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## COUPLERS FOR COLOR PHOTOGRAPHY

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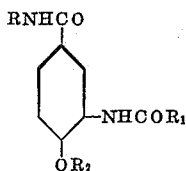
16 Claims. (Cl. 95-6)

This invention relates to photography and particularly to compounds which form dyes on coupling with the developing agent to produce colored images.

It is known that colored photographic images may be formed by using a developer which produces a colored compound on development. The colored compound thus formed is deposited adjacent the silver grains of the silver image during development. It is also known that a colored image may be formed by adding to said developer solution or by incorporating in the silver halide emulsion before or after exposing a compound which couples during development with the oxidation product of the developing agent and which forms a colored compound which is likewise deposited adjacent the silver grains of the silver image during development. Such a compound which is employed in conjunction with a developing agent for the silver and which couples with the oxidation product of the developing agent during development is referred to herein as a coupling compound or coupler.

The present invention concerns new or improved emulsions containing a coupler as defined herein after as well as color-forming developers containing a coupler of the invention in addition to a primary aromatic amino silver halide developing agent.

We have found that the compounds of the following structure are valuable couplers for color photography and produce dye images of improved absorption characteristics on color development.



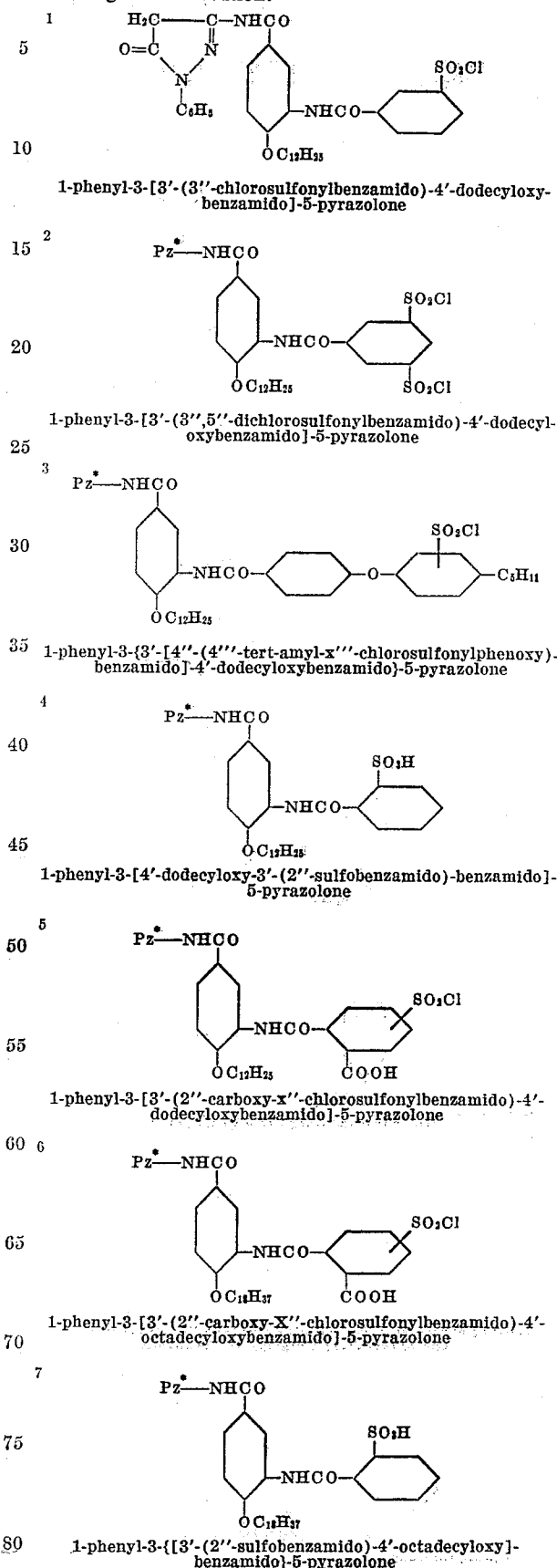
wherein R represents a coupler group free to react with the oxidation product of a primary aromatic amino silver halide developing agent to form a dye image, R<sub>1</sub> represents a mononuclear aryl group of the benzene series containing an alkali solubilizing group, and R<sub>2</sub> represents a saturated alkyl group containing from 10 to 20 carbon atoms.

