

[54] SILVER HALIDE EMULSION CONTAINING KETOMETHYLENE PHOTOGRAPHIC COLOR-FORMING COUPLERS

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[75] Inventor: Stanley S. Kertel, Webster, N.Y.

Primary Examiner—J. Travis Brown
Attorney, Agent, or Firm—John T. Lewis

[73] Assignee: Eastman Kodak Company, Rochester, N.Y.

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[57] ABSTRACT

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This invention relates to photographic elements and to photographic emulsions and photographic color developer compositions that contain certain color-forming couplers of the 1,2,4-benzothiadiazine-1,1-dioxide class having an open chain ketomethylene group on the carbon atom in the 3-position.

[51] Int. Cl. G03c 1/40

[58] Field of Search 96/100, 56.2, 56.3, 56.6

[56] References Cited
UNITED STATES PATENTS

2,435,173 1/1948 Bavley 96/100

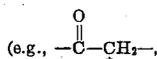
21 Claims, No Drawings

SILVER HALIDE EMULSION CONTAINING KETOMETHYLENE PHOTOGRAPHIC COLOR-FORMING COUPLERS

This invention relates to a new class of cyclic ketomethylene color coupler compounds. The color couplers of this invention are readily synthesized benzothiazine compounds which can be efficiently reacted with an oxidized color developing agent to obtain stable, yellow photographic dyes.

BACKGROUND

Colored photographic images are typically obtained in the photographic art by coupling a by-product from the silver image development process (i.e., an oxidized primary aromatic amino developing agent) with a color-forming coupler compound. The subtractive process of color formation is ordinarily employed. Coupler compounds employed to produce yellow or magenta photographic dyes, for instance, are generally of the so-called "open chain ketomethylene" type, as described for instance on pages 822-823 of Kirk-Othmer, *ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY*, Volume 5, Copyright 1964 and in the Barr et al. U.S. Pat. No. 3,701,783. Open-chain ketomethylene couplers couple at the carbon atom forming the methylene moiety adjacent the carbonyl group



* denoting the coupling position). The majority of such couplers are characterized in requiring the development of four silver halide molecules in order to ultimately produce one molecule of dye.

The suitability of an organic compound as a color-forming coupler depends upon more than general reactivity. Consideration must also be given to the color balance, contrast, grain size and general sharpness of the dye images obtained. A coupler should also be stable and produce stable photographic dyes having precise spectral absorption characteristics upon reaction with oxidized developer.

Successful couplers must also possess a number of important ancillary characteristics. It is often desirable, for instance, to utilize non-diffusible couplers. These usually require only minimal amounts of high-boiling coupler solvents and thereby enable the use of thinner and more durable photographic elements. Non-diffusible couplers should also be capable of precise incorporation into a silver halide emulsion without adversely affecting emulsion viscosity, adhesion characteristics of the emulsion layer, or the unity of an emulsion layer during modern high-speed multilayer coating.

Several separate layers may be applied to a film base to obtain a color photographic element. For this reason, coupler-induced changes in the physical properties of the coating can be as important as coupler reactivity with oxidized developer.

OBJECTS

It is an object of this invention to provide a new class of color-forming couplers which will satisfy the numerous requirements for a commercially acceptable color-forming photographic coupler.

It is a further object of this invention to provide new compounds which will readily and efficiently react with oxidized color developer to produce dyes having acceptable stability under normal photographic use conditions.

It is a still further object of this invention to provide novel photographic elements in which the couplers of this invention can be used advantageously.

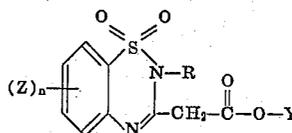
It is still another object of this invention to provide novel photographic emulsion compositions that contain such yellow dye-forming couplers; said emulsion compositions being useful in the manufacture of photographic elements containing at least one layer in which such color couplers are present in a non-diffusible form.

It is still another object of this invention to provide novel photographic color developer compositions which contain, dissolved therein, one or more of such yellow dye-forming color couplers.

DESCRIPTION OF THE INVENTION

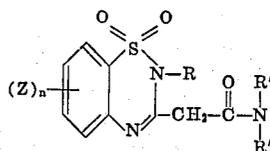
These and other objects of this invention are obtained through the utilization of a class of color-forming coupler compounds capable of forming a dye when reacted with oxidized aromatic primary amino color developing agent and represented by formula (1) or (2):

(1)



or

(2)



wherein

R is hydrogen, or an alkyl group containing up to 15 carbon atoms;

Y is an alkyl or aryl radical;

R' is hydrogen or an alkyl group containing 1-5 carbon atoms;

R'' is an alkyl or aryl group; and

Z is individually defined at each occurrence as a halo group, an alkoxy group or an alkyl group containing 1-18 carbon atoms; and

n is 0-2.

