

PATENT SPECIFICATION

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 798 79Y KD KM KR KS KW KY KZ
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(54) YELLOW COUPLER COMPOUNDS

(71) We, KONISHIROKU PHOTO INDUSTRY CO. LTD., a Japanese body Corporate of 1—10, 3-Chome, Nihonbachi-Muro-Nachi, Chuo-ku Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to new compounds and their use as yellow couplers in photography. In a particular aspect, the present invention pertains to a process for forming yellow dye images in color photographic elements using the new compounds as 2-equivalent yellow dye image-forming couplers.

15 A photographic process for forming a dye image by exposing a photographic element containing couplers and then developing the exposed photographic element with a developer containing an aromatic primary amine type developing agent as active ingredient is already well known. Among the couplers used in the abovementioned process, the yellow
 20 coupler has an active methylene group which is useful for forming a yellow dye by coupling with an oxidation product of the aromatic amine type developing agent. In the case where this active methylene has not been substituted, 4 molecules of silver halide are required in order to form 1 molecule of the dye at the time of development. Accordingly, the said coupler is called a 4-equivalent coupler. It is also well known, however, that the same
 30 dye as in the case of the above-mentioned coupler having the said active methylene can be formed from a coupler, in which one of the hydrogen atoms of the active methylene contained therein has been substituted by a halogen atom, e.g. a chlorine atom. In this case, the halogen atom is released during the color development reaction and 2 molecules of developed silver halide can form 1 molecule of a dye, so that the said coupler is called a

2-equivalent coupler. The 2-equivalent coupler has such advantages as mentioned below over the 4-equivalent coupler.

1. The coupling rate is more enhanced than in the case of the conventional 4-equivalent coupler.

2. The amount of silver halide may be decreased to one half of the amount required for formation of the same dye as in the case of the 4-equivalent coupler, so that the production cost of photographic material can be reduced.

3. The emulsion layer can be made thinner, and the color image obtained is improved in resolution and sharpness.

4. In the case of a multi-layered photographic element, the permeation of light into the lower layers is improved to provide an excellent photographic speed.

Due to the above-mentioned advantages, the use of the 2-equivalent coupler makes it extremely successful for formation of a color image in a multi-layered color photographic element.

Such 2-equivalent coupler as mentioned above is a yellow image-forming coupler containing an active methylene group, one of the hydrogen atoms of which has been substituted, and the substituent contained in said active methylene group has the property that it is liberated at the time of color development.

A 2-equivalent coupler is known which tends to form color stains such as fog and the like and has a property of disturbing the developability of a photographic material containing said coupler. However, the 2-equivalent coupler of the present invention is not only colorless but also high in reactivity and scarcely forms stains. Further, a yellow dye formed at the time of color development from the yellow coupler of the present invention is excellent in fastness to light, humidity and heat, has no unnecessary absorption in the long wavelength region, has less absorption in the

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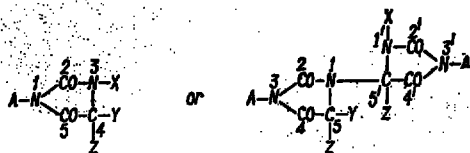
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green light region of the spectrum, shows sharp absorptions, and provides an extremely favorable hue at the time of color reproduction.

- 5 The present invention provides compounds of the general formula:



wherein A represents a group derivable by removing a hydrogen atom from an active methylene group of an active methylene group-containing yellow image-forming coupler; X represents a hydrogen atom, or an alkyl, acyl, carboxymethyl, alkoxy-carbonylmethyl, carbamylmethyl, aryl or aralkyl group, the aryl or aralkyl group being substituted or unsubstituted in the aromatic ring, or a nitro or amino group; and each of Y and Z independently represents a hydrogen atom, or an alkyl, ureido, aryl or aralkyl group, the aryl or aralkyl group being substituted or unsubstituted in the aromatic ring, or a styryl or anilino group, or Y and Z together represent a benzylidene group.

In the above formula Y and Z preferably both represent hydrogen atoms or methyl groups or one represents phenyl, *p*-methylbenzyl or ureido and the other a hydrogen atom.

Preferred meanings of X are a hydrogen atom or an alkyl, acetyl, phenyl, substituted phenyl, benzyl or ethoxycarbonylmethyl group.

The group A is preferably derivable by removing one of the hydrogen atoms from a group $-\text{CH}_2-\text{CO}-$, i.e. a group having a $-\text{CH}_2-$ group activated by being adjacent to carbonyl, present in a yellow image-forming coupler. The $-\text{CH}_2-$ group may have two neighbouring carbonyl groups, i.e. be present as $-\text{CO}-\text{CH}_2-\text{CO}-$. Examples of suitable A groups are those present in the exemplified compounds (1) to (16) hereinafter described.

The invention further provides a process for forming a yellow dye image, which process comprises developing an exposed light-sensitive silver halide emulsion carried on a support, the emulsion containing as a coupler a compound of the invention, or which process comprises color developing an exposed light-sensitive silver halide emulsion carried on a support, the emulsion not containing said coupler, with a developer liquid containing said coupler.