It will be noted that the compounds of the invention possess a central nucleus to which is attached through the acid amide linkage, a group R conferring a coupler function, a group R<sub>1</sub> conferring solubility to the coupler, and the alkyl group R<sub>2</sub> which serves to prevent wandering of the coupler from emulsion layer to emulsion layer. There is thus provided a method for selectively varying the reactive coupler group, the solubilizing group or the alkoxy group which controls the diffusion, independently to obtain the desired solubility and diffusion characteristics and spectral absorption characteristics in the dye images obtained therefrom.

The compounds of our invention are prepared in general by condensing a m-nitro-p-alkoxy benzoyl chloride with a coupler compound, reducing the meta-nitro group and acylating the resultant amino group with an aromatic acid chloride or anhydride containing the desired solubilizing group.

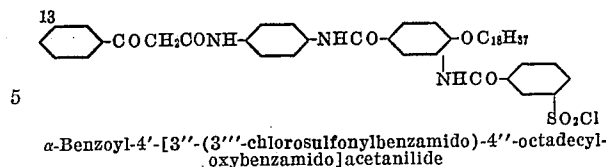
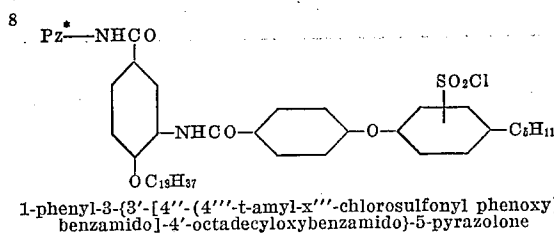
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The following compounds are useful as couplers according to our invention:

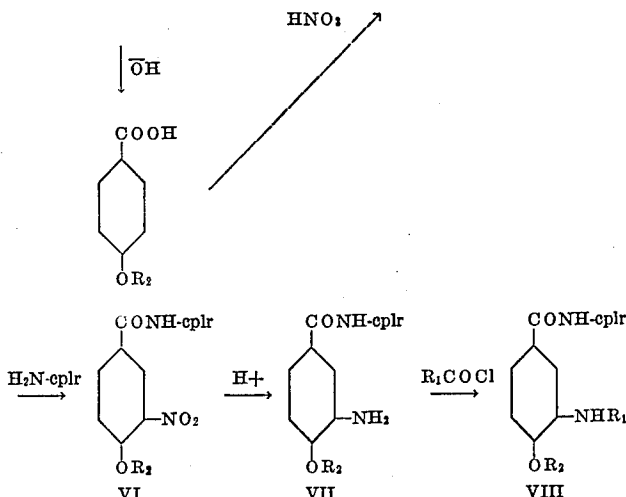
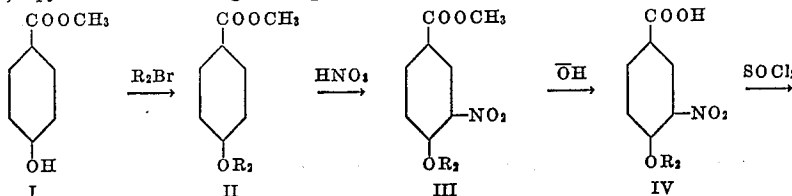


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10 The couplers of our invention may be prepared by the general procedure following.



#### PROCEDURE

##### Methyl-4-octadecyloxybenzoate (II)

To 2.3 grams of metallic sodium in a 500 cc. flask were added dropwise 50 cc. of methyl alcohol and when the sodium was completely dissolved, 15.2 grams of methyl-4-hydroxy benzoate and 33.3 grams of octadecyl bromide were added. The resultant 2-phase composition was heated under reflux with occasional stirring for 48 hours. 100 cc. of sodium hydroxide solution were then added and heating continued under reflux for three hours. Upon cooling, the oily top layer crystallized to a white cake which was broken up and purified by recrystallization from methyl alcohol to obtain the compound II having a melting point of 69–70° C. Subsequent syntheses gave purer material with M. P. up to 76° C.