Preferred color coupler compounds of this invention are those in which, in formula (1) or (2) above, R is hydrogen or an alkyl group containing up to 5 carbon atoms (for example, methyl, isopropyl or butyl); Y is an alkoxy group containing up to 25 carbon atoms (such as methoxy, isopropoxy, dodecyloxy), an aryloxy group containing up to 15 carbon atoms (such as phenoxy or naphthoxy), or a halo-, alkoxy-, or alkyl-substituted aryloxy group containing up to 20 carbon atoms (such as chlorophenoxy and decylphenoxy); R' is hydrogen; R'' is alkyl containing 1-22 carbon atoms or aryl such as a mono- or di-substituted phenyl group wherein the substituent(s) on the phenyl group is preferably halo, alkyl, carboxyl, sulfonamido, or alkoxy; and Z is prefer-

ably chloro, alkoxy containing 1-5 carbon atoms or alkyl containing 1-5 carbon atoms when Z is present.

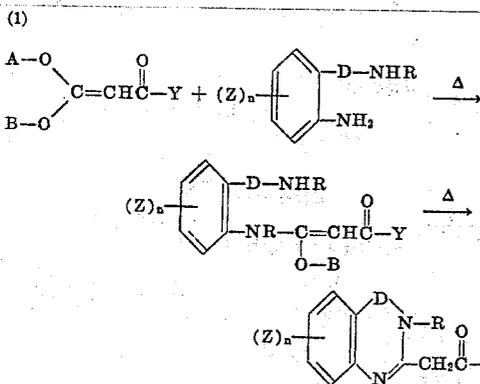
Still further preferred are the following coupler compounds:

- a. 3-(carboxymethyl)-1,2,4-benzothiadiazine-1,1-dioxide
- b. 3-[(4-ethoxyphenyl)carbamyl]methyl-1,2,4-benzothiadiazine-1,1-dioxide
- c. 3-(carboxymethyl)-6-chloro-1,2,4-benzothiadiazine-1,1-dioxide
- d. 3-(phenylcarbamyl)methyl-6-chloro-1,2,4-benzothiadiazine-1,1-dioxide
- e. 3-[(2-chloro-5-methylphenyl)carbamyl]methyl-6-chloro-1,2,4-benzothiadiazine-1,1-dioxide.

This invention relates to the aforementioned coupler compounds, to color developer and photographic emulsion compositions containing them, and to photographic elements in which such coupler compounds are contained in layers which also contain photosensitive silver halide.

Methods of Manufacture

Compounds having the structure of formula (1), above can be prepared via the following general reaction:



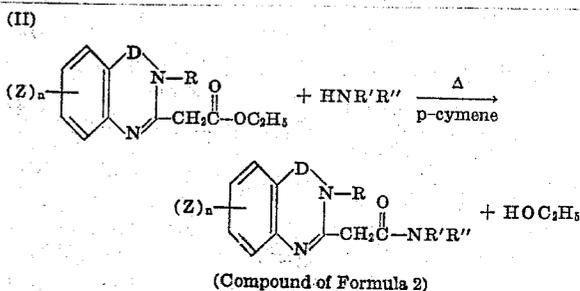
wherein R, Y, Z and n have the same meanings as in formula (1) above, D is a sulfo (SO₂) group, and A and B are preferably lower alkyl such as ethyl.

Generally, the initial reaction to obtain an alkyl ester of formula (1) can be most conveniently effected by contacting and heating an alkoxyacrylate with a substantial amount of an appropriate benzene sulfonamide, preferably in about equimolar amounts under

reflux conditions at atmospheric pressure in the presence of a low boiling aliphatic alcohol (i.e., methyl, ethyl and/or isopropyl alcohol) as reaction solvent. If desired, however, the reaction can also be successfully carried out with an excess (i.e., more than theoretical amount) of sulfonamide reactant and/or in the absence of a reaction solvent and at a temperature up to about 170° C. The reaction is often aided by the presence of acetic acid as catalyst in the reaction mixture.