Also within the scope of the invention are (1) a photographic element which comprises a support carrying a layer of a light-sensitive silver halide emulsion, which element includes a yellow image-forming layer comprising a compound of the invention and (2) a developer

for exposed light-sensitive silver halide color photographic emulsions which comprises a *p*-phenylenediamine type developing agent and a compound of the invention as coupler.

Typical examples of the heterocyclic substituent of the coupler used in the present invention are as follows:

2,5-Dioxo-1-imidazolidinyl

3-Methyl-2,5-dioxo-1-imidazolidinyl

3-Ethyl-2,5-dioxo-1-imidazolidinyl

3-Propyl-2,5-dioxo-1-imidazolidinyl

3-Isopropyl-2,5-dioxo-1-imidazolidinyl

3-Phenyl-2,5-dioxo-1-imidazolidinyl

3-(*p*-Chlorophenyl)-2,5-dioxo-1-imidazolidinyl

3-(*o*-Tolyl)-2,5-dioxo-1-imidazolidinyl

3-(*m*-Tolyl)-2,5-dioxo-1-imidazolidinyl

3-(*p*-Tolyl)-2,5-dioxo-1-imidazolidinyl

3-(4-Bromo-*m*-tolyl)-2,5-dioxo-1-imidazolidinyl

3-(2,4-Xylyl)-2,5-dioxo-1-imidazolidinyl

3-Mesityl-2,5-dioxo-1-imidazolidinyl

3-(*p*-Methoxyphenyl)-2,5-dioxo-1-imidazolidinyl

3-(*p*-Ethoxyphenyl)-2,5-dioxo-1-imidazolidinyl

3-(2-Bromo-4-ethoxyphenyl)-2,5-dioxo-1-imidazolidinyl

3-Acetyl-2,5-dioxo-1-imidazolidinyl

3-Carboxymethyl-2,5-dioxo-1-imidazolidinyl

3-Methoxycarbonylmethyl-2,5-dioxo-1-imidazolidinyl

3-Ethoxycarbonylmethyl-2,5-dioxo-1-imidazolidinyl

3-Carbamylmethyl-2,5-dioxo-1-imidazolidinyl

4-Methyl-2,5-dioxo-1-imidazolidinyl

3,4-Dimethyl-2,5-dioxo-1-imidazolidinyl

3,4-Diethyl-4-methyl-2,5-dioxo-1-imidazolidinyl

4-Ethyl-2,5-dioxo-1-imidazolidinyl

3-Phenyl-4-methyl-2,5-dioxo-1-imidazolidinyl

3-(*o*-Tolyl)-4-ethyl-2,5-dioxo-1-imidazolidinyl

3-Acetyl-4-methyl-2,5-dioxo-1-imidazolidinyl

4,4-Dimethyl-2,5-dioxo-1-imidazolidinyl

3,4,4-Trimethyl-2,5-dioxo-1-imidazolidinyl

3-Naphthyl-4,4-dimethyl-2,5-dioxo-1-imidazolidinyl

4,4-Diethyl-2,5-dioxo-1-imidazolidinyl

4-Phenyl-2,5-dioxo-1-imidazolidinyl

4-(*p*-Chlorophenyl)-2,5-dioxo-1-imidazolidinyl

3-Methyl-4-phenyl-2,5-dioxo-1-imidazolidinyl

3-Benzyl-2,5-dioxo-1-imidazolidinyl

3-(*p*-Methylbenzyl)-2,5-dioxo-1-imidazolidinyl

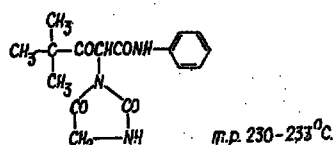
3-Benzyl-4-methyl-2,5-dioxo-1-imidazolidinyl

- 4-Benzyl-2,5-dioxo-1-imidazolidinyl
 4-Phenethyl-2,5-dioxo-1-imidazolidinyl
 4,4-Diphenyl-2,5-dioxo-1-imidazolidinyl
 4-Ureido-2,5-dioxo-1-imidazolidinyl
 5 3-Methyl-4-ureido-2,5-dioxo-1-imidazolidinyl
 3-Nitro-2,5-dioxo-1-imidazolidinyl
 3-Amino-2,5-dioxo-1-imidazolidinyl
 3-Nitro-4-methyl-2,5-dioxo-1-imidazolidinyl
 10 4-Benzylidene-2,5-dioxo-1-imidazolidinyl
 4-Styryl-2,5-dioxo-1-imidazolidinyl
 4-Anilino-4-phenyl-2,5-dioxo-1-imidazolidinyl
 15 2,4,2',4'-Tetraoxo-1,5'-biimidazolidine-3,3'-diyl.

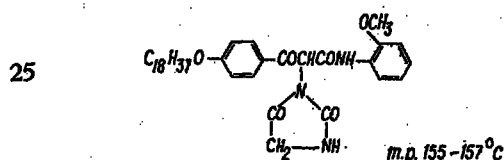
Typical examples of the couplers of the present invention are shown below.