##### Methyl-3-nitro-4-octadecyloxybenzoate (III)

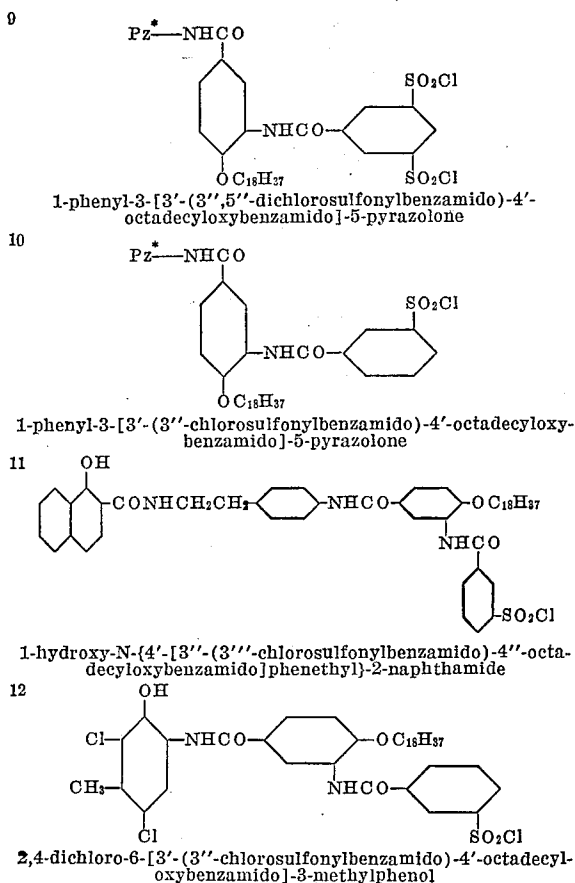
To 100 cc. of concentrated nitric acid heated to 95° C. in a flask equipped with a stirrer, were added 10 grams of II prepared as above described and heating and stirring were carried out for 1½ hours. The product was then poured on to one kilogram of cracked ice, filtered and washed. The residue on the filter was then dissolved in 30 cc. of ethyl acetate, the solution decolorized, filtered and the product recrystallized from methyl alcohol to yield the ester III having a melting point of 80–1° C.

##### 3-nitro-4-octadecyloxybenzoic acid (IV)

33 grams of compound III prepared as above described were added to an alcoholic potassium hydroxide solution and heated under reflux for 45 minutes to saponify the ester. The reaction mixture was cooled, acidified with hydrochloric acid solution, filtered and washed. The product was recrystallized from alcohol to yield the acid IV having a melting point of 100–2° C.

##### 3-nitro-4-octadecyloxybenzoyl chloride (V)

To 2.5 grams of the acid IV prepared as above described were added 20 cc. of thionyl chloride and the mixture heated in a flask under reflux over a water bath



\* 3-pyrazolyl nucleus as in compound 1.

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for one hour. The reaction mixture was allowed to stand overnight and the excess of thionyl chloride removed under vacuum. The acid chloride V remaining had a melting point of 52–3° C.

*1-phenyl-3-(3'-nitro-4'-octadecyloxy)-benzamido-5-pyrazolone (VI)*

This coupler was prepared from the acid chloride V as follows:

To 5.8 gm. of 1-phenyl-3-amino-5-pyrazolone dissolved in 75 ml. of dioxan were added 15 gm. of the acid chloride V, prepared as described above. The solution was refluxed for 40 min., then diluted with 500 ml. of ethyl alcohol, filtered hot through Darco, chilled in ice, and the crystalline product, amounting to 6.1 gm., collected on a Büchner funnel. The product softens at 135°, melts at 155–160°.

*1-phenyl-3(3'-amino-4'-octadecyloxy-benzamido)-5-pyrazolone (VII)*

A mixture of five grams of compound VI, 50 cc. of 90 percent acetic acid solution and five grams of iron filings were refluxed for ten minutes, after which the reaction mixture was poured into water to yield a gray granular precipitate. The precipitate was then extracted with 200 cc. of hot acetonitrile and the residue recrystallized from 30 cc. of 90 percent acetic acid to yield a white solid, VII having a melting point of 138–42° C.