Lower alkoxy acrylates such as the ethoxy acrylate reactants useful in the manufacture of compounds of formula (1), above are readily obtainable from the corresponding known alkoxy ester of cyanoacetic acid, and α-amino benzene sulfonamide reactants are obtainable commercially (ref. cpd. No. A4543-2; Aldrich Chemical Co., Catalog No. 15, 1970).

Compounds having the structure of formula (2), above, can be prepared via the following general reaction:



wherein D is a sulfo (SO₂) group and R', R'', Z and n have the same meaning as in formula (2) above.

In carrying out reaction (II) set out above to convert an intermediate alkyl ester reactant to the corresponding desired amido product (formula 2), the alkyl ester reactant is preferably contacted and heated with about an equimolar amount of an amine compound of the formula NHR'R'' as above defined, the reaction can be optionally carried out in an inert organic solvent such as xylene or p-isopropyltoluene under reflux conditions and at a temperature up to about 160°C.

Details Concerning the Invention

Typical, non-limiting examples of the valuable color forming coupler compounds of this invention are exemplified with respect to formulae (3) and (4) in Table I, below:

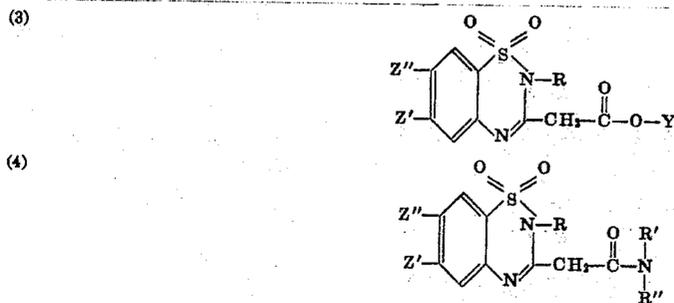


TABLE I

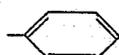
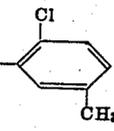
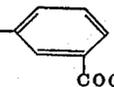
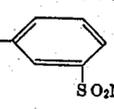
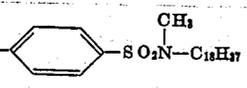
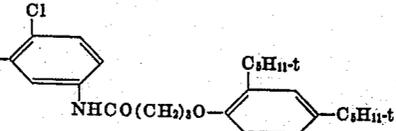
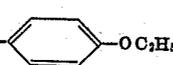
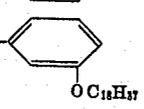
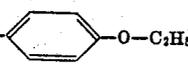
Coupler number	R	R'	Y	R''	Z'	Z''
I.....	H		-C ₂ H ₅		H	H
II.....	H	H			H	H

Table I-Continued

Coupler number	R	R'	Y	R''	Z'	Z''
III	H		-C ₂ H ₅		Cl	H
IV	H	H			Cl	H
V	H	H			Cl	H
VI	H	H			Cl	H
VII	H	H			Cl	H
VIII	H	CH ₃		-C ₁₈ H ₃₇	Cl	H
IX	H	H			Cl	H
X	H	H			Cl	H
XI	H	H			Cl	H
XII	H	H			Cl	H
XIII	H		-CH ₃			
XIV	C ₂ H ₅		-C ₂ H ₅		C ₁₈ H ₃₇	H
XV	C ₁₀ H ₂₁	H			H	H
XVI	CH ₃		-C ₂ H ₅		Cl	H
XVII	H		-C ₂ H ₅		Cl	Cl
XVIII	H	H			Cl	Cl
XIX	CH ₃		-C ₂ H ₅		H	Cl
XX	C ₂ H ₅		-CH ₃		Cl	Cl

Included in Table I are examples of both diffusible and non-diffusible couplers. Thus, it can be appreciated that the non-ballasted coupler materials of this invention can be utilized as part of a color developing solution. The ballasted coupler materials of this invention can be initially incorporated into one or more of the silver halide emulsion layers of a photographic element by known solution and emulsification techniques. Upon reaction of such compounds with oxidized developing agent, either diffusible or non-diffusible dyes can be produced depending upon the attached ballasting and/or solubilizing groups. In addition, the presence of certain substituent groups (such as an alkyl, chloro or bromo) on the benzothiazine nucleus will generally favor a bathochromic shift in maximum light absorption of the resulting dye to a lower wavelength.