Exemplified couplers:

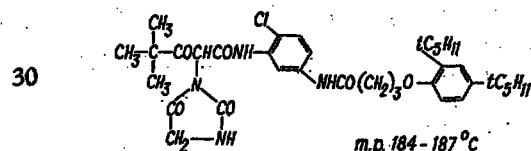
- 20 (1) α - (2,5-Dioxo-1-imidazolidinyl) - α - pivalyl - acetanilide



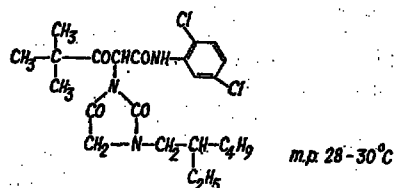
- (2) α - (2,5-Dioxo-1-imidazolidinyl) - α - (p-octadecyloxybenzoyl) - 2-methoxy - acetanilide



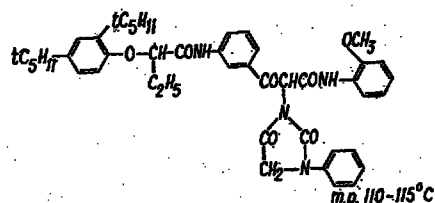
- (3) α - (2,5-Dioxo-1-imidazolidinyl) - α - pivalyl - 2-chloro-5-[γ -(2,4-di-t-amylphenoxy)-butyramido]-acetanilide



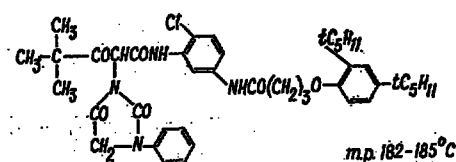
- (4) α - [3-(2-Ethylhexyl)-2,5-dioxo-1-imidazolidinyl] - α - pivalyl - 2,5-dichloroacetanilide



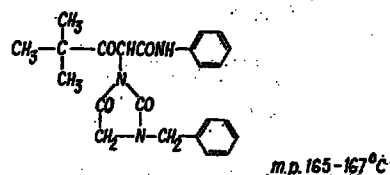
- (5) α - (3-Phenyl-2,5-dioxo-1-imidazolidinyl) - α - {3-[α -(2,4-di-t-amylphenoxy)butyramido]-benzoyl} - 2-methoxyacetanilide 35



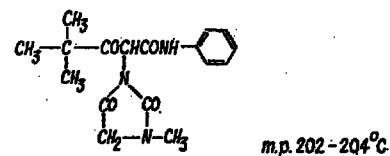
- (6) α - (3-Phenyl-2,5-dioxo-1-imidazolidinyl) - α - pivalyl - 2-chloro-5-[γ -(2,4-di-t-amylphenoxy)-butyramido]-acetanilide 40



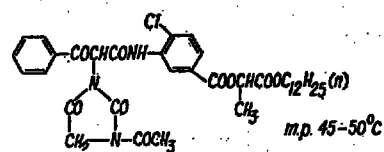
- (7) α - (3-Benzyl-2,5-dioxo-1-imidazolidinyl) - α - pivalyl - acetanilide 45



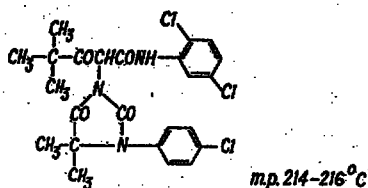
- (8) α - (3-Methyl-2,5-dioxo-1-imidazolidinyl) - α - pivalyl - acetanilide 50



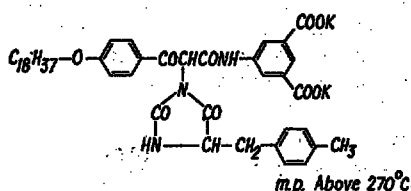
- (9) α - (3-Acetyl-2,5-dioxo-1-imidazolidinyl) - α - benzoyl - 2-chloro-5-[1-(n-dodecyloxy-carbonyl)ethoxycarbonyl]-acetanilide 55



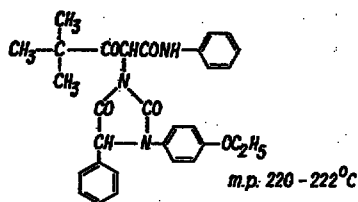
- (10) α - [3-(p-Chlorophenyl)-4,4-dimethyl-2,5-dioxo-1-imidazolidinyl] - α - pivalyl - 2,5-dichloroacetanilide 60



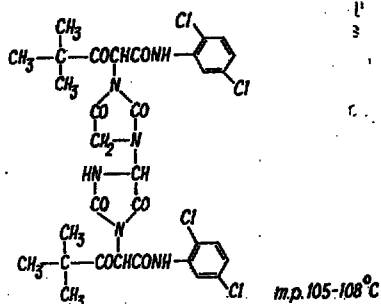
- (11) α - [4 - (p - Methylbenzyl) - 2,5-dioxo - 1 - imidazolidinyl] - α - (p-octadecyloxybenzoyl) - 3,5 - dicarboxyacetanilide dipotassium salt



