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8 Claims 10

lower alkoxy > hydrogen $\approx$ lower alkyl > aryloxy $\approx$ halogen

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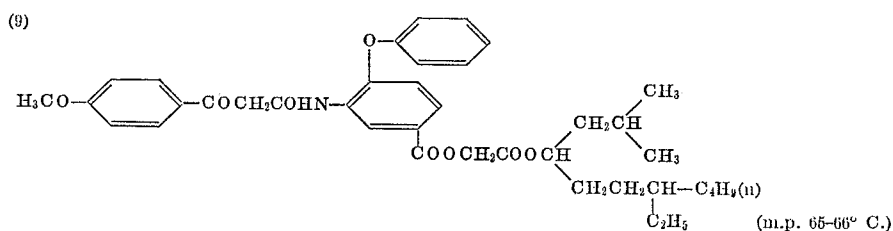
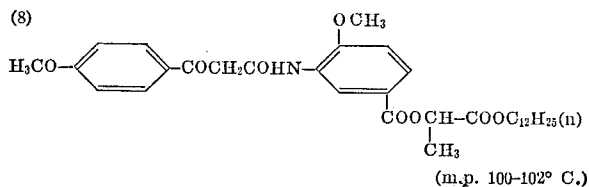
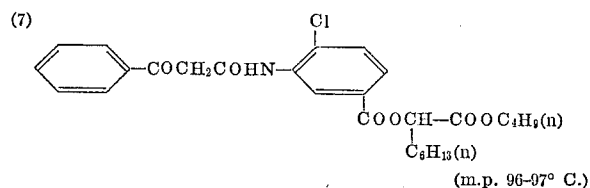
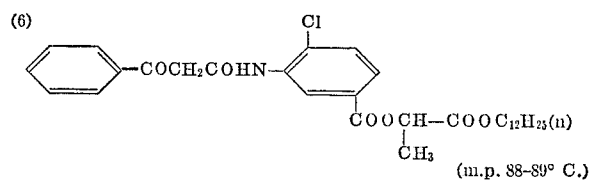
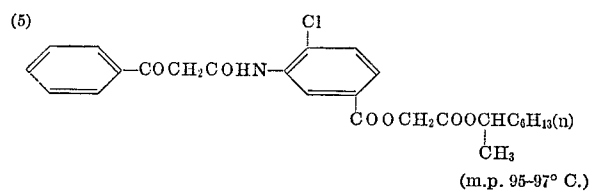
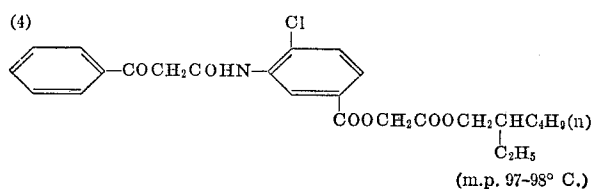
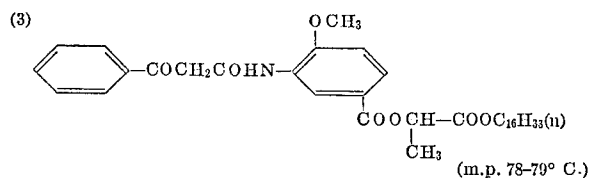
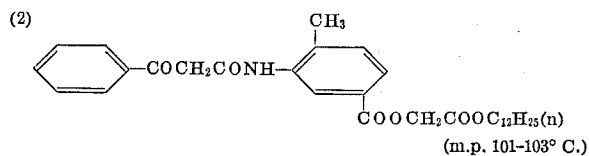
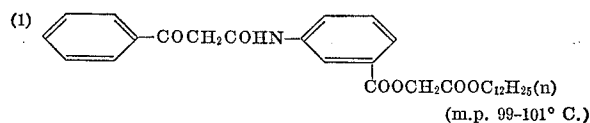
For example, solubility of the coupler having a chlorine atom as Y is reduced to $\frac{1}{3}$ – $\frac{1}{5}$ of that of the coupler having a methoxy group as Y.