Diffusible coupler compounds are illustrated in Table I by couplers I-VII. This type of compound is generally introduced into a color photographic element by inclusion within a developer solution in accordance with art-recognized techniques as summarized, for instance, on

lines 50-65 of Section XXII of PRODUCT LICENSING INDEX, Volume 92, Publication 9232 (December, 1971). An effective amount of diffusible couplers for color photographic purposes can preferably range from about 0.5 grams per liter to 1.9 grams per liter of developer solution. Varying concentrations outside of this range are useful, however, depending upon the desired image processing conditions and the like.

Ballasted, non-diffusible hydrophobic coupler compounds encompassed by this invention (such as, for example, couplers VIII-X in Table I) can be conveniently incorporated into a photographic element either as part of a photographic silver halide emulsion layer or as part of a layer contiguous thereto. This is most conveniently accomplished by initially dissolving the coupler into a high-boiling and/or one or more low-boiling organic solvents. The resulting solution is then dispersed into an aqueous gelatin solution with the aid of an emulsifier, and this coupler dispersion is set, noddled, washed and then melted and dispersed into a light sensitive silver halide gelatin dispersion and thereafter coated onto

a suitable support. Suitable solvents and techniques for this purpose are disclosed, for instance, in U.S. Pat. Nos. 2,949,360; 2,801,171; 2,322,827; and 2,304,939. See, for instance, in section XXII, page 110, lines 1-50 of PRODUCT LICENSING INDEX, Volume 92, Publication 9232 (December, 1971). One or more silver chloride, silver bromide, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide, and silver chloroiodide salts are usually included in photographic elements in which the present couplers are utilized. An effective amount of non-diffusible coupler for color photographic purposes can range from about 25-200 mg/ft² of coated material, a concentration of 30-50 mg/ft² being generally preferred.

Photographic elements suitable according to the present invention comprise:

1. a support such as described in Section X of PRODUCT LICENSING INDEX, Vol. 92, Publication 9232 (December, 1971). Included among the possible supports are layers or films comprising hydrophobic resins which have been electron bombarded as described, for instance, in British Pat. Nos. 971,058; 1,060,526 and U.S. Pat. Nos. 2,864,755 and 2,864,756 to improve adhesion of hydrophilic colloid layers coated over them. Such resin layers or films may be either self-supporting or may be coated over another support layer. Specific supports having useful hydrophobic surfaces include poly(ethylene terephthalate) films electron-bombarded to have a contact angle less than 45° (U.S. Pat. No. 3,220,842), an electron-bombarded surface comprising a chromium halide (U.S. Pat. No. 3,117,865), or electron-bombarded hardened gelatin coated papers (Belgian Pat. No. 671,661), etc. The support layer can be overcoated, if desired, with an antistatic layer to prevent or minimize the build-up of static electricity to objectionable levels during the manufacture and/or processing of the photographic element. Some conventional antistatic layers are described in Section IX of PRODUCT LICENSING INDEX, Vol. 92, p. 108, Publication 9232 (December, 1971).

2. an antihalation layer (attached to the support either directly or indirectly by means of a subbing layer) such as dye-containing gelatin, starch, or the like, as described, for instance, in Glafkides "Photographic Chemistry," Volume 1, pages 470-471, Arrowsmith Ltd. 1958;

3. one or more, and preferably three or more, light-sensitive and differently sensitized silver halide emulsion layers coated onto the support; the layers conveniently comprising (a) a red-sensitized layer containing at least one phenolic or α -naphtholic cyan-dye-forming coupler, (ref. Kirk-Othmer—"Encyclopedia of Chemical Technology," Vol. 5, pages 825-826, (1964); (b) a green-sensitized layer containing at least one 5-pyrazolone magenta dye-forming coupler (ref. Kirk-Othmer—"Encyclopedia of Chemical Technology," Vol. 5, pages 823-824 (1964); and (c) a blue-sensitized layer containing at least one coupler compound of the present invention. A Carey-Lea filter layer is preferably interposed between the blue- and green-sensitized layers. See also Sections XV (spectral sensitization) and XXII (Color materials) of PRODUCT LICENSING INDEX, Volume 92, pages 108-110 (December, 1971).

Suitable light-sensitive silver halide emulsions and references describing their preparation and chemical

sensitization thereof are summarized, for instance, on page 107 in Section I and III of PRODUCT LICENSING INDEX, Volume 92, Publication 9232 (December, 1971), and includes emulsions of silver chloride, silver bromide, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide, and silver chloroiodide.

