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UNITED STATES PATENT OFFICE

2,448,939

THIOGLYCOLIC AMIDE COUPLERS

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19 Claims. (Cl. 95—6)

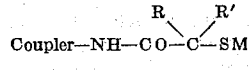
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This invention relates to photographic color-forming or coupling compounds and particularly to coupler compounds which are non-diffusing when incorporated in sensitive emulsion layers.

In Peterson U. S. Patent 2,296,306, granted September 22, 1942, and U. S. Patent 2,353,754, granted July 18, 1944, there are described couplers which contain a heterocyclic ring and a free imino or mercapto group which is capable of forming a metallic salt in photographic emulsions. These compounds are quite non-diffusing in photographic emulsions but combine with the development product of primary aromatic amino developing agents to form colored images in the well known manner. Upon fixing, the metallic atom attached to the imino or mercapto group is removed and the unused coupler may be washed from the layer. Some of the couplers previously used are not, however, readily washed from the emulsion layer after fixing and tend to decompose and discolor the final image.

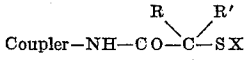
It is, therefore, an object of the present invention to provide a new class of coupler compounds from which insoluble metallic salts may be formed in the emulsion layer. A further object is to provide coupler compounds which are readily soluble in the fixing bath and which may be readily removed from the emulsion layer. Other objects will appear from the following description of our invention.

These objects are accomplished by incorporating in the emulsion layer a thioglycolic amide derivative of a coupler having the following probable formula:



where R and R'=hydrogen or alkyl groups, and M=a heavy metal.

These insoluble couplers are produced from coupling compounds of the following probable formula:



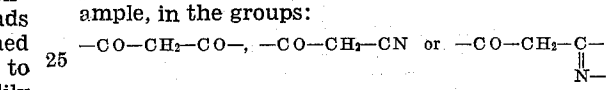
where R and R'=hydrogen or alkyl groups and X=hydrogen or acetyl.

These couplers are formed by introducing the thioglycolic amide portion of the molecule into any well known type of coupler compound, such as those described in Fisher U. S. Patent 1,055,155, Mannes and Godowsky U. S. Patents 2,039,730, 2,108,602, and 2,113,330 or Mannes, Godowsky, and Peterson U. S. Patents 2,115,394 and 2,126,337. It is to be understood that when we refer to introducing the thioglycolic amide portion into

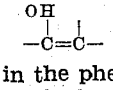
2

coupler compounds, we do not mean that the final compound is necessarily formed by simple substitution starting with these two materials. The final compound may be formed by any suitable reaction which results in a compound having a thioglycolic amide portion as described above and a coupling portion or portions containing at least one group capable of reacting with the development product of the developing agent to form a dye image.

The "coupler" portion of the molecule indicated in the general formulas above contains the functional or reactive group common to coupler compounds which react with primary aromatic amino developing agents to form colored images. This functional or reactive group is usually a reactive methylene or reactive ethenol group and may occur at various positions or more than a single position in the coupler molecule. By reactive methylene, we mean a CH_2 group which is reactive in the coupling process. This group is usually present between two negative centers as, for example, in the groups:

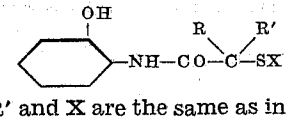


in a ring system or chain compound. One or both of the hydrogen atoms of the methylene group may be substituted by certain groups without destroying the chemical activity of the group. By reactive ethenol, we mean the group:

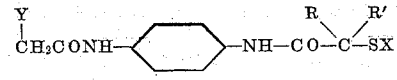


This group occurs in the phenolic and naptholic coupler compounds which are reactive in the ortho or para portion with respect to the position of the hydroxyl group.

The compounds which we propose to use may have the following structure:



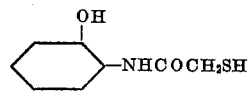
where R, R' and X are the same as in the formula above, and the phenol nucleus may contain other substituents, as long as it is unsubstituted or contains a replaceable substituent, such as halogen, in the position para to the hydroxyl group; or the following structure:



where R, R' and X are the same as in the formula above, and Y is an acyl group such as acetyl or benzoyl, or a cyano group.

