United States Patent Office

3,669,671

Patented June 13, 1972

3,669,671

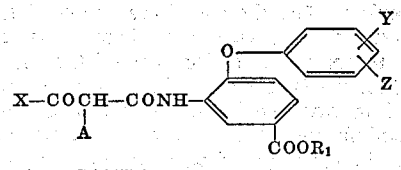
LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC EMULSIONS CONTAINING YELLOW COUPLERS

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

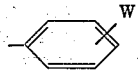
No Drawing. Filed Dec. 12, 1969, Ser. No. 884,751
Int. Cl. G03c 1/40
U.S. Cl. 96—100 7 Claims

ABSTRACT OF THE DISCLOSURE

New compounds of the general formula



wherein X is —$C(CH_3)_3$ or



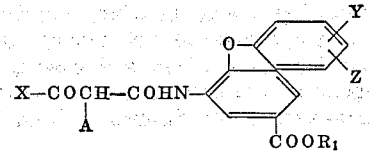
W is hydrogen, C_{6-18} acylamino, lower alkoxy, halogen or lower alkyl;

R_1 is an aliphatic hydrocarbon radical having 1–18 carbon atoms; Y and Z are each hydrogen, halogen, lower alkoxy, lower alkyl or —$COOR_2$; A is hydrogen, halogen or —$OCOR_3$;

R_2 and R_3 are each lower alkyl

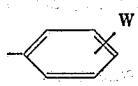
are found to be useful as yellow-forming color couplers of the protected type in light-sensitive silver halide photographic emulsions. These compounds can be synthesized from readily available starting materials with ease and at cheap cost.

This invention relates to a light-sensitive color photographic emulsion, more particularly, to a light-sensitive color photographic emulsion containing a yellow coupler of the formula given hereinafter as a so-called protected type coupler.



wherein

X is —$C(CH_3)_3$ or



W is hydrogen, C_{6-18} acylamino, lower alkoxy, halogen or lower alkyl;

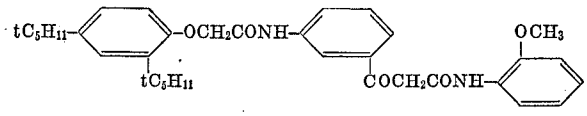
R_1 is an aliphatic hydrocarbon radical having 1–18 carbon atoms;

Y and Z are each hydrogen, halogen, lower alkoxy, lower alkyl or —$COOR_2$;

A is hydrogen, halogen or —$OCOR_3$;

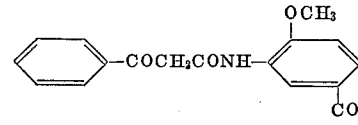
R_2 and R_3 are each lower alkyl)

A number of compounds have heretofore been proposed as yellow couplers used as protected type couplers which are dispersed in a photographic emulsion as a solution in high boiling solvent. Very few are found, however, which can be prepared at a low price and in high purity. For example, a very expensive starting material must be used for the production of the coupler of the formula



(I)

which is disclosed in U.S. Pat. 2,875,057. The above known coupler has good solubility in a high boiling solvent but is liable to cause separation in the emulsion under high concentration conditions because the melting point thereof is relatively high. Further, the coupler of the formula



(II)

which is disclosed in Japanese patent publ. No. 5,582/1967 gives a less transparent dye image and also tends to separate in the emulsion under high concentration conditions though its melting point is lower than that of the above coupler of U.S. Pat. 2,875,057.

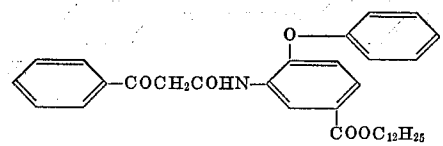
Thus, it has long been desired to find a coupler which can be prepared at a reasonable price and have good solubility in high boiling solvents without causing any separation in a photographic emplsion. Under the circumstances, we have found that the yellow coupler of the afore-mentioned formula is very advantageous as the protected type coupler.

The novel coupler is readily soluble in a high boiling solvent such as dibutyl phthalate, tricresyl phosphate, etc. and does not cause any separation in the photographic emulsion even at high concentration.

Further, the new coupler has a low melting point and accordingly is free from crystallization in the emulsion or even in a dried coating on a support. Moreover, a dye image obtained from the coupler has good spectral absorption characteristics and high transparency. The dye image has further advantages that it is fast to light, heat and humidity. Thus, the novel coupler which is free from the foregoing disadvantages of the prior couplers is particularly useful as a protected type coupler. The above advantageous characteristics of the novel coupler are considered attributed to an aryloxy group and an alkoxycarbonyl group introduced at the 2- and 5-positions, respectively, of the anilide moiety.