4. One or more gelatin spacer layers between the light-sensitive emulsion layers or the emulsion layers and Carey-Lea filter layer as above described; and

5. a protective, water-permeable overcoat layer, such as gelatin, poly(N-vinyl lactam), gum arabic, hydrophilic copolymer of N-acrylamidoalkyl betain (ref. U.S. Pat. No. 2,833,650), cellulose ethers and esters alkali soluble poly(vinyl phthalate) (ref. U.S. Pat. No. 2,798,004); also water-soluble polymers having varying degrees of solubility, such as poly(vinyl alcohol) (optimally with surfactant), poly(vinyl pyrrolidone), poly(alkylene oxides), poly(vinyl alcohol) and its derivatives such as its partial esters, ethers and acetals exemplified by hydrolyzed and partially hydrolyzed poly(vinylacetate), poly(vinyl acetaldehyde acetal), poly(vinyl butyraldehyde acetal), poly(vinyl sodium o-sulfobenzaldehyde acetal), poly(vinyl disodium 2,4-disulfobenzaldehyde acetal); and water-soluble copolymers and interpolymers exemplified by copoly (methyl vinyl ether/maleic anhydride), copoly(acrylic acid/methacrylic acid, ethyl ester maleic anhydride) and copoly(maleic anhydride/acrylic acid/vinyl acetate). The overcoat layer(s) may conveniently contain an aldehyde scavenger such as described, for instance, in U.S. Pat. Nos. 3,236,652; 3,287,135; 3,220,839; 2,403,927 and British Pat. No. 623,448, and other ingredients such as buffering agents (e.g., an acidic or basic material), lubricating agents, matting agents, and ultraviolet light absorbers such as 2,2'-di-hydroxy 4,4'-dimethoxybenzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diazidostilbene-2,2'-disulfonic acid sodium salt, and sodium-(α -phenylhydrazone).

In addition, photographic materials and elements utilizing the present dye-forming couplers can usefully contain brighteners, such as stilbenes, triazines etc. spectral sensitizing dyes, supersensitizing addenda, and also absorbing and filter dyes as summarized, for instance, on page 109-110 in Sections XIV, XV and XVI of PRODUCT LICENSING INDEX, Volume 92 (December, 1971).

A still further embodiment of the present invention includes photographic elements such as x-ray films which can contain at least one fluorescing screen (such as those described in U.S. Pat. Nos. 3,300,311 and 3,617,285), and one or more silver halide emulsion layers applied directly or indirectly to a support layer. One or more couplers of the present invention can be used in optional combination with one or more cyan dye-forming couplers in one or more layers of an x-ray element. Thus, when an element containing such a combination of couplers plus photosensitive silver halide is exposed and then developed with an aromatic primary amino oxidizable color developer, neutral silver and dye images having increased maximum densities will be produced. This density increase permits the use of a lower silver halide concentration without sacrificing the quality or amount of information obtained from the resulting x-ray picture.

The following preparations and examples are in-

cluded to provide a better understanding of the invention. Preparations A through G, below, illustrate methods of preparing some of the preferred coupler compounds of this invention. Some of the valuable end uses and properties of the coupler compounds of this invention are set out in Examples 1 through 3.

Preparation A (Coupler III in Table I, above)

Into a 1 liter three-necked flask, equipped with a mechanical stirrer and a steam-heated condenser, were placed 0.1 mole of ethyl- β,β -diethoxyacrylate and 0.1 mole of 2-amino-4-chlorobenzenesulfonamide. The reaction mixture was heated in an oil bath at 120°C–130°C for about 1½ hours until distillation of ethanol was completed. The resulting product was recrystallized from methanol to obtain a compound identified as coupler III (M.P. 141°–143°C.) in Table I.

Preparation B (Coupler I in Table I, above)

By utilizing 0.1 mole of 2-aminobenzenesulfonamide and 0.1 mole ethyl- β,β -diethoxyacrylate in accordance with the process described in Preparation A there is obtainable a compound identified as coupler I in Table I.

Preparation C (Coupler IX in Table I, above)

A mixture of 0.01 mole of coupler No. III, 0.01 mole 4-(N-methyl-N-octadecylsulfonamido)aniline and 30 ml p-cymene were placed in a 100 ml flask equipped with a steam-heated condenser and heated to reflux until the distillation of ethanol was completed. After the reaction mixture had cooled, the resulting solid residue was collected with suction then washed with hexane and with acetonitrile. The resulting product was identified as coupler IX (M.P. 168°–170°C) in Table I.