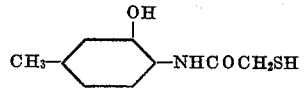
The following compounds are examples of couplers containing the thioglycolic amide structure which may be employed according to our invention:

(1)



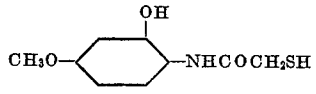
2-hydroxy-thioglycolic anilide

(2)



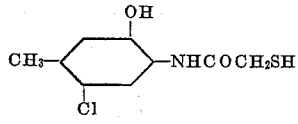
2-hydroxy-4-methyl-thioglycolic anilide

(3)



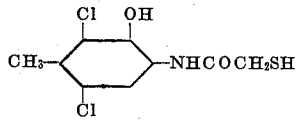
2-hydroxy-4-methoxy-thioglycolic anilide

(4)



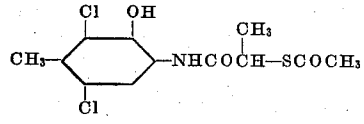
2-hydroxy-4-methyl-5-chloro-thioglycolic anilide

(5)



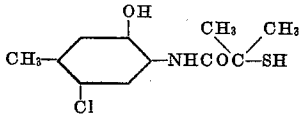
2-hydroxy-3,5-dichloro-4-methyl-thioglycolic anilide

(6)



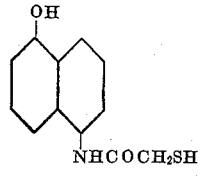
2-(α-acetylmercaptopropionamido)-4,6-dichloro-5-methylphenol

(7)



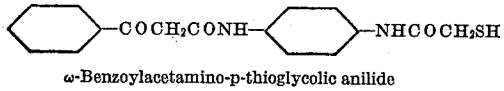
2-hydroxy-4-methyl-5-chloro-(α-dimethylthioglycolic anilide)

(8)



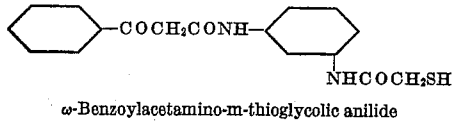
5-(thioacetylamino)-1-naphthol

(9)



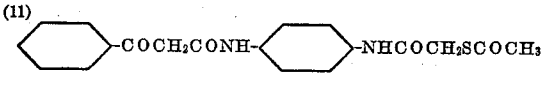
ω-Benzoylacetamino-p-thioglycolic anilide

(10)



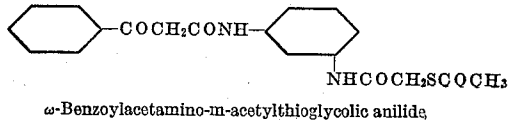
ω-Benzoylacetamino-m-thioglycolic anilide

(11)



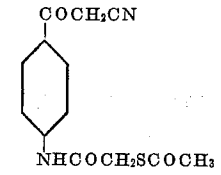
ω-Benzoylacetamino-p-acetylthioglycolic anilide

(12)



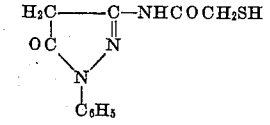
ω-Benzoylacetamino-m-acetylthioglycolic anilide

(13)



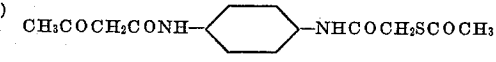
p-Acetylthioglycolylamino-ω-cyanoacetophenone

(14)



1-phenyl-3-(thioglycolylamino)-5-pyrazolone

(15)



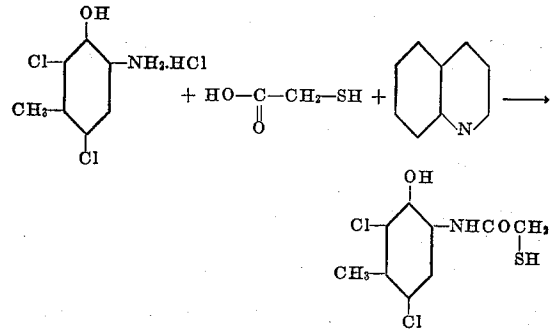
Acetoacetylamino-p-acetylthioglycolicanilide