Solubility of the couplers can, however, be particularly increased, when an alkyl group is introduced as R_2 or a branched-chain alkyl group is substituted for a straight-chain alkyl group as R_3 . Conversion of the substituent may be effected by using an agent selected depending on purpose. For example, monochloroacetic acid, α -bromopropionic acid, α -bromo-n-butyric acid, α -bromoiso-butyric acid, α -bromo-caprylic acid, α -bromo-lauric acid, etc. are used for converting R_2 and lauryl alcohol, 2-ethyl hexanol, 2-octyl alcohol, 7-ethyl-2-methylundecanol-4, di-isobutylcarbinol, etc. are used for the conversion of R_3 . These fatty acids and alcohols are all readily commercially available. Among the rest, α -halogeno fatty acid esters can be synthesized in good yield and in such high purity that no admixture of starting material is observed in a crude product by reacting α -halogeno fatty acid with alcohol in an equivalent molar ratio. Further, the intermediate of the Formula IV which is obtainable by the reaction of a substituted or unsubstituted aminobenzoic acid with α -halogeno fatty acid ester in an equivalent molar ratio is so pure that no admixture of starting material is observed in the crude product, and there is not needed any complicated isolation and purification steps. Because of such high purity of the intermediate (IV), the condensation with β -keto-ester proceeds smoothly and thus a resulting condensation product is readily isolated. It is therefore evident from the foregoing that the couplers according to this invention can be prepared at a low cost and are particularly useful from the industrial viewpoint.

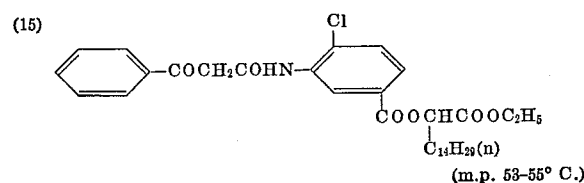
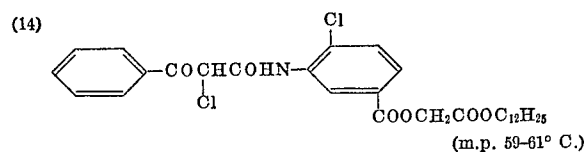
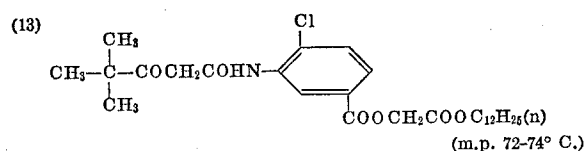
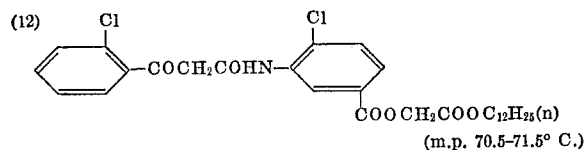
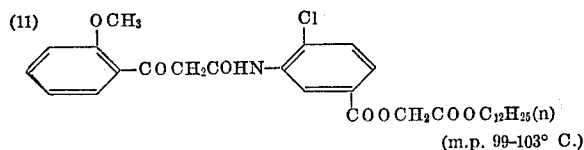
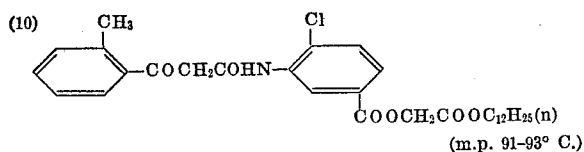
In addition to the above advantages, the couplers used in this invention exhibit improved photographic properties. They can form a highly dense dye image and are reduced in fogging and desensitization. Further, a color photographic material which can yield a highly transparent color image can be obtained from the emulsion of this invention in which the coupler is well dispersed because of its good solubility in high boiling solvent. Dye image obtainable from the couplers used in the present invention has good spectral absorption characteristics and is particularly fast to light, heat and humidity and does not suffer from discoloring or fading caused by various chemicals. In particular, a coupler containing as R_1 a tert. butyl group or o-substituted phenyl group produces an outstandingly fast dye image. Further, it has been found that maximum absorption of dye image is shifted to a long wavelength region when the carbon chain of R_2 in the Formula III is longer, as compared with the case where R_2 is hydrogen or short-chained alkyl group. For example, the couplers of the Formulas 6 and 7 as given hereinafter show the maximum absorption at 450 m μ and 460 m μ , respectively. This means that the preparation of a light-sensitive color photographic material properly meeting selected purposes is possible when the proper length of the carbon chain of alkyl group contained as R_2 is selected.