Preparation D (Coupler XI in Table I, above)

A mixture of 0.01 mole of coupler No. III, 0.01 mole 4-ethoxyaniline and 30 ml p-cymene were reacted as in Preparation C to obtain a product identified as coupler XI (M.P. 268°–270°C) in Table I.

Preparation E (Coupler V in Table I, above)

A mixture of 0.01 mole of coupler No. III, 0.01 mole 2-chloro-5-methylaniline, and 30 ml xylene were reacted as in Preparation C to obtain a product identified as coupler V (M.P. 180°C) in Table I.

Preparation F (Coupler IV in Table I, above)

A mixture of 0.01 mole of coupler No. III, 0.01 mole aniline, and 30 ml cymene were reacted as in Preparation C to obtain a product identified as coupler IV (M.P. 285°C) in Table I.

Preparation G (Coupler XVII in Table I, above)

By utilizing 0.1 mole of ethyl- β,β -diethylacrylate and 0.1 mole of 2-amino-4,5-dichlorobenzenesulfonamide in accordance with the process of Preparation A there is obtainable a coupler identified as coupler XVII in Table I.

Example 1

A 1% solution of coupler IX (see Table I, above) in butyl alcohol was added in equal volume to a 5% sodium carbonate solution and then admixed with 50 ml of a color developing composition A (described below) and an oxidant ($K_2S_2O_8$) to obtain a yellow dye extractable in the organic phase and with a λ max absorption at 475 nm. Acidification with dilute HCl caused a reversible bathochromic dye shift to obtain an orange-red solution.

Developing Composition A

Benzyl alcohol	4.0	ml
Sodium hexametaphosphate	0.5	g
Na_2SO_3	2.0	g
40% NaOH solution	0.4	ml
$Na_2CO_3 \cdot H_2O$	50.0	g
50% NaBr solution	1.72	ml
4-Amino-3-methyl-N-ethyl-N- β -(methanesulfonamide)ethyl-aniline	5.0	g
Water to	1000	ml
pH adjusted to	10.75	

Example 2

A 1% solution of coupler IV (product of Preparation F) in methanol was converted to the corresponding dye solution in accordance with Example 1 and a strip of mordanted receiver immersed in the dye solution for 1 minute. After washing and drying, it was determined that the captured dye has a λ max of 420 m μ .

Example 3

Four test film strips identified respectively as T-1, T-2, T-3 and T-4 were prepared by coating a film support with a single gelatin-silver bromiodide emulsion containing silver (206 mg/ft²), gelatin (685 mg/ft²), di-n-butyl phthalate (80 mg/ft²) and coupler IX (161 mg/ft²) or an equivalent amount of α -[3- α -(2,4-ditert-amylphenoxy)butyramido]-benzoyl]-2-methoxyacetanilide as a control coupler. The test strips were then exposed to a graduated-density test and developed at 20°C in the usual way in Developing Composition A (Example 1) or in Developing Composition B as described below:

Developing Composition B

Benzyl alcohol	4.0	ml
Sodium hexametaphosphate	0.5	g
Na_2SO_3	2.0	g
40% NaOH solution		
$Na_2CO_3 \cdot H_2O$	20.0	g
50% NaBr solution	3.46	ml
4-Amino-3-methyl-N,N-diethyl-aniline hydrochloride	2.0	g
Water to	1000	ml
pH adjusted to	10.86	

The test strips were then bleached, fixed, washed and dried in the usual manner and the results evaluated in Table III.

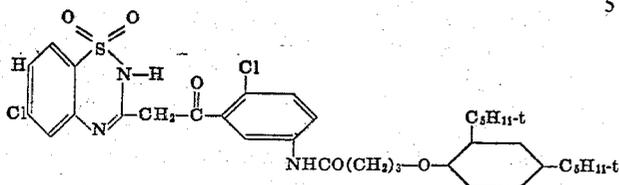
Table II

Strip	Coupler	λ max*	Dmax	Fog	amma	Developing Composition
T-1 (Invention)	IX	504	1.92	.06	1.21	A
T-2	Control Coupler	445	1.90	.10	1.46	A
T-3 (Invention)	IX	514	2.47	.07	1.60	B
T-4	Control Coupler	450	2.30	.12	1.49	B

*wavelength at absorption maximum

Example 4

Example 3 was repeated, except that Coupler X (Table I) was used in place of Coupler IX. The structure of Coupler X is:



In Table III is shown data resulting from a photographic test performed on the resulting test strips.