The coupler compounds used according to our invention are generally incorporated in the emulsion layer by first forming a solution of the sodium or other soluble salt of the coupler and then incorporated in a silver halide emulsion whereupon part of the silver of the silver halide replaces the sodium to form the silver salt of the coupler. Other heavy metal salts such as gold, nickel, mercury, cadmium or tin may be formed before the coupler is incorporated in the silver halide emulsion. Silver salts are preferred, however, since a silver salt is ordinarily used in the production of sensitive layers and common silver salts, such as silver chloride or silver bromide are suitable for the purpose of our invention. Other silver salts which may be used are silver ferricyanide, silver ortho phosphate, silver arsenate, silver oxalate, silver cyanate and silver citrate. In the case of the acetyl derivatives of the thioglycolic amides, it is possible that the reaction with the silver results in the formation of a complex rather than a pure salt. The formation of such additional complexes is suggested by P. Pfeiffer "Organische Molekulverbindungen" (1922), pages 60, 125*f*, 153 and 289.

The non-diffusing metal salts made according to our invention may be incorporated in single or multi-layer gelatin emulsion coatings or in layers of other colloidal materials such as cellulose esters or natural or synthetic resins, and mixtures of the couplers may be used in a single layer.

The couplers which we propose to use are made in general by condensing thioglycolic acid or acetyl thioglycolyl chloride with the appropriate amine. The methods used in the preparation of the specific examples above were as follows:

Compound 5 is prepared as follows:



In a 1-liter round-bottomed flask is placed 163 grams (0.715 mole) of purified 2-amino-4,6-dichloro-5-methylphenol hydrochloride. To the hydrochloride is added 210 grams (0.238 mole) of

thioglycolic acid and 109.5 grams (0.845 mole) (100 cc.) of quinoline. The mixture is stirred well and the flask is immersed in the steam bath and covered with a towel. The heating is continued for 5 hours with shaking at intervals. The reaction mixture is a brown liquid with some undissolved hydrochloride. The mixture is cooled to about 35° and then stirred into 1 liter of water; at first a liquid forms which rapidly changes to a mass of soft lumps. The crude anilide is filtered, washed with 1 liter of water and sucked almost dry on the filter. The product is then dried in a vacuum desiccator over the week-end. Yield of crude product is 145 grams (76.0%) M. P. 130–134°.

Purification

The 145 grams of crude grey anilide is dissolved in 1200 cc. of boiling benzene, filtered and the filtrate is chilled rapidly to about 10°. The anilide crystallizes in small colorless crystals which are filtered and washed on the filter with 150 cc. of cold (10°) benzene. The product is then sucked dry on the filter. Recovery is 116 grams (80%) M. P. 138–139°.

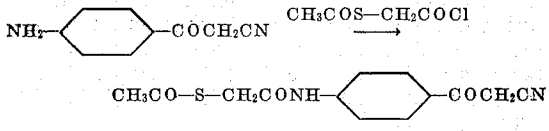
The 116 grams of anilide is recrystallized a second time from 1200 cc. of boiled benzene, filtered and then chilled to 10°. The crystals are filtered and washed with 150 cc. of cold benzene. Recovery is 109 grams (91.5%) M. P. 138.5–139.5°.

The third and final crystallization is carried out by dissolving the 109 grams of anilide in 1300 cc. of boiled chloroform, filtering and chilling to 0°. The product crystallizes in small crystals which are filtered off and then washed with 200 cc. of ice-cold chloroform. The product is sucked dry on the filter. The anilide is placed in a vacuum desiccator overnight. Recovery is 87 grams (80%) M. P. 139–140°. Yield of purified product is 46%.

Compounds 1, 2, 3, 4, 8 and 14 are prepared in a similar manner, using the corresponding amine in place of 2-amino-4,6-dichloro-5-methylphenol hydrochloride.

Compound 7 is prepared by a method similar to that used in the preparation of compound 5, using the corresponding amine and α-mercaptoisobutyric acid (Billmann, Ann. 348, 129) instead of thioglycolic acid. The free base of the amine is employed, rather than the hydrochloride, and no quinoline is necessary.