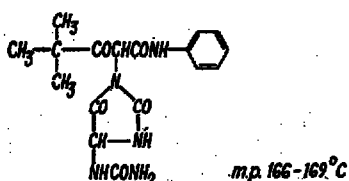
- (12) α - [3 - (p - Ethoxyphenyl) - 4-phenyl - 2,5 - dioxo - 1 - imidazolidinyl] - α - pivalyl - acetanilide



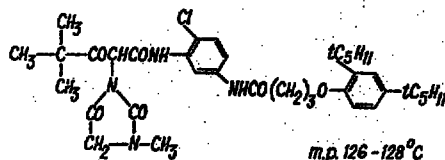
- (13) α, α' - (2,4,2',4' - Tetraoxo - 1,5'-biimidazolidine - 3,3' - diyl) - bis - (α -pivalyl - 2,5 - dichloroacetanilide)



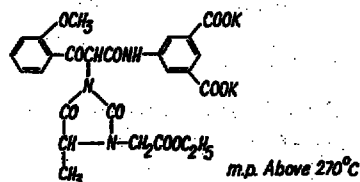
- (14) α - (4 - Ureido - 2,5 - dioxo - 1-imidazolidinyl) - α - pivalyl - acetanilide



- (15) α - (3 - Methyl - 2,5 - dioxo - 1-imidazolidinyl) - α - pivalyl - 2-chloro - 5 - [γ - (2,4 - di - *t* - amylphenoxy) - butyramido] - acetanilide



- (16) α - (4 - Methyl - 3 - ethoxycarbonylmethyl - 2,5 - dioxo - 1 - imidazolidinyl) - α - (o - methoxybenzoyl) - 3,5-dicarboxyacetanilide dipotassium salt



The compounds of the invention can be synthesized by reacting a yellow image-forming coupler having an active methylene group, in which one of the hydrogen atoms of the active methylene group which is bonded to two carbonyl groups has been substituted by a halogen atom, with a substituted or unsubstituted hydantoin or bihydantoin.

Procedures for synthesizing the couplers used in the present invention are set forth below with reference to Synthesis Examples.

Synthesis Example 1.

Synthesis of the exemplified coupler (1):

A mixture comprising 12.6 g. of α -pivalyl- α -chloroacetanilide and 10 g. of hydantoin potassium salt was reacted under reflux for 6 hours in 200 ml. of acetonitrile. Thereafter, the liquid reaction mixture was filtered, and the filtrate was vaporized to dryness under reduced pressure. The residue obtained was recrystallized from a mixed solvent comprising *n*-hexane and alcohol to obtain 6 g. of white crystalline needles, m.p. 230°-233°C.

Elemental analysis:

	C	H	N
Calculated (%)	60.55	6.03	13.24
Found (%)	60.62	5.86	13.53

Synthesis Example 2.

Synthesis of the exemplified coupler (3):

A mixture comprising 25 g. of α -pivalyl- α -chloro - 2 - chloro - 5 - [γ - (2,4 - di - *t* - amylphenoxy)butyramido] - acetanilide and 8 g. of hydantoin potassium salt was reacted under reflux for 2 hours in 250 ml. of acetonitrile. Thereafter, the liquid reaction mixture was filtered, and the filtrate was

05 vaporized to dryness under reduced pressure. The residue obtained was recrystallized from a mixed solvent comprising *n*-hexane and alcohol to obtain 15 g. of white crystalline powder, m.p. 184—187°C.

Elemental analysis:

	C	H	N	Cl
Calculated (%)	64.60	7.38	8.37	5.92
Found (%)	64.57	7.42	8.34	5.00

Synthesis Example 3.

Synthesis of the exemplified coupler (5):

2 A mixture comprising 22.3 g. of α - {3-[α - (2,4 - di - t - amylphenyl)butyramido]-benzoyl} - α - bromo - 2 - methoxyacetanilide and 10 g. of 1-phenylhydantoin potassium salt was reacted under reflux for 1 hour in 200 ml. of acetonitrile. Thereafter, the liquid reaction mixture was filtered, and the filtrate was vaporized to dryness under reduced pressure. The residue obtained was dissolved in 300 ml. of ethyl acetate, and the resulting solution was washed 2 times with 100 ml. portions of an aqueous 1N-NaOH solution, 1 time with 100 ml. of an aqueous 1N-HCl solution, and 3 times with 100 ml. portions of water. Subsequently, the ethyl acetate solution was vaporized to dryness under reduced pressure, and the residue was washed 3 times with 50 ml. of hot *n*-hexane to obtain 13 g. of a pale yellow powder, m.p. 110—115°C.

Elemental analysis:

	C	H	N
Calculated (%)	71.02	6.88	7.36
Found (%)	71.03	7.15	7.09

Synthesis Example 4.

Synthesis of the exemplified compound (10):

35 A mixture comprising 7.4 g. of α -pivalyl- α - bromo - 2,5 - dichloroacetanilide and 6.2 g. of 1 - (*p* - chlorophenyl) - 5,5 - dimethylhydantoin and 4 g. of triethylamine was reacted under reflux for 4 hours in 150 ml. of acetonitrile. Thereafter, the liquid reaction mixture was vaporized to dryness, and the residue was charged with water and filtered to obtain crystals. The crystals were recrystallized from alcohol to obtain 4 g. of white crystalline mass, m.p. 214—216°C.