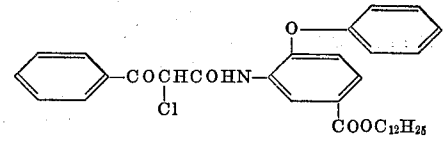
Typical couplers included in the general formula given hereinbefore are exemplified below. It should be noted that couplers usable in the invention are not limited only to these compounds.

(1)



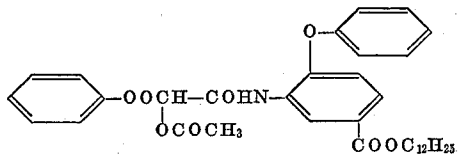
(m.p. 94–95° C.)

(2)



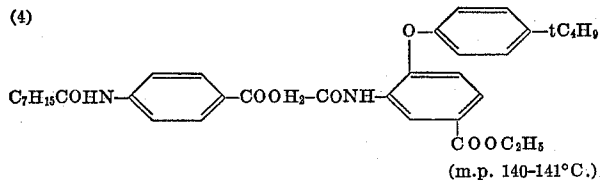
(olly; Ref. Index n_D^{20} 1.5628)

(3)



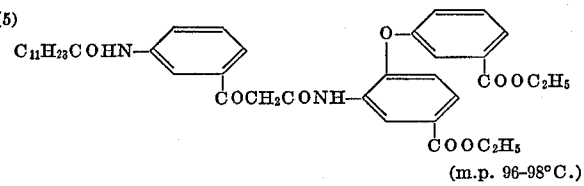
(m.p. 65-66°C.)

(4)



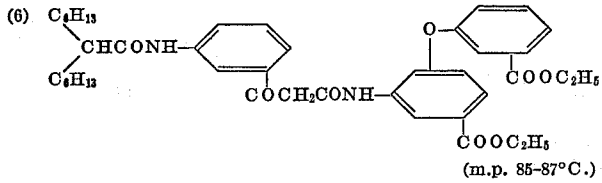
(m.p. 140-141°C.)

(5)



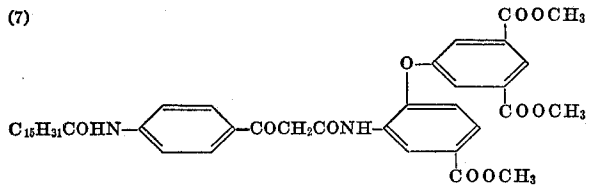
(m.p. 96-98°C.)

(6)



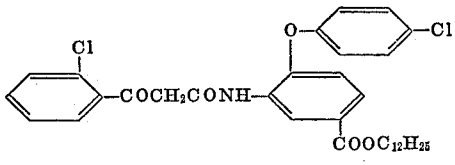
(m.p. 85-87°C.)

(7)



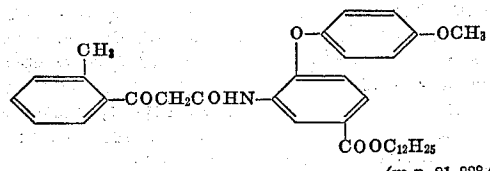
(m.p. 129-131°C.)

(8)



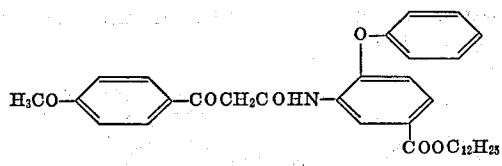
(oily)

(9)



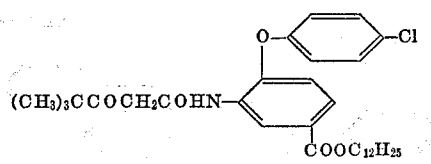
(m.p. 81-82° C.)

(10)



(m.p. 128-129° C.)

(11)



m.p.72-73°C.)

Synthesis of the yellow coupler may be made, in general, by condensing an aniline having an aryloxy group and alkoxycarbonyl group at the 2- and 5-positions, respectively, to the amino group with a β-keto acid ester in an inert solvent or by condensing an aminobenzoylacetanilide having 2-aryloxy and 5-alkoxycarbonyl groups in the anilide moiety with an acid chloride in an inert solvent.