Compound 13 is prepared as follows:



Twenty grams (0.125 mole) of p-amino-ω-cyanoacetophenone was dissolved in 300 cc. of dioxane, at 50° in a 500 cc. Erlenmeyer flask. The solution was filtered and cooled to 20°. Synthetic quinoline (16.1 grams) (0.125 mole) was then added and then 19.1 grams (0.125 mole) of acetylthioglycolyl chloride was added to the well stirred solution. The temperature rises quickly and a precipitate forms. This precipitate was stirred occasionally over a period of about an hour. The materials were poured into a beaker and 300 cc. of water was added. The precipitate was thoroughly washed with water and then with alcohol. Twenty-seven grams of product was recrystallized from 1500 cc. of alcohol. The product was decolorized with Darco. The material was recrystallized a second time, the solution standing overnight in the refrigerator before filtering. Yield:

20 grams of recrystallized material (61% of the theoretical), M. P. 195°.

Acetylthioglycolic acid

$$CH_3COCl + HSCH_2COOH \rightarrow CH_3COSCH_2COOH + HCl$$

In a 500-cc. 3-necked flask fitted with a condenser, stirrer, and dropping funnel was placed 139 cc. (2 moles) of thioglycolic acid. Then 175 cc. (2.5 moles) of acetyl chloride was added through the dropping funnel to the stirred mixture at such a rate as to cause rapid, but not too vigorous, evolution of HCl. The mixture warms spontaneously. It was transferred to a 500-cc. modified Claisen flask with a 10-inch column and distilled under reduced pressure. A forerun of about 50 grams B. P_{15}=50–100°, was collected. Then the mixture was cooled slightly, and the distillation continued using a high-vacuum. The fraction, B. $P_{2.5}$=115–118°, was collected as acetylthioglycolic acid. It amounted to 170–175 grams (65%). (See Ber. 46, 1913, 2105.)

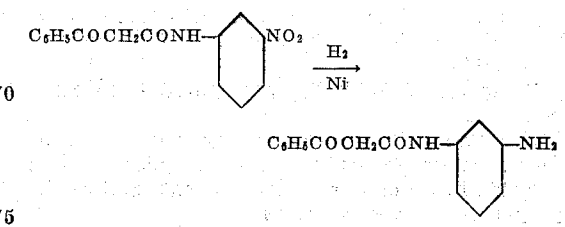
Acetylthioglycolyl chloride

$$CH_3COSCH_2CO_2H + SOCl_2 \rightarrow CH_3COSCH_2COCl + SO_2 + HCl$$

A 500-cc. 3-necked round-bottomed flask fitted with a thermometer, stirrer, outlet tube, and an addition funnel is charged with 102 grams (0.75 mole) of acetyl thioglycolic acid. The flask is immersed in a water bath maintained at about 20° as 93 cc. (1.27 moles) of thionyl chloride is added dropwise to the stirred solution at such a rate as to cause evolution of HCl and SO_2 and to keep the temperature of the reaction mixture at 25–30°. After about 30% of the thionyl chloride is added, the vigor of the reaction subsides considerably so that the remainder may be added rapidly. The mixture is stirred overnight at room temperature. The excess thionyl chloride is removed at reduced pressure; heating the flask gently by means of a water bath which is gradually warmed from 25–65°. Then 50 cc. of dry benzene is added; this is removed at reduced pressure. After repeating this process once more, the water bath is gradually warmed to 100° as the last traces of benzene and thionyl chloride are removed. Finally the product is distilled through a short column using two water pumps to take care of decomposition at the initial part of the distillation. The fraction boiling at 98–101° under 16–18 mm. is collected as pure acetylthioglycolyl chloride. The yield is 73 grams (64%). (Ber. 46, 2105.)