Table III

St-rip	Coupler	λ max*	Dmax	Fog	gamma	Developing Composition
1	Control	445	2.08	0.11	1.30	A
2	X	473	2.58	0.12	1.46	A
3	Control	451	2.62	0.12	1.75	B
4	X	473	3.66	0.12	2.21	B

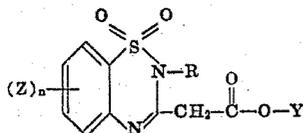
*wavelength at absorption maximum

The invention has been described in detail with particular reference to preferred embodiments thereof, but, it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

What is claimed is:

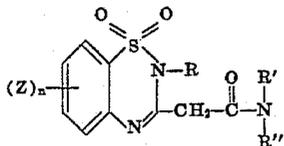
1. A light-sensitive photographic element comprising a photographic support having coated thereon at least one photosensitive silver halide emulsion layer containing at least one color coupler capable of forming a yellow dye when reacted with oxidized primary amino color developing agent; said color coupler being represented by the formula:

(1)



or

(2)



wherein

R is defined as hydrogen, or an alkyl group containing up to 15 carbon atoms;

Y is defined as an alkyl or an aryl group;

R' is hydrogen or an alkyl group containing 1-5 carbon atoms;

R'' is an alkyl or an aryl group; and

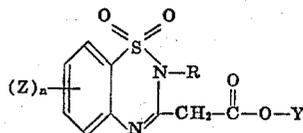
Z is individually defined at each occurrence as a halo group, an alkoxy group or an alkyl group containing 1-18 carbon atoms; and

n is 0-2.

2. A light-sensitive photographic element comprising a photographic support having coated thereon at least one photosensitive silver halide emulsion layer containing at least one color coupler capable of forming a yellow dye when reacted with oxidized primary amino color developing agent; said color coupler being represented by the formula:

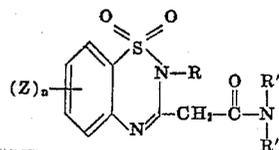
low dye when reacted with oxidized primary amino color developing agent; said color coupler being represented by the formula:

5 (1)



or

15 (2)



wherein

R is hydrogen or alkyl containing 1-5 carbon atoms;

Y is an alkyl or an aryl group containing 1 to 15 carbon atoms, or a halo-, alkoxy- or alkyl-substituted aryloxy group containing 1 to 15 carbon atoms;

R' is hydrogen;

R'' is an alkyl group containing 1-22 carbon atoms or an aryl or mono- or di-substituted phenyl group in which the substituents are halo, alkyl, carboxyl, alkoxy or sulfonamido groups;

Z is chloro, an alkoxy group containing 1-5 carbon atoms or an alkyl group containing 1-5 carbon atoms; and

n is 0-2.

3. A photographic element as in claim 2, wherein said element has the structure of formula (1) and Z is hydrogen, R is hydrogen and Y is an alkyl group.

4. A photographic element as in claim 2, wherein said element has the structure of formula (2) and Z is H or chlorine, R is H, R' is H and R'' is a substituted phenyl group.

5. A photographic element as in claim 2, wherein said element has the structure of formula (2) and n is O, R is H, R' is H and R'' is alkyl.

6. A photographic light-sensitive element comprising a photographic support having coated thereon at least one photosensitive silver halide emulsion layer containing 3-(carboethoxy) methyl-1,2,4-benzothiadiazine-1,1-dioxide.

7. A photographic light-sensitive element comprising a photographic support having coated thereon at least one photosensitive silver halide emulsion layer containing 3-[(4-ethoxyphenyl)carbonyl]methyl-1,2,4-benzothiadiazine-1,1-dioxide.

8. A photographic light-sensitive element comprising a photographic support having coated thereon at least one photosensitive silver halide emulsion layer containing 3-(carboethoxy)methyl-6-chloro-1,2,4-benzothiadiazine-1,1-dioxide.

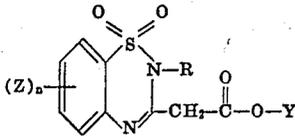
9. A photographic light-sensitive element comprising a photographic support having coated thereon at least one photosensitive silver halide emulsion layer containing 3-(phenylcarbonyl)methyl-6-chloro-1,2,4-benzothiadiazine-1,1-dioxide.