In preparing a light-sensitive color photographic material using the yellow coupler of the aforementioned general formula, the coupler is dissolved in a high boiling solvent having a boiling point of 175° C. or higher, such as tricresyl phosphate, dibutyl phthalate and the like, or a low boiling solvent such as butyl acetate, butyl propionate and the like. On occasion, the coupler may be dissolved in a mixture of the above solvents. The resulting solution is mixed with an aqueous gelatine solution containing a surface active agent. The mixture is emulsified in a high speed rotary mixer or colloid mill and then immediately added to a light-sensitive silver halide photographic emulsion. The photographic emulsion thus treated is coated on a support such a film base or baryta paper and dried to remove a major part of the low boiling solvent. Alternatively, the emulsified mixture is previously set by cooling, extruded in noodle form and freed from the low boiling solvent by, for example, washing with water, and thereafter added with warming to the photographic emulsion, which is then treated in a similar manner as described above to give a light-sensitive color photographic material. This preparation of photographic material is not limited to the above method but any other modification may be practicable.

The coupler is preferably added to the photographic emulsion in an amount of 10–100 g. per mol of a silver halide contained in the emulsion. The above range is not, however, critical. The photographic emulsion used in this invention may contain any silver salt such as silver chloride, silver iodide and silver bromoiodide. Further, the emulsion may be sensitized with a chemical sensitizer, for example, sulfur sensitizer, natural sensitizer found in gelatine, reducing sensitizer and noble metal salt sensitizer. Said photographic emulsion may further contain photographic additives ordinarily used, such as anti-foggants, stabilizers, anti-stain agents, anti-irradiation agents, polymeric modifiers, coating aids, etc. As the optical sensitizer used in the photographic emulsion, any known carbocyanine dye or merocyanine dye may be used.

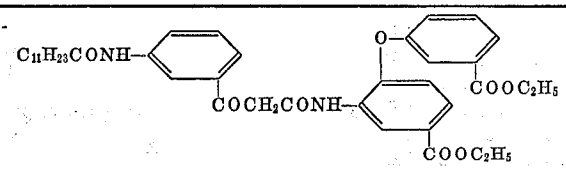
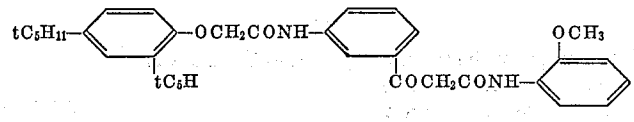
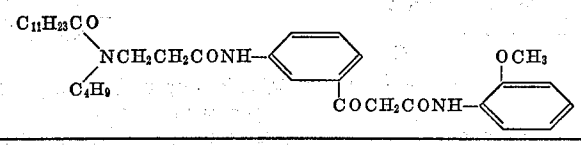
The light-sensitive photographic material thus obtained is then exposed to light and thereafter treated with a developing agent principally comprising p-phenylenediamine series developer. After bleaching and fixing, there appears a yellow dye image of high density having good spectral absorption characteristics and showing the maximum absorption at near 440 mμ. Said image is also excellent in transparency and fastness to light, heat and humidity.

Typical developing agents used in this invention for the treatment of light-sensitive photographic material are sulfates, sulfites and hydrochlorides of the following compounds:

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.

As shown by the Table 1 given hereinafter, the novel coupler used in this invention, which is substituted at the 2- and 5-positions in the anilide moiety with an aryloxy group and an alkoxycarbonyl group, respectively, has a lower melting point than known couplers.

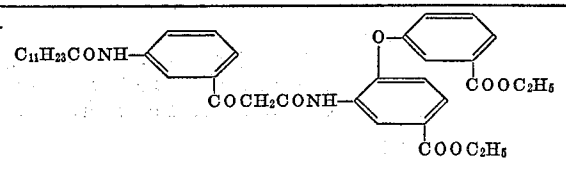
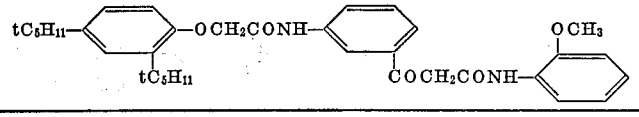
TABLE 1

	Formula	Melting Point (° C.)
Novel coupler (5)		96–98
Known coupler (cf. United States Patent 2,875,057).		126–127
Known coupler (cf. Japanese Patent Publication No. 2,837/1964).		110

Because of the above lower melting point, crystallization of the present coupler in the photographic emulsion or in the dried coating can be prevented and highly transparent photographic material is obtainable.

The fact that the coupler used in this invention has good solubility in a high boiling solvent is proved by the test which is effected by measuring an amount (ml.) of dibutyl phthalate required for dissolving 1.0 g. of coupler at 60° C. The result of the test is shown in the following Table 2.