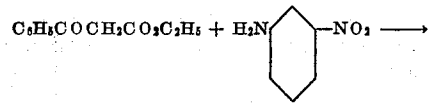
Compounds 11 and 12 are prepared by condensing p-(benzoylacetamino)-aniline or m-(benzoylacetamino)-aniline with acetylthioglycolyl chloride in a manner similar to that used in the preparation of compound 13. m-(Benzoylacetamino)-aniline is prepared as follows, and p-(benzoylacetamino)-aniline is similarly prepared, using ethyl acetate as a solvent instead of alcohol:

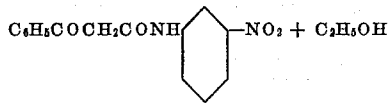
m-(Benzoylacetamino)-aniline



Twenty-five grams of ω-benzoyl-m-nitroacetanilide, suspended in 200 cc. of alcohol, is shaken in an atmosphere of hydrogen and in the presence of Raney nickel at a temperature of 80–90° until the theoretical amount of hydrogen is absorbed. The catalyst is filtered off and the solution is concentrated in vacuo to 25 cc. Thus 13.5 grams of m-(benzoylacetamino)-aniline melting at 156° is obtained.

ω-Benzoyl-m-nitroacetanilide

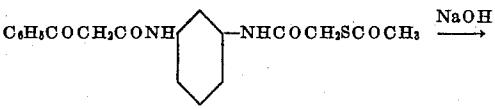


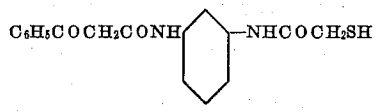


Forty-five grams of ethyl benzoylacetate, in an open beaker, is heated on an oil bath to 170–180°. Then 22 grams of m-nitroaniline is added in small increments during 15 minutes, always allowing time between each addition for the alcohol to be evolved and for the temperature of the solution to rise above 165°. Heating is continued for another 15 minutes, and, after the solution is allowed to cool somewhat, 75 cc. of benzene is added. The bright yellow crystalline product is filtered and washed with ether. The yield is 25 grams of ω-benzoyl-m-nitroacetanilide; M. P. 136–137°.

Compound 10 is prepared as from compound 12 as follows:

ω-Benzoylacetamino-m-thioglycolic anilide





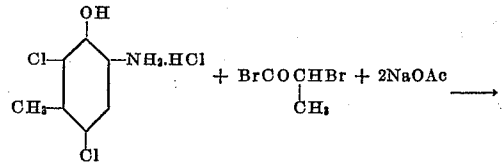
To a suspension of 1.85 gram (0.005 mole) of benzoylacetamino - m - acetylthioglycolic anilide in 5 cc. of alcohol is added 10 cc. of 5 per cent sodium hydroxide (0.0125 mole), and the mixture is stirred until solution is effected. The solution is diluted to 25 cc., filtered and let stand 10 minutes. The alkaline solution is kept at room temperature (25° C.) throughout. The product separates as a gum when the solution is acidified with 10 cc. of 10 per cent acetic acid. After washing several times with water, the gum slowly crystallizes. There is obtained 1.25 grams of ω-benzoylacetamino-m-thioglycolic anilide melting at 148–149°.

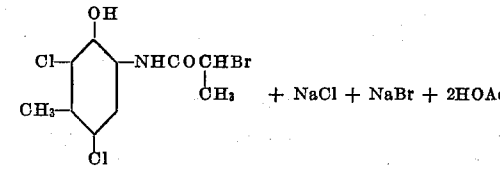
Compound 9 is similarly prepared from compound 11.

Compound 15 is prepared by condensing p-(acetoacetamino)-aniline wth acetylthioglycolyl chloride in a manner similar to that used in the preparation of compound 13.

Compound 6 is prepared as follows:

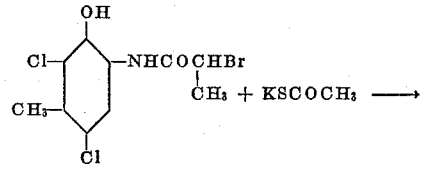
2-(α-bromopropionamido)-4,6-dichloro-5-methylphenol

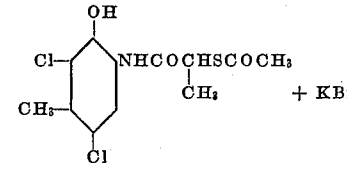




To a well stirred suspension of 22.8 grams (0.1 mole) of 2-amino-4,6-dichloro-5-methylphenol hydrochloride and 17.5 grams (0.2 mole) of anhydrous sodium acetate in 200 cc. of glacial acetic acid was added 21.6 grams (0.1 mole) of α-bromopropionyl bromide. The mixture was stirred at 50° for two hours, and then flooded with water. The oil was extracted with ether, and the ether layer washed, dried and concentrated. The residue was recrystallized from benzene, M. P. 144–146°.