*1-phenyl-3-[3'-(3''-chlorosulfonylbenzamido)-4'-octadecyloxy-benzamido]-5-pyrazolone VIII*

One gram of the amide VII prepared as above described was dissolved in 100 cc. of dioxane and 0.8 cc. of m-chlorosulfonyl benzoyl chloride was added. The temperature of the reaction mixture gradually rose from 20 to 24° C. and within one-half hour a copious precipitate had formed. After allowing the reaction mixture to stand overnight, the precipitate was filtered off and washed with dioxane and acetonitrile to obtain the product VIII having a melting point of from 152–5° C.

Coupler VIII prepared as above, has the structure of compound No. 10 in the above tabulation.

Compound No. 9 was prepared as follows: one gram of the intermediate VII prepared as above described, was dissolved in 10 cc. of glacial acetic acid containing 0.2 gram of sodium acetate. There was then added 0.66 gram of 3,5-dichlorosulfonyl benzoyl chloride dissolved in about 5 cc. of acetic acid. The temperature of the reaction mixture rose slightly and a copious precipitate formed. After standing for one hour, the precipitate was filtered off, washed with 95 percent acetic acid solution and petroleum ether and dried to produce desired product having a melting point of from 148–150° C.

Coupler No. 8 was prepared from intermediate VII as follows: 0.33 gram of sodium acetate was dissolved in 20 cc. of glacial acetic acid. 2.0 grams of VII were then dissolved in the solution and 1.6 grams of x-chlorosulfonyl-4-t-amyl phenoxybenzoyl chloride dissolved in 5 cc. of glacial acetic acid were added to the solution at 55° C. After standing for several hours at room temperature, the product was filtered, washed with 90 percent acetic acid solution and dried to yield the desired compound having a melting point of 128–30° C.

Compound No. 7 was prepared by dissolving two grams of the amine VII in 20 cc. of glacial acetic acid and after warming the solution of 55° C. adding a solution of 0.72 gram of o-sulfobenzoic anhydride in 5 cc. of acetic acid solution. A white precipitate immediately formed which gradually reverted on cooling to a pink solid which was filtered off and washed with ethyl acetate, benzene and acetonitrile to yield the product having a melting point of 210–12° C.

Compound No. 6 was prepared by dissolving 1.5 grams of the amine VII in 20 cc. of warm ethyl acetate and adding a solution of 0.66 gram of m-chlorosulfonyl phthalic anhydride in 5 cc. of ethyl acetate. The solution was then decolorized and allowed to stand overnight, following which the solution was diluted with petroleum ether which caused the formation of a finely divided precipitate which was removed from the liquid in a centrifuge. The produce was then washed with petroleum ether containing a small amount of hydrochloric acid and after drying, a product was obtained having a melting point of 142–3° C.

Compounds Nos. 1 to 5 were prepared in a manner similar to that described above for the preparation of compounds 6 to 10, substituting methyl 4-dodecycloxyben-

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zoate for methyl 4-octadecycloxybenzoate II in the above detailed synthesis.

In the above syntheses it may be desirable to hydrolyze compounds of the type of II before nitration. Accordingly, rather than first nitrating II, a compound of this type can first be hydrolyzed to the corresponding 4-alkoxybenzoic acid, then nitrated to yield the desired 3-nitro-4-alkoxybenzoic acid IV which is then converted to the acid chloride and condensed with the desired coupler group as shown in the general procedure outlined above.

Compound No. 11 and similar compounds can be prepared in the manner described for compound 10 using the intermediate V and condensing with 1-hydroxy-N-(4'-amino phenethyl)-2-naphthamide followed by reduction of the nitro group and condensation with m-chlorosulfonyl benzoyl chloride or the acid halides or anhydrides used in the preparation of compounds 6 to 9.

Compound No. 12 and similar compounds can be prepared from the intermediate V condensed with 2-amino-4,6-dichloro-5-methyl phenol, followed by reduction of the nitro group and condensation with any of the acid halides or anhydrides used in the preparation of compounds 6 to 10.

Compound No. 13 and similar couplers can be prepared by condensing the acid chloride V with  $\alpha$ -benzoyl-4'-aminoacetanilide followed by reduction of the nitro group and condensation with any of the acid halides or anhydrides used in the preparation of compounds 6 to 10.