Elemental analysis:

	C	H	N	Cl
Calculated (%)	54.92	4.60	8.06	20.26
Found (%)	54.90	4.74	8.21	20.29

Synthesis Example 5.

Synthesis of the exemplified compound (13):

55 A mixture comprising 6.4 g. of α -chloro- α - pivalyl - 2,5 - dichloroacetanilide and 2.8 g. of 1,5'-bihydantoin dipotassium salt was reacted under reflux for 3 hours in 150 ml. of acetonitrile. Thereafter, the liquid reaction mixture was poured into 500 ml. of

water, and deposited white crystals were recovered by filtration. The recovered crystals were recrystallized from a mixed solvent comprising *n*-hexane and ethanol to obtain 4 g. of a white powder, m.p. 105—108°C.

Elemental analysis:

	C	H	N	Cl
Calculated (%)	49.88	4.18	10.90	18.40
Found (%)	49.61	4.30	11.12	18.27

A developing agent used for development in the present process for forming yellow images of light-sensitive color photographic materials is a phenylenediamine type silver halide-developing agent or a *p*-aminophenol type developing agent in which the amino group has not been substituted. Examples of the developing agent are as shown below.

Diethyl - <i>p</i> - phenylenediamine hydrochloride	
Monomethyl - <i>p</i> - phenylenediamine hydrochloride	80
Dimethyl - <i>p</i> - phenylenediamine hydrochloride	
2 - Amino - 5 - diethylaminotoluene hydrochloride	85
2 - Amino - 5 - (N - ethyl - N - dodecylamino) toluene	
N - Ethyl - N - β - methanesulfonamidoethyl - 3 - methyl - 4 - aminoaniline hydrochloride	90
N - Ethyl - N - β - methanesulfonamidoethyl - 4 - aminoaniline	
4 - N - Ethyl - N - β - hydroxyethylaminoaniline.	

Some of the couplers used in the present invention are incorporated in an alkaline developer. The developer may contain a sulfite, carbonate, bisulfite, bromide, or iodide of an alkali metal.

An example of the composition of a typical developer containing the coupler which is used in the present invention is as follows:

2 - Amino - 5 - diethylamino-toluene hydrochloride	2.0 g.	
Anhydrous sodium sulfite	2.0 g.	105
Anhydrous sodium carbonate	20.0 g.	
Potassium bromide	1.0 g.	
Exemplified coupler (1)	2.0 g.	
Water to make	1,000 ml.	

In order to incorporate the couplers used in the present invention in light-sensitive color photographic emulsions, any of the known procedures may be adopted. For example, there may be adopted the following procedure:

One or a mixture of the couplers is dissolved in a high boiling solvent (having a boiling point of more than 175°C.) such as tricresyl phosphate or dibutyl phthalate or in

a low boiling solvent such as ethyl acetate or butyl propionate, or in a mixture of high and low boiling solvents. The resulting solution is mixed with an aqueous gelatin solution containing a surface active agent and then emulsified and dispersed by means of a high speed rotary mixer or a colloid mill. The thus obtained coupler dispersion is incorporated directly in a silver halide photographic emulsion, which is then coated on a support, followed by drying. Alternatively, the above-mentioned coupler dispersion is set, extruded into the form of noodles, freed from any low boiling solvent by water-washing or the like means, and incorporated in a silver halide photographic emulsion, which is then coated on a support, followed by drying. In this case, the amount of the coupler to be incorporated is preferably 10 to 300 g. per mole of the silver halide used, though the amount may be varied according to the application purpose of the resulting photographic element.

Among the 2-equivalent yellow dye image-forming couplers used in the present invention, the exemplified couplers (5), (6) and (9) can be dispersed into a photographic emulsion according to the above-mentioned procedure without using the high boiling solvent; the exemplified coupler (11) can be dispersed in a photographic emulsion according to the Fischer's dispersion method; the exemplified coupler (1) can be incorporated into a developer; and the exemplified coupler (4) can be used for diffusion transfer since it forms a diffusing dye.

For the preparation of photographic emulsions used in the present invention, various silver halides such as silver chloride, silver iodobromide and silver chlorobromide may be used. Further, the emulsions may have been subjected to chemical sensitization or optical sensitization using a carbocyanine dye or merocyanine dye, and may contain ordinary photographic additives, for example, anti-foggant, stabilizer, anti-stain agent, anti-irradiation agent, high molecular additive, hardener, and coating aid.

A light-sensitive color photographic element containing the coupler of the present invention may also contain an ultraviolet absorber, whereby the resulting color image can further be enhanced in fastness. Further, the color developer may contain a develop-

ment-controlling agent such as citrazinic acid in addition to the aforesaid developing agent. The present invention is illustrated in further detail below with reference to Examples.

Example 1.

20.0 Grams of each of the exemplified couplers (3), (6) and (9) were completely dissolved at 60°C. in a mixed solvent comprising 20 ml. of dibutyl phthalates and 60 ml. of ethyl acetate. This solution was mixed with 10 ml. of a 6% aqueous solution of Alkanol B (alkylnaphthalenesulfonate) and 200 ml. of a 6% aqueous gelatin solution, and the mixed solution was emulsified and dispersed by means of a colloid mill to form a coupler dispersion.