TABLE 2

	Formula	Required dibutyl phthalate (ml.)
Novel coupler (5)		2.0
Known coupler (cf. United States Patent 2,875,057).		7.5

As evidently shown in the foregoing Tables 1 and 2, the novel coupler used in this invention melts at a lower temperature and has better solubility in a high boiling solvent that known couplers and therefore it will be understood that use of the new coupler results in an increase of the density of the developed dye image and, on the other hand, a decrease in the required amount of high boiling solvent and thus such new coupler is more preferable and useful as a protected type coupler.

The following examples will explain the present invention in detail, without limiting its scope thereto.

EXAMPLE 1

20 g. of the foregoing couple (1) is dissolved at 60° C. in a mixture of 20 ml. of dibutyl phthalate and 60 ml. of butyl acetate. The resulting solution is mixed with 10 ml. of an aqueous solution of 10% Alkanol B (alkyl naphthalene sulfonate produced by Du Pont, U.S.A.) and 200 ml. of an aqueous 5% gelatin solution. The resulting mixture is treated in a colloid mill. The coupler dispersion thus obtained is added to 1 kg. of a high speed gelatino-silver iodobromide photographic emulsion, which is then coated on a film base and dried.

The light-sensitive photographic material thus obtained is exposed to light in the ordinary manner and then treated to 20° C. for 10 minutes with a developing solution of the following formulation:

	G.
N,N-diethyl-p-phenylenediamine hydrochloride	2.5
Anhydrous sodium sulfite	2.0
Sodium carbonate monohydrate	82.0
Potassium bromide	2.0
Water to make up 1000 ml.	

The developed film is subjected to ordinary stopping and fixing and then, after washing with water for 10–15 minutes, treated for 5 minutes with a bleaching bath of the following formulation:

	G.
Potassium ferricyanide	100
Potassium bromide	50
Water to make up 1000 ml.	

The film is washed with water for 5 minutes and further treated for 5 minutes in a fixing bath of the following formulation:

Sodium thiosulfate pentahydrate—250 g.
Water to make up 1000 ml.

The film is washed with water for 20–25 minutes and dried. A brilliant yellow dye image having absorption maximum at 440 mμ is obtained. This dye image was outstandingly excellent more in transparency than the dye image obtained from the known coupler (II) as aforementioned in the same manner as above.

EXAMPLE 2

10 g. of the coupler (5) is dissolved at 50° C. in a mixture of 10 ml. of tricresyl phosphate and 30 ml. of butyl acetate. The resulting solution is mixed with 5 ml. of an aqueous solution of 10% Alkanol B and 800 ml. of an aqueous solution of 5% gelatine. The mixture is treated in a colloid mill. The resulting dispersion is added

to 500 g. of a gelatino-silver iodobromide emulsion, which is then coated on a film base and dried.

The photographic material thus obtained is exposed to light and treated at 20° C. for 10 minutes with a developing solution of the following formulation:

	G.
Metal	3.0
Anhydrous sodium sulfite	60.0
Hydroquinone	6.0
Anhydrous sodium carbonate	50.0
Potassium bromide	1.0
Water to make up 1000 ml.	

After being subjected to ordinary stopping, hardening and water-washing steps, the material is exposed to white light and then treated at 20° C. for 10 minutes with a developing solution of the following formulation:

	G.
N,N-diethyl-p-phenylenediamine hydrochloride	5.0
Anhydrous sodium sulfite	2.0
Sodium carbonate (monohydrate)	82.0
Potassium bromide	1.0
Water to make up 1000 ml.	

The developed material is further subjected to stopping, fixing, water washing and bleaching steps and then washed for 20 minutes with running water. After drying, a highly transparent yellow positive dye image having absorption maximum at 445 mμ is obtained.

EXAMPLE 3

10 g. of the coupler (9) is dissolved at 50° C. in 20 ml. of dibutyl phthalate. The resulting solution is mixed with 5 ml. of an aqueous solution of 10% Alkanol B and 200 ml. of an aqueous 5% gelatine solution. The mixture is passed through a colloid mill several times to form a dispersion. The resulting dispersion is added to 500 g. of a gelatino-silver chlorobromide emulsion, which is then coated on a baryta paper and dried.

The light-sensitive photographic material thus formed is exposed to light and then treated at 20° C. for 10 minutes with a developing solution of the following formulation:

	G.
N - ethyl - N - hydroxyethyl - p - phenylenediamine sulfate	2.5
Anhydrous sodium sulfite	2.0
Hydroxylamine hydrochloride	1.0
Sodium carbonate (monohydrate)	82.0
Water to make up 1000 ml.	