Other pyrazolones such as those following can be used for condensation with the intermediate V in which cases, as above; the resultant nitro compound is then reduced and condensed with the desired acid chloride or anhydride providing the required solubilizing group: 1-p-cyanophenyl-3-amino-5-pyrazolone, 1-sym. trichlorophenyl-3-amino-5-pyrazolone, 1-[4'-(4''-tert. butylphenoxy)phenyl]-3-amino-5-pyrazolone.

It will be noted that the couplers such as compounds Nos. 1 to 3 contain a sulfonyl chloride group. Accordingly, it is desirable to hydrolyze this group preferably just before incorporation of the coupler into a photographic emulsion or developing solution. This may be accomplished by hydrolyzing the group in alcoholic alkali solution as described in the Salminen et al., U. S. patent application Serial No. 774,890, filed September 18, 1947, published April 24, 1951. The couplers containing the free sulfonic acid group are incorporated into silver halide emulsions in the required quantity.

In case the coupler is to be used in a color developing solution, the following example illustrates a developing solution which may be used with the compounds of our invention.

A

	Grams
p-Aminodiethylaniline sulfate.....	2
Sodium sulfite (anhydrous).....	5
Sodium carbonate (anhydrous).....	20
Potassium bromide.....	2
Water to 1 liter.	

B

Coupler compound.....	grams... 2
Sodium hydroxide (2% sol.).....	cc... 50

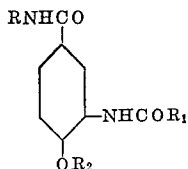
For use, B is added to A. In case the coupler has been hydrolyzed in alcoholic alkali solution as above described, this solution can replace B and a corresponding quantity of the solution is added to A. Other well known primary aromatic amino color developing agents can be used in the developer solution in place of that indicated. These developing agents possess an unsubstituted amino group which enables the oxidation products of the developer to couple with the color forming compounds of the invention to form a dye image in the region of exposure and development of the emulsion layer whether the coupler is in the emulsion or developer solution.

The couplers of our invention may be employed for the production of colored photographic images in layers of gelatin or other carrier for the silver halide such as collodion, cellulose organic acid esters or synthetic resins. The support for the emulsion may be a transparent material such as glass, cellulose ester or a nontransparent reflecting material such as paper or an opaque cellulose ester layer. The emulsion containing the couplers of the invention may be coated as a single layer on the support or as superposed layers on one or both sides of the support. The superposed layers may be differentially sen-

sitized to form natural color photographic images in the well known manner. For example, in a multilayer material sensitized to red, green and blue light, respectively, our couplers can be used in any of the layers, preferably the pyrazolone couplers in the green sensitive layer, the phenolic hydroxyl couplers in the red sensitive layer and the acylacetanilide couplers in the blue sensitive layer. In such use, the couplers of our invention will be found to exhibit little or no diffusion in the emulsion layer in spite of the presence of the solubilizing group on the molecule and the couplers couple readily with the oxidation products of the developer.

What we claim is:

1. A photographic emulsion for forming colored images comprising a silver halide emulsion having incorporated therein a coupler compound having the formula



wherein R represents a coupler group free to react with the oxidation product of a primary aromatic amino silver halide developing agent to form a dye image, R1 represents a mononuclear aryl group of the benzene series containing an alkali solubilizing group and R2 represents a saturated alkyl group of from 10 to 20 carbon atoms.

2. A photographic emulsion for forming colored images comprising a silver halide emulsion having incorporated therein a coupler compound having the formula set forth in claim 1, wherein R represents a substituent containing a methylene group reactive with the oxidation product of a primary aromatic amino silver halide developing agent to form a dye image, R1 represents a mononuclear aryl group of the benzene series containing an alkali solubilizing group, and R2 represents a saturated alkyl group of from 10 to 20 carbon atoms.

3. A photographic emulsion for forming colored images comprising a silver halide emulsion having incorporated therein a coupler compound having the formula set forth in claim 1, wherein R represents a phenolic hydroxyl group, R1 represents a mononuclear aryl group of the benzene series containing an alkali solubilizing group, and R2 represents a saturated alkyl group of from 10 to 20 carbon atoms.

