer containing a p-phenylenediamine type developing agents as an active ingredient, and then bleached, desilvered and fixed to obtain a high density color image which is excellent in spectral absorption characteristics and durability and high in transparency.

A color photographic material using the coupler of the present invention may be incorporated with an UV-absorber of the benzophenone type (e.g. 2-hydroxy-4-dodecyloxybenzophenone) or the triazole type [e.g. 2(2'-hydroxy-3',5'-di-tert-butylphenyl) benzotriazole], whereby the resulting image can further be increased in durability.

Typical examples of the developing agent used for development of the light-sensitive color photographic material of the present invention are sulfates, sulfites and hydrochlorides of N,N - diethyl - p - phenylenediamine, N-ethyl - N - β - methanesulfonamidoethyl - 3-methyl-4-aminoaniline, N - ethyl - N - hydroxyethyl - p - phenylenediamine, N - ethyl - N - hydroxyethyl - 2 - methyl-p-phenylenediamine and N,N - diethyl - 2 - methyl-p-phenylenediamine. Further, the developer may contain a development-controlling agent, e.g. citrazinic acid, in addition to the above-mentioned active ingredient.

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

EXAMPLE 1

10 grams of the exemplified coupler (3) was added to a mixed solution comprising 10 ml. of tricresyl phosphate and 30 ml. of butyl acetate, and the resulting mixture was heated to 50° C., whereby the coupler was completely dissolved. This solution was mixed with 5 ml. of a 10% aqueous solution of Alkanol B and 800 ml. of a 5% aqueous solution of gelatin, and the resulting mixture was subjected to a colloid mill to form a dispersion. This dispersion was added to 500 g. of a gelatin silver iodobromide emulsion, which was then coated on a film base and dried to obtain a photographic material having a stable film coating. This photographic ma-

terial was exposed and then developed at 21° C. for 12 minutes with a developer of the following composition:

	G.
Metol	3.0
Anhydrous sodium sulfite	50.0
Hydroquinone	6.0
Anhydrous sodium carbonate	40.0
Potassium bromide	3.5
Potassium rhodanide	2.0
Water to make 1,000 ml.	

Thereafter, the material was subjected to ordinary stopping, film-hardening and water-washing treatments, and then subjected to second exposure by use of a white light. Subsequently, the thus treated material was developed at 21° C. for 13 minutes with a developer of the following composition:

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

Thereafter, the material was subjected to ordinary stopping, water-washing, bleaching and fixing treatments, washed with running water for 20 minutes and then dried to obtain a blue positive color image which had an absorption maximum at 675 mμ and was excellent in transparency.

EXAMPLE 2

A mixture comprising 10 g. of the exemplified coupler (4) and 20 ml. of dibutyl phthalate was heated to 50° C. to form a solution. This solution was mixed with 5 ml. of a 10% aqueous Alkanol B solution and 200 ml. of a 5% aqueous gelatin solution, and the resulting mixture was subjected several times to a colloid mill to form a dispersion. This dispersion was added to 500 g. of a gelatin silver chlorobromide emulsion, which was then coated on a baryta paper and dried to prepare a light-sensitive material.

The thus prepared material was exposed and then developed at 25° C. for 10 minutes with a developer of the following composition:

N-ethyl-N-β - methanesulfonamidoethyl-3-methyl-N - ethyl - N - β-methanesulfonamidoethyl-3-methyl-4aminoaniline sulfate	g.	8.5
Sodium tertiary phosphate (dodecahydrate)	g.	15.0
Sodium metaborate	g.	10.0
Anhydrous sodium sulfite	g.	7.0
Hydroxylamine sulfate	g.	2.0
Potassium bromide	g.	0.5
6-nitrobenzimidazole nitrate	g.	0.04
Benzyl alcohol	ml.	10
Diethylene glycol	ml.	20
Caustic soda	g.	1.2
Water to make 1,000 mil.		

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

Ammonium thiosulfate	g.	120
Potassium metabisulfite	g.	20
Glacial acetic acid	cc.	10
Water to make 1,000 mil.		

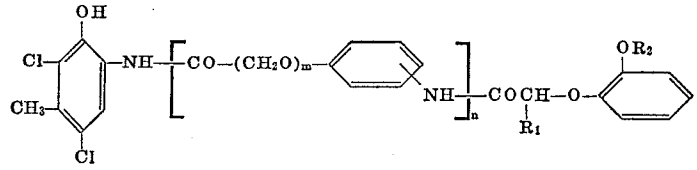
Subsequently, the material was washed with water for 5 minutes and then bleached at 25° C. for 3 minutes in a bath of the following composition:

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

Thereafter, the thus treated material was washed with water for 10 minutes, dipped in a stabilization bath for 2 minutes and then dried to obtain a cyan color image which had an absorption maximum at 670 mμ and was excellent in resistance to light and moisture.

What we claim is:

1. A light-sensitive silver halide color photographic material characterized by containing as a coupler a compound of the general formula,



wherein R_1 is a hydrogen atom or a lower alkyl group; R_2 is an aliphatic hydrocarbon residue having 8 to 18 carbon atoms; n is zero or 1; and m is zero or 1.

2. A light sensitive silver halide color photographic material as claimed in claim 1 wherein the coupler is 2-[α-(2 - octyloxyphenoxy)butylamide]-4,6 - dichloro-5-methylphenol.

3. A light sensitive silver halide color photographic material as claimed in claim 1 wherein the coupler is 2-(2-decyloxyphenoxy acetamide)-4,6 - dichloro-5-methylphenol.

4. A light sensitive silver halide color photographic material as claimed in claim 1 wherein the coupler is 2-(2-dodecyloxy acetamide) - 4,6 - dichloro-5-methylphenol.

5. A light sensitive silver halide color photographic material as claimed in claim 1 wherein the coupler is 2-[α-(2-dodecyloxyphenoxy)butylamide] - 4,6 - dichloro-5-methylphenol.

6. A light sensitive silver halide color photographic material as claimed in claim 1 wherein the coupler is 2-[α-(2 - tetradecyloxyphenoxy)propionamide] - 4,6-dichloro-5-methylphenol.

7. A light sensitive silver halide color photographic material as claimed in claim 1 wherein the coupler is 2-[α-(2-dodecyloxyphenoxy)butylamide] - 4,6-dichloro-ro-5-methylphenol.

8. A light sensitive silver halide color photographic material as claimed in claim 1 wherein the coupler is 2-(2-octadecyloxyphenoxy acetamide) - 4,6-dichloro-5-methylphenol.

9. A light sensitive silver halide color photographic material as claimed in claim 1 wherein the coupler is 2-[4-(α-2 - dodecyloxyphenoxy butylamide]benzamide-4, 6-dichloro-5-methylphenol.

10. A light sensitive silver halide color photographic material as claimed in claim 1 wherein the coupler is 2-[3-(2 - dodecyloxyphenoxy acetamide)benzamide]-4, 6-dichloro-5-methylphenol.

11. A light sensitive silver halide color photographic material as claimed in claim 1 wherein the coupler is 2-[4-(α - 2 - dodecyloxyphenoxy butylamide)phenoxy acetamide]-4,6-dichloro-5-methylphenol.

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J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

260—559