2-α-acetylmercaptopropionamido)-4,6-dichloro-5-methylphenol





To a solution of potassium thioacetate prepared from 0.4 gram of thioacetic acid and 0.23 gram of potassium hydroxide in 15 cc. of ethyl alcohol was added 1.6 grams of 2-(α-bromopropionamido)-4,6-dichloro-5-methylphenol. The clear solution warmed to 35° and potassium bromide separated. After standing overnight, water was added and the solid collected on a filter. It was recrystallized from diluted alcohol; M. P. 132–133°.

The preparation of the couplers used according to our invention is described in our divisional U. S. Patent 2,412,700, granted December 17, 1946.

The following examples, which are illustrative only, indicate a method of forming a multi-layer photographic element, using the couplers of our invention:

A cyan coupler solution is prepared by dissolving 6.9 grams (0.03 mole) of 2-hydroxy-4-methyl-5-chloro-thioglycolic anilide in 120 cc. of 2% sodium hydroxide. A very fine silver chloride emulsion is prepared by a well-known procedure containing 6.4 grams (0.045 mole) of silver chloride in 880 cc. of a 2.3% gel solution. The cyan coupler solution is added with rapid stirring to this very fine grain silver chloride emulsion. This forms a silver salt of the cyan coupler in very fine dispersion. This coupler dispersion may then

be mixed with an equal volume of a higher speed red-sensitized emulsion and coated on a support, spreading 45 grams of coupler per thousand square feet.

A magenta coupler solution is prepared by dissolving 5.5 grams (0.02 mole) of p-acetylthioglycolylamino-ω-cyanoacetophenone in 72 cc. of 2% sodium hydroxide. A very fine grain silver chloride emulsion is prepared by a well-known method containing 4.3 grams (0.03 mole) of silver chloride in 928 cc. of a 1.1% gel solution. The magenta coupler solution is added with rapid stirring to this very fine grain silver chloride emulsion. This forms a silver salt of the magenta coupler in very fine dispersion. This coupler dispersion may then be mixed with one-half the volume of a higher speed green-sensitized emulsion and coated on the red-sensitized cyan layer spreading 60 grams of coupler per thousand square feet.

A yellow filter layer is coated over the red and green-sensitive layers to protect them from the blue light to which they are inherently sensitive. This filter layer may consist of a very fine dispersion of silver prepared by the Carey-Lea dextrin method. It should be coated so it has a density of 2.0 to light of wave length 420 mμ.

The yellow coupler is prepared by dissolving 7.4 grams of (0.02 mole) of ω-benzoylacetamino-p-acetylthioglycolic anilide in 80 cc. of 2% sodium hydroxide. A very fine silver chloride emulsion is prepared by a well-known procedure containing 4.3 grams (0.03 mole) of silver chloride in 920 cc. of 1.1% gel solution. The yellow coupler solution is added with rapid stirring to this very fine grain silver chloride emulsion. This forms a silver salt of the yellow coupler in very fine dispersion. This coupler dispersion may then be mixed with one-half the volume of a higher speed unsensitized emulsion and coated over the filter layer. This layer of yellow coupler is the top and final coat of the multi-layer coating. The layer should be spread at about 120 grams per thousand square feet.

The emulsion layers coated in this way produce respectively cyan, magenta and yellow images upon development with a primary aromatic amino developing agent such as diethyl-p-phenylenediamine. The element may be exposed and developed directly to form a negative colored image or a positive image may be obtained by first developing in an ordinary black-and-white developer followed by color development of the residual silver halide.

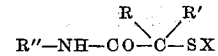
The emulsions containing our coupler compounds are developed with any suitable primary aromatic amino developing agent, such as the solutions described in Peterson U. S. Patents 2,296,306 and 2,353,754. Development is preferably carried out for about 5 minutes at 65° F. after which the element is treated with a weak acid stop bath, such as acetic acid followed by ferricyanide and hypo baths to remove the silver and any undeveloped silver halide which the film contains. These baths also remove any unused coupler.