4. A photographic emulsion for forming colored images comprising a silver halide emulsion having incorporated therein a coupler compound having the formula set forth in claim 1, wherein R represents a 3-pyrazolyl-5-one group unsubstituted in the 4-position, R1 represents a solubilizing group selected from the class consisting of sulfophenyl, carboxyphenyl and phenyl sulfonylhalide groups, and R2 represents a saturated alkyl group of from 10 to 20 carbon atoms.

5. A photographic emulsion for forming colored images comprising a silver halide emulsion having incorporated therein a coupler compound having the formula set forth in claim 1, wherein R represents a 3-pyrazolyl-5-one group unsubstituted in the 4-position, R1 represents a sulfophenyl group and R2 represents a saturated alkyl group of from 10 to 20 carbon atoms.

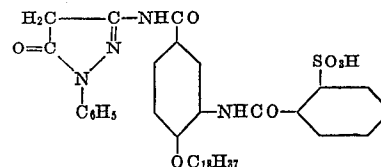
6. A photographic emulsion for forming colored images comprising a silver halide emulsion having incorporated therein a coupler compound having the formula set forth in claim 1, wherein R represents a 3-pyrazolyl-5-one group unsubstituted in the 4-position, R1 represents a sulfophenyl group and R2 represents a dodecyl group.

7. A photographic emulsion for forming colored images comprising a silver halide emulsion having incorporated therein a coupler compound having the formula set forth in claim 1, wherein R represents a 3-pyrazolyl-5-one group unsubstituted in the 4-position, R1 represents a sulfophenyl group and R2 represents an octadecyl group.

8. A photographic emulsion for forming colored images comprising a silver halide emulsion having incorporated therein a coupler compound having the formula set forth in claim 1, wherein R represents a 3-pyrazolyl-5-one group unsubstituted in the 4-position, R1 represents an o-sulfo-phenyl group and R2 represents a dodecyl group.

9. A photographic emulsion for forming colored images comprising a silver halide emulsion having incorporated therein a coupler compound having the formula set forth in claim 1, wherein R represents a 3-pyrazolyl-5-one group unsubstituted in the 4-position, R1 represents an o-sulfo-phenyl group and R2 represents an octadecyl group.

10. A photographic emulsion for forming colored images comprising a silver halide emulsion having incorporated therein a coupler compound having the formula

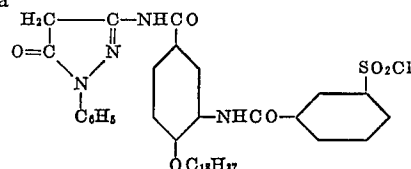


11. A photographic emulsion for forming colored images comprising a silver halide emulsion having incorporated therein a coupler compound having the formula set forth in claim 1, wherein R represents a 3-pyrazolyl-5-one group unsubstituted in the 4-position, R1 represents a phenylsulfonyl halide group and R2 represents a saturated alkyl group of from 10 to 20 carbon atoms.

12. A photographic emulsion for forming colored images comprising a silver halide emulsion having incorporated therein a coupler compound having the formula set forth in claim 1, wherein R represents a 3-pyrazolyl-5-one group unsubstituted in the 4-position, R1 represents a phenyl-o-sulfonyl halide group and R2 represents a saturated alkyl group of from 10 to 20 carbon atoms.

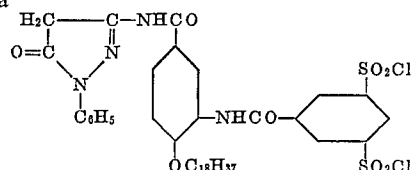
13. A photographic emulsion for forming colored images comprising a silver halide emulsion having incorporated therein a coupler compound having the formula set forth in claim 1, wherein R represents a 3-pyrazolyl-5-one group unsubstituted in the 4-position, R1 represents a phenyl-m-sulfonyl halide group and R2 represents an octadecyl group.

14. A photographic emulsion for forming colored images comprising a silver halide emulsion having incorporated therein a coupler compound having the formula



15. A photographic emulsion for forming colored images comprising a silver halide emulsion having incorporated therein a coupler compound having the formula set forth in claim 1, wherein R represents a 3-pyrazolyl-5-one group unsubstituted in the 4-position, R1 represents a phenyl-di-sulfonylhalide group and R2 represents an octadecyl group.

16. A photographic emulsion for forming colored images comprising a silver halide emulsion having incorporated therein a coupler compound having the formula



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