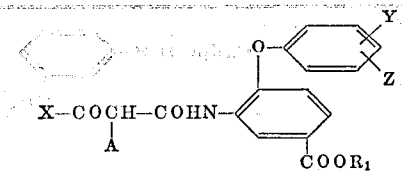
The developed material is then treated with a stopping solution which comprises 10 ml. of glacial acetic acid, 3.0 g. of sodium hydroxide and 1000 ml. of water and immediately thereafter with an acidic hardening fixing solution for 4 minutes. After washing with water for 10 minutes, the material is subsequently treated at 20° C. for 8 minutes with a bleaching bath of the following formulation:

	G.
Ethylenediaminetetraacetic acid disodium salt	40.0
Ferric salt	30.0
Sodium carbonate (monohydrate)	20.0
Potassium bromide	30.0
Sodium thiosulfate	200.0
Water to make up 1000 ml.	

The material is washed with water for 20 minutes and then treated for 8 minutes in a stabilizing bath and dried. A yellow dye image having an absorption maximum at 440 mμ and excellent in fastness to light and heat as well as in storability is obtained.

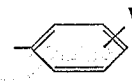
What we claim is:

1. A light-sensitive silver halide color photographic emulsion characterized by inclusion of a yellow coupler of the general formula



wherein

X is $-C(CH_3)_3$ or



W is hydrogen, C_{6-18} acylamino, lower alkoxy, halogen or lower alkyl;

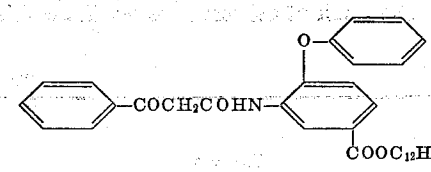
R_1 is an aliphatic hydrocarbon radical having 1–18 carbon atoms;

Y and Z are each hydrogen, halogen, lower alkoxy, lower alkyl or $-COOR_2$;

A is hydrogen, halogen or $-OCOR_3$;

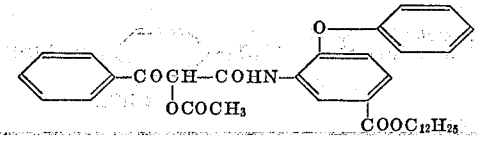
R_2 and R_3 are each lower alkyl.

2. A light-sensitive silver halide color photographic emulsion as claimed in claim **1**, wherein said yellow coupler is one having the following formula



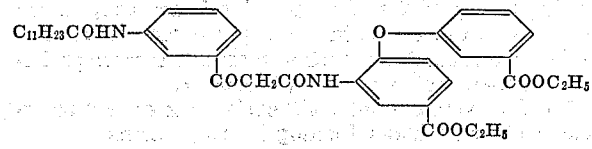
(m.p. 94–95° C.)

3. A light-sensitive silver halide color photographic emulsion as claimed in claim **1**, wherein said yellow coupler is one having the following formula



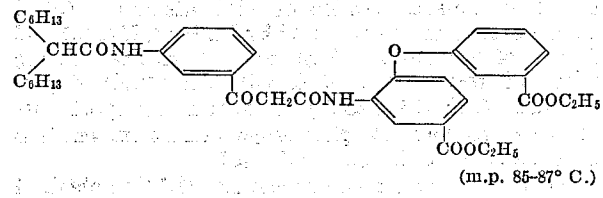
(m.p. 65–66° C.)

4. A light-sensitive silver halide color photographic emulsion as claimed in claim **1**, wherein said yellow coupler is one having the following formula



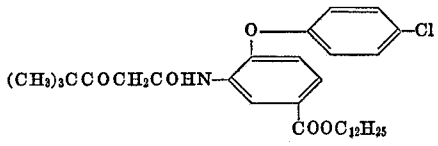
(m.p. 96–98° C.)

5. A light-sensitive silver halide color photographic emulsion as claimed in claim **1**, wherein said yellow coupler is one having the following formula



(m.p. 85–87° C.)

6. A light-sensitive silver halide color photographic emulsion as claimed in claim 1, wherein said yellow coupler is one having the following formula



(m.p. 72-73°C)

7. A light-sensitive silver halide color photographic material which comprises a support and, coated thereon, the light-sensitive color photographic emulsion of claim 1.

References Cited

UNITED STATES PATENTS

3,409,439	11/1968	Yoshida et al.	96—100
3,447,928	6/1969	Loria	96—100

J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

96—55