10. A photographic light-sensitive element comprising a photographic support having coated thereon at least one photosensitive silver halide emulsion layer containing 3-[(2-chloro-5-methylphenyl)carbonyl]methyl-6-chloro-1,2,4-benzothiadiazine-1,1-dioxide.

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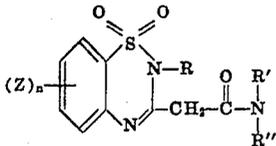
11. A light-sensitive silver halide emulsion containing a non-diffusible color coupler compound of the formula

(1)



or

(2)



wherein

R is hydrogen or alkyl containing up to 15 carbon atoms;

Y is an alkyl group or an aryl group;

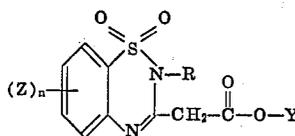
R' is hydrogen or an alkyl group containing 1-5 carbon atoms;

R'' is an alkyl or an aryl group containing up to 20 carbon atoms;

Z is a halo, an alkoxy group or an alkyl group; and n is 0-2.

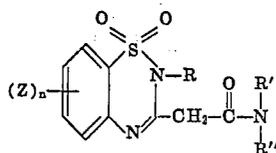
12. A light-sensitive, photographic silver halide emulsion containing a non-diffusible color coupler compound of the formula:

(1)



or

(2)



wherein

R is hydrogen or alkyl containing 1-5 carbon atoms;

Y is an alkyl, aryl, or halo-substituted, alkoxy-substituted, or alkyl-substituted aryl group containing 1 to 15 carbon atoms;

R' is hydrogen;

R'' is alkyl containing 1-22 carbon atoms; and n=0.

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13. A light-sensitive, photographic silver halide emulsion as in claim 12, wherein said R'' is a mono-substituted phenyl group or a di-substituted phenyl group in which the substituents are halo, alkyl, carboxyl or sulfonamido radicals.

14. A light-sensitive, photographic silver halide emulsion as in claim 12, wherein said R'' is phenyl.

15. A light-sensitive, photographic silver halide emulsion as in claim 12, wherein said R'' is an alkoxy group.

16. A light-sensitive, photographic silver halide emulsion as in claim 12, wherein said color coupler is 3-(carboxy) methyl-1,2,4-benzothiadiazine-1,1-dioxide.

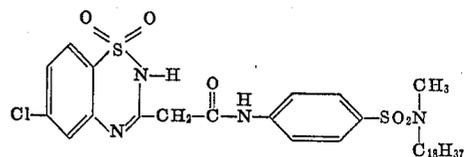
17. A light-sensitive, photographic silver halide emulsion as in claim 12, wherein said color coupler is 3-[(4-ethoxyphenyl)carbonyl]methyl-1,2,4-benzothiadiazine-1,1-dioxide.

18. A light-sensitive, photographic silver halide emulsion as in claim 12, wherein said color coupler is 3-(carboxy)methyl-6-chloro-1,2,4-benzothiadiazine-1,1-dioxide.

19. A light-sensitive, photographic silver halide emulsion as in claim 12, wherein said color coupler is 3-(phenylcarbonyl)methyl-6-chloro-1,2,4-benzothiadiazine-1,1-dioxide.

20. A light-sensitive, photographic silver halide emulsion as in claim 12, wherein said color coupler is 3-[(2-chloro-5-methylphenyl)carbonyl]methyl-6-chloro-1,2,4-benzothiadiazine-1,1-dioxide.

21. A photographic element comprising a photographic support having coated thereon at least three emulsion layers containing photosensitive silver halide, each of said emulsion layers being sensitized to a different wavelength region of the visible spectrum, and one of said emulsion layers containing from about 25 to about 200 mg per square foot of said support of a ballasted, non-diffusible coupler compound capable of forming a yellow dye when reacted with 4-amino-3-methyl-N-β-(methane-sulfonamide) ethylaniline; said coupler compound being represented by the formula:



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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,841,880 Dated October 15, 1974

Inventor(s) Stanley S. Kertel

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Title page, line 3 of the Abstract, "container" should read ---contain---;

Column 10, line 56, "III" should read ---II---;

Column 10, approximate columnar line 60, in Table II, "amma" should read ---Gamma---; and

Column 11, line 20, "amma" should read ---Gamma---.

Signed and sealed this 4th day of February 1975.

(SEAL)
Attest:

McCoy M. Gibson Jr.
Attesting Officer

C. Marshall Dann
Commissioner of Patents