The above-mentioned coupler dispersion was added to 1 kg. of a high speed silver iodobromide emulsion, which was then coated on a film base and dried to prepare a light-sensitive photographic element in the form of a stable film. The photographic element was exposed according to an ordinary procedure, and then developed at 20°C. for 10 minutes with a developer of the following composition:

N - Ethyl - N - β - methane-			
sulfonamidoethyl-3-methyl-			
4-aminoaniline sulfate	5.0 g.		
Anhydrous sodium sulfite	2.0 g.		
Benzyl alcohol	3.8 g.		
Sodium carbonate (mono-			
hydrate)	50.0 g.		
Potassium bromide	1.0 g.		
Sodium hydroxide	0.55 g.		
Water to make	1000 ml		

Subsequently, the developed photographic element was subjected to ordinary stopping, fixing and bleaching treatments.

The absorption maximum (λ -max), maximum density (D-max) and storability of each of the thus obtained color images were as set forth in Table 1, in which are also shown those of color images formed by using light-sensitive color photographic elements prepared in the same manner as above, except that the couplers used were identical in structure with those used in the above but had not been substituted in hydrogen atoms of active methylene groups.

TABLE I

Run No.	Coupler	λ -max (m μ)	D-max	Color image	
				Ratio of residual dye	
				Light fastness	Humidity fastness
1	Control	447	1.22	96	99
2	Exemplified coupler (3)	447	2.40	96	99
3	Control	447	1.23	95	99
4	Exemplified coupler (6)	447	2.12	97	100
5	Control	452	1.90	75	100
6	Exemplified coupler (9)	453	2.40	78	100

Control: Active methylene - unsubstituted type coupler otherwise identical in structure with the exemplified coupler.

5 λ -max and D-max: Calculated by measuring the spectral absorption and density of each color image.

Ratio of residual dye: Ratio (%) of residual dye after treating each color image at a portion where the initial density was 1.0.

10 Treatment conditions:

Light fastness: Xenon arc lamp, 50°C. 30 hrs.

15 Humidity fastness: 50°C. 80% RH, 7 days.

As shown in Table 1, the couplers of the present invention display favorable characteristics and are usable in multi-layered and multicolor photographic elements.

20 Example 2.

In the same manner as in Example 1, each of the exemplified couplers (6) and (15) was dispersed in a gelatin-silver iodobromide emulsion. The amount of the silver halide used was the same as in Example 1. Subsequently, the emulsion was treated in the same manner as in Example 1 to prepare a light-sensitive photographic element containing each of the exemplified couplers (6) and (15).

30 For comparison, a control photographic element was prepared in the same manner as above, except that the coupler used was a coupler not substituted at an active methylene group but identical in other structure with the coupler of the present invention and therefore a 4-equivalent coupler.

35 Each of the thus prepared photographic elements was exposed and then developed

with the same developer as in Example 1.

The density of yellow dye formed at each stage by exposing each photographic element to blue light was measured by means of a densitometer and shown in the accompanying drawing, in which the horizontal axis represents the amount of exposure (log E) and the vertical axis represents the density. In the drawing, the curve 1 shows the case of the control photographic element containing the 4-equivalent coupler, and the curves 2 and 3 show the cases of the photographic elements containing the exemplified couplers (6) and (15), respectively. The amount of silver halide contained in each of the photographic elements according to the present invention was identical with that of the control photographic element. As is clear from the drawing, the 2-equivalent couplers of the present invention are sufficiently useable even when the amount of silver is reduced to one half of the amount used hitherto.

(1): Unsubstituted type coupler identical in other structure with the coupler of the present invention.

(2): Exemplified coupler (6).

(3): Exemplified coupler (15).

Example 3.

The exemplified coupler (11) was dispersed in a mixed solvent comprising ethanol and water, and then dissolved by addition of a 10% caustic soda solution. This solution was mixed with an aqueous gelatin solution containing 12% of gelatin and 5.13 g. of Alkanol B, and the mixed solution was neutralized with acetic acid.

Subsequently, the solution was dispersed in a silver halide emulsion containing silver iodobromide, and the emulsion was coated on a support and then dried to prepare a photographic element. The thus prepared photographic material was exposed according to an ordinary procedure, and then treated in the same manner as in Example 1.

The photographic properties of the result-

ing color image were as set forth in Table 2, in which are also shown the photographic properties of a color image obtained by use of a control photographic element prepared in the same manner as above, except that the coupler used was an unsubstituted type coupler identical in other structure with the coupler of the present invention.

TABLE 2

Coupler	Fog	λ -max (m μ)	D-max
Exemplified coupler (11)	0.12	450	2.06
Unsubstituted type coupler	0.10	450	1.85

As is clear from Table 2, the coupler of the present invention shows favorable results even when used according to Fischer's dispersion method.

Example 4.