Typical couplers used in this invention are shown below by way of exemplification only.

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A light-sensitive color photographic material is prepared in the following manner: A yellow coupler as shown above is dissolved in a high boiling solvent having

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a boiling point of 180° C. or higher such as tricresyl phosphate, dibutyl phthalate, etc. or a low boiling solvent such as butyl acetate, butyl propionate, etc. On occasion, the coupler may be dissolved in a mixture of these 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 obtained is coated on a support such as a film base or baryta paper and dried to remove a major part of the low boiling solvent. Alternatively, the emulsified mixture is set by cooling, extruded to noodle form and freed from 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 above to give a light-sensitive color photographic material. The preparation of photographic materials 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 an antifoggant, stabilizer, anti-stain agent, anti-irradiation agent, polymeric modifier, coating aid, etc. As the optical sensitizer used in the photographic emulsion, any known carbocyanine dye or merocyanine dye may be used. When the photographic emulsion having the spectral sensitivity in the same region is coated in double layers, the coupler according to the present invention may be included in either layer or both layers.

The light-sensitive photographic material thus obtained is then exposed to radiation ray, X-ray visible ray, infrared ray, etc. and thereafter treated with a developing agent principally comprising a p-phenylenediamine series developer. After bleaching and fixing, there appears a yellow dye image of high density having good

TABLE 1

Formula	M.P. (° C.)	Required dibutyl phthal- ate (ml.)
Novel coupler..... 	88-89	2
Known coupler (cf. Japanese Patent Publication No. 5,582/1967) 	98-100	4
Novel coupler..... 	72-74	0.5
Known coupler (cf. United States Patent 3,265,506) 	130-140	10

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spectral absorption characteristics and showing a maximum absorption at 450–465 $m\mu$. Said dye image is also excellent in transparency and fastness to light, heat and humidity.

Typical developing agents used in this invention for the treatment of the light-sensitive photographic material are the 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.

The couplers used in this invention are compared with known couplers having similar structural formulas in melting point and solubility in high boiling solvent. The solubility is determined by measuring an amount (ml.) of dibutyl phthalate required for completely dissolving 1 g. of coupler at 60° C. The results are shown in Table 1.

As evident from the above Table 1, the novel couplers used in this invention melt at a lower temperature and have better solubility in a high boiling solvent as compared with known couplers and therefore it will be understood that such new couplers are very useful as protected type couplers.

The present invention will be explained in detail by the following examples which are given by way of illustration only and do not intend to limit the scope of the invention thereto.

EXAMPLE 1

20 g. of the present coupler (3) is dissolved at 80° 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% gelatine solution. The resulting mixture is treated in a colloid mill. The coupler dispersion 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 at 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:

	G.
Sodium thiosulfate pentahydrate	250
Water to make up 1000 ml.	

The film is washed with water for 20–25 minutes and dried. A brilliant yellow dye image having a maximum absorption at 455 $m\mu$ is obtained.

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EXAMPLE 2

10 g. of the present coupler (13) is dissolved at 60° 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 200 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.
Metol	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 12 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 washed for 20 minutes with running water and dried. A yellow dye image having good transparency and showing a maximum absorption at 450 $m\mu$ is obtained.

EXAMPLE 3

10 g. of the present coupler (6) 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-phenylene - diamine sulfite	2.5
Anhydrous sodium sulfite	2.0
Hydroxylamine hydrochloride	1.0
Sodium carbonate (monohydrate)	82.0
Potassium bromide	2.0
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 chloride	30.0
Sodium carbonate (monohydrate)	20.0
Potassium bromide	30.0
Sodium thiosulfate (pentahydrate)	200.0
Water to make up 1000 ml.	

The material is washed with water for 20 minutes and then treated for 2 minutes in a stabilizing bath and dried.