A photographic emulsion containing the exemplified coupler (4) was coated on a support and then dried to prepare a light-sensitive photographic element. This photographic element was exposed and then treated with an alkaline developer (pH 13) containing 2 g/l of Na₂SO₃ and 11 g/l of 4 - N - ethyl - N - β - hydroxyethyl amino-aniline. The resulting negative was brought into close contact at 24°C. for 3 minutes with an image-receiving sheet containing dimethyl - β - hydroxyethyl - γ - stearamidopropylammonium dihydrogen phosphate (mordant). Thereafter, the image-receiving sheet was peeled off, whereby the yellow dye

formed had transferred to the image-receiving sheet to give an excellent positive image.

Example 5.

An ordinary silver iodobromide emulsion was coated on a support and then dried to prepare a light-sensitive element. This photographic element was subjected to an ordinary external development using the exemplified coupler (1)-containing developer mentioned previously.

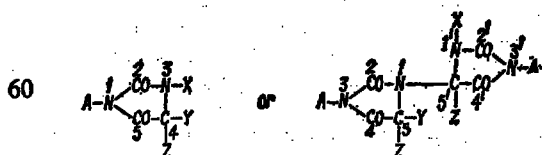
The photographic properties of the resulting color image were as set forth in Table 3, in which are also shown the photographic properties of a color image obtained by treating the photographic element with an external developer containing an unsubstituted type coupler identical in other structure with the coupler of the present invention.

TABLE 3

Coupler	Fog	λ -max (m μ)	D-max
Exemplified coupler (1)	0.05	442	2.01
Unsubstituted type coupler	0.04	443	1.47

WHAT WE CLAIM IS:—

1. Compounds of the general formula:



wherein A represents a group derivable by removing a hydrogen atom from an active methylene group of an active methylene group-containing yellow image-forming coupler; X represents a hydrogen atom, or an alkyl, acyl, carboxymethyl, alkoxycarbonylmethyl, carbamylmethyl, aryl or aralkyl group, the aryl or aralkyl group being substituted or unsubstituted in the aromatic ring,



Subsequently, the solution was dispersed in a silver halide emulsion containing silver iodobromide, and the emulsion was coated on a support and then dried to prepare a photographic element. The thus prepared photographic material was exposed according to an ordinary procedure, and then treated in the same manner as in Example 1.

The photographic properties of the result-

ing color image were as set forth in Table 2, in which are also shown the photographic properties of a color image obtained by use of a control photographic element prepared in the same manner as above, except that the coupler used was an unsubstituted type coupler identical in other structure with the coupler of the present invention.

TABLE 2

Coupler	Fog	λ -max (m μ)	D-max
Exemplified coupler (11)	0.12	450	2.06
Unsubstituted type coupler	0.10	450	1.85

As is clear from Table 2, the coupler of the present invention shows favorable results even when used according to Fischer's dispersion method.

Example 4.

A photographic emulsion containing the exemplified coupler (4) was coated on a support and then dried to prepare a light-sensitive photographic element. This photographic element was exposed and then treated with an alkaline developer (pH 13) containing 2 g/l of Na_2SO_3 and 11 g/l of 4-N-ethyl-N- β -hydroxyethyl amino-aniline. The resulting negative was brought into close contact at 24°C. for 3 minutes with an image-receiving sheet containing dimethyl- β -hydroxyethyl- γ -stearamidopropylammonium dihydrogen phosphate (mordant). Thereafter, the image-receiving sheet was peeled off, whereby the yellow dye

formed had transferred to the image-receiving sheet to give an excellent positive image.

Example 5.

An ordinary silver iodobromide emulsion was coated on a support and then dried to prepare a light-sensitive element. This photographic element was subjected to an ordinary external development using the exemplified coupler (1)-containing developer mentioned previously.

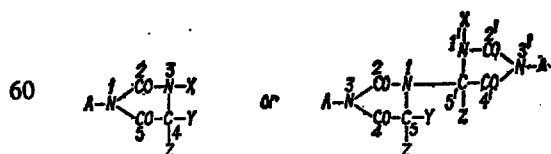
The photographic properties of the resulting color image were as set forth in Table 3, in which are also shown the photographic properties of a color image obtained by treating the photographic element with an external developer containing an unsubstituted type coupler identical in other structure with the coupler of the present invention.

TABLE 3

Coupler	Fog	λ -max (m μ)	D-max
Exemplified coupler (1)	0.05	442	2.01
Unsubstituted type coupler	0.04	443	1.47

WHAT WE CLAIM IS:—

1. Compounds of the general formula:



wherein A represents a group derivable by removing a hydrogen atom from an active methylene group of an active methylene group-containing yellow image-forming coupler; X represents a hydrogen atom, or an alkyl, acyl, carboxymethyl, alkoxy-carbonylmethyl, carbamylmethyl, aryl or aralkyl group, the aryl or aralkyl group being substituted or unsubstituted in the aromatic ring,

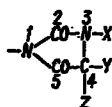


or a nitro or amino group; and each of Y and Z independently represents a hydrogen atom, or an alkyl, ureido, aryl or aralkyl group, the aryl or aralkyl group being substituted or unsubstituted in the aromatic ring,

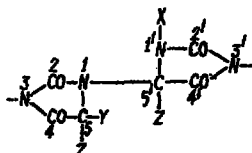
5 2. Compounds according to claim 1 wherein Y and Z both represent hydrogen atoms or methyl groups or one represents phenyl, *p*-methylbenzyl or ureido and the other a hydrogen atom.