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A yellow dye image having a maximum absorption at 450 m μ is obtained. This image is excellent in fastness to light and heat as well as in storability.

When the present coupler (7) is used in a similar manner as above in place of the coupler (6), a yellow dye image having the maximum absorption at 460 m μ and excellent in fastness to light and heat as well as in storability is obtained.

EXAMPLE 4

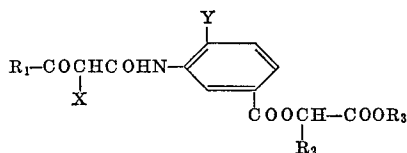
2.0 g. of the present coupler (12) is dissolved in 5 ml. of butyl acetate. The resulting solution is mixed with 1.5 ml. of an aqueous solution of 10% Alkanol B and 20 ml. of an aqueous 5% gelatine solution and the mixture is treated in a mill.

The coupler dispersion thus obtained is added to 100 g. of a blue light-sensitive high speed gelatino-silver bromide emulsion, which is then coated on a film base and dried.

The light-sensitive photographic material thus obtained is then exposed to light and treated with the developing solution as used in Example 1. A brilliant yellow dye image having a maximum absorption at 460 m μ is obtained.

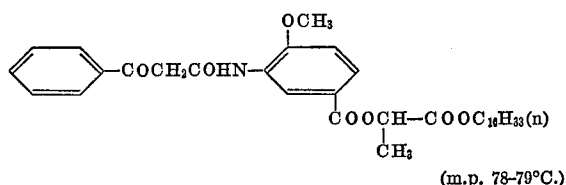
What we claim is:

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



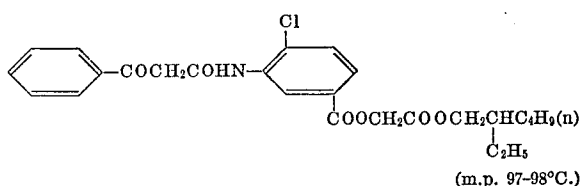
wherein X is hydrogen or halogen; Y is hydrogen, lower alkyl, lower alkoxy, aryloxy or halogen, R₁ is tert. butyl or a phenyl group; R₂ is hydrogen or C₁₋₁₄ alkyl which may contain a branched chain; R₃ is C₁₋₁₈ alkyl which may contain a branched chain; sum of carbon atoms of R₂ and R₃ being 8 or more.

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

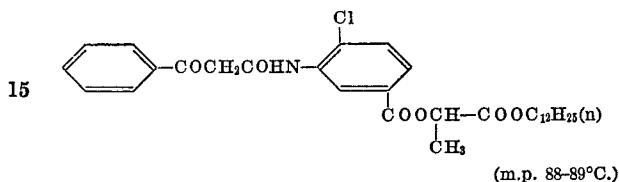


3. A light-sensitive silver halide color photographic emulsion as claimed in claim 1, wherein said yellow coupler is one having the following formula

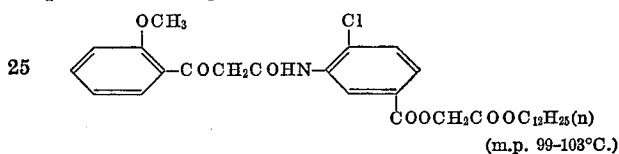
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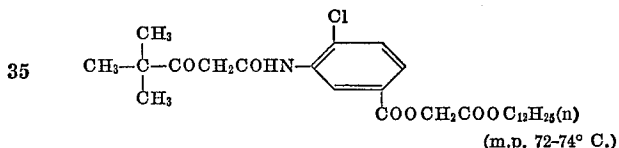
4. A light-sensitive silver halide color photographic emulsion as claimed in claim 1, wherein said yellow coupler is one having the following formula



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



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



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.

8. A light-sensitive silver halide color photographic emulsion as claimed in claim 1 wherein the phenyl group is a substituted phenyl group whose substituents are selected from the group consisting of alkyl, alkoxy and halo groups.

References Cited

UNITED STATES PATENTS

3,551,155 12/1970 Yoshida et al. 96-100

J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

96-55