10 3. Compounds according to claim 1 or 2 wherein X represents a hydrogen atom, or an alkyl, acetyl, phenyl, substituted phenyl, benzyl or ethoxycarbonylmethyl group.

15 4. Compounds according to claim 1 wherein the group



or



20 is any one of the 1-imidazolidinyl or 1,5'-biimidazolidine-3,3'-diyl groups specifically hereinbefore listed.

25 5. Compounds according to any preceding claim wherein A represents a group derivable by removing one of the hydrogen atoms from a group $\text{—CH}_2\text{—CO—}$ present in a yellow image-forming coupler.

30 6. Compounds according to claim 5 wherein A represents a group derivable by removing one of the hydrogen atoms from a group of $\text{—CO—CH}_2\text{—CO—}$ present in a yellow image-forming coupler.

35 7. Compounds according to any preceding claim wherein the A group is any of those present in the compounds (1) to (16) hereinbefore set forth.

40 8. The compounds α - (2,5 - dioxo - 1-imidazolidinyl) - α - pivalyl - acetanilide, α - (2,5 - dioxo - 1 - imidazolidinyl) - α - (*p* - octadecyloxybenzoyl) - 2 - methoxyacetanilide, α - (2,5 - dioxo - 1 - imidazolidinyl) - α - pivalyl - 2 - chloro - 5 - [γ - (2,4 - di - *t* - amylphenoxy) - butyramido] - acetanilide, α - [3 - (2 - ethylhexyl) - 2,5-dioxo - 1 - imidazolidinyl] - α - pivalyl - 2,5 - dichloroacetanilide, α - (3 - phenyl - 2,5 - dioxo - 1 - imidazolidinyl) - α - {3 - [α - (2,4 - di - *t* - amylphenoxy)butyramido] - benzoyl} - 2 - methoxy - acetanilide, α - (3 - phenyl - 2,5 - dioxo - 1 -

imidazolidinyl) - α - pivalyl - 2 - chloro - 5 - [γ - (2,4 - di - *t* - amylphenoxy) - butyramido] - acetanilide, α - (3 - benzyl - 2,5-dioxo - 1 - imidazolidinyl) - α - pivalyl - acetanilide, α - (3 - methyl - 2,5 - dioxo - 1 - imidazolidinyl) - α - pivalyl - acetanilide, α - (3 - acetyl - 2,5 - dioxo - 1 - imidazolidinyl) - α - benzoyl - 2 - chloro - 5 - [1 - (*n* - dodecyloxycarbonyl)ethoxycarbonyl] - acetanilide, α - [3 - *p* - chlorophenyl] - 4,4-dimethyl - 2,5 - dioxo - 1 - imidazolidinyl - α - pivalyl - 2,5 - dichloroacetanilide, α - [4 - (*p* - methylbenzyl) - 2,5 - dioxo - 1 - imidazolidinyl] - α - (*p* - octadecyloxybenzoyl) - 3,5 - dicarboxyacetanilide dipotassium salt, α - [3 - (*p* - ethoxyphenyl) - 4 - phenyl - 2,5 - dioxo - 1 - imidazolidinyl] - α - pivalyl - acetanilide, α , α' - (2,4,2',4' - tetraoxo - 1,5' - biimidazolidine, 3,3' - diyl) - bis - (α - pivalyl - 2,5 - dichloroacetanilide), α - (4 - ureido - 2,5 - dioxo - 1 - imidazolidinyl) - α - pivalyl - acetanilide, α - (3 - methyl - 2,5 - dioxo - 1 - imidazolidinyl) - α - pivalyl - 2 - chloro - 5 - [γ - (2,4 - di - *t* - amylphenoxy) - butyramido] - acetanilide and α - (4 - methyl - 3 - ethoxycarbonylmethyl - 2,5 - dioxo - 1 - imidazolidinyl) - α - (*o* - methoxybenzoyl) - 3,5 - dicarboxyacetanilide dipotassium salt.

9. A process for forming a yellow dye image, which process comprises developing an exposed light-sensitive silver halide emulsion carried on a support, the emulsion containing as a coupler a compound claimed in claim 1, or which process comprises color-developing an exposed light-sensitive silver halide emulsion carried on a support, the emulsion not containing said coupler, with a developer liquid containing said coupler.

10. A process according to claim 9 wherein the coupler is a compound claimed in any one of claims 2—8.

11. A support carrying a yellow dye image obtained by a process claimed in claim 9 or 10.

12. A photographic element which comprises a support carrying a layer of a light-sensitive silver halide emulsion, which element includes a yellow image-forming layer comprising a compound claimed in any one of claims 1—8.

13. A developer for exposed light-sensitive silver halide color photographic emulsions which comprises a *p*-phenylenediamine type developing agent and as a coupler a compound claimed in any one of claims 1—8.

J. A. KEMP & CO.,
Chartered Patent Agents,
14 South Square,
Gray's Inn, London, WC1R 5EU.