It will be apparent that the emulsion layers made with the couplers of our invention may be coated on any suitable support such as cellulose nitrate, cellulose acetate, glass or synthetic resins or on opaque supports, such as paper or pigmented cellulose esters.

The modification and examples included herein are illustrative only and it will be understood that our invention is to be taken as limited only by the scope of the appended claims.

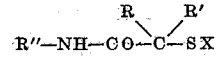
We claim:

1. The method of producing a colored photographic image in a silver halide emulsion layer which comprises incorporating in said layer a metallic salt of a coupler compound having the formula:



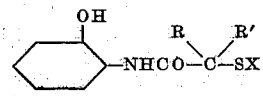
where R'' is selected from the class consisting of 2-hydroxy mononuclear aryl radicals, 5-hydroxynaphthyl radicals, 1-benzoyl acetanilido radicals, acetoacetylanilido radicals, omega-cyano acetophenone radicals, and 3-(1-phenyl-5-pyrazolone) radicals, R and R' are selected from the class consisting of hydrogen and alkyl groups, and X is selected from the class consisting of hydrogen and acetyl groups, exposing said layer and developing it with a primary aromatic amino developing agent.

2. The method of producing a colored photographic image in a silver halide emulsion layer which comprises incorporating in said layer a metallic salt of a coupler compound having the formula:



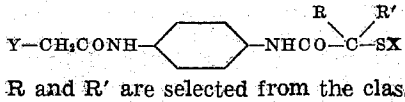
where R'' is a 2-hydroxy mononuclear aryl radical and R and R' are selected from the class consisting of hydrogen and alkyl groups, and X is selected from the class consisting of hydrogen and acetyl groups, exposing said layer and developing it with a primary aromatic amino developing agent.

3. The method of producing a colored photographic image in a silver halide emulsion layer which comprises incorporating in said layer a metallic salt of a coupler compound having the formula:



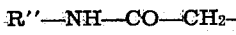
where R and R' are selected from the class consisting of hydrogen and alkyl groups, and X is selected from the class consisting of hydrogen and acetyl groups, exposing said layer and developing it with a primary aromatic amino developing agent.

4. The method of producing a colored photographic image in a silver halide emulsion layer which comprises incorporating in said layer a metallic salt of a coupler compound having the formula:



where R and R' are selected from the class consisting of hydrogen and alkyl groups, X is selected from the class consisting of hydrogen and acetyl groups, and Y is selected from the class consisting of acyl and cyano groups, exposing said layer and developing it with a primary aromatic amino developing agent.

5. The method of producing a colored photographic image in a silver halide emulsion layer which comprises incorporating in said layer a metallic salt of a coupler compound having the formula:



where R'' is selected from the class consisting of 2-hydroxy mononuclear aryl radicals, 5-hydroxynaphthyl radicals, 1-benzoyl acetanilido radicals, acetoacetylanilido radicals, omega-cyano aceto-

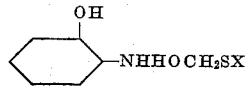
phenone radicals, and 3-(1-phenyl-5-pyrazolone) radicals, and X is selected from the class consisting of hydrogen and acetyl groups, exposing said layer and developing it with a primary aromatic amino developing agent.

6. The method of producing a colored photographic image in a silver halide emulsion layer which comprises incorporating in said layer a metallic salt of a coupler compound having the formula:

$$R''—NH—CO—CH_2—SX$$

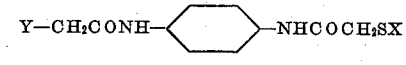
where R'' is a 2-hydroxy mononuclear aryl radical and X is selected from the class consisting of hydrogen and acetyl groups, exposing said layer and developing it with a primary, aromatic amino developing agent.

7. The method of producing a colored photographic image in a silver halide emulsion layer which comprises incorporating in said layer a metallic salt of a coupler compound having the formula:



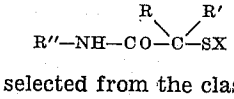
where X is selected from the class consisting of hydrogen and acetyl groups, exposing said layer and developing it with a primary aromatic amino developing agent.

8. The method of producing a colored photographic image in a silver halide emulsion layer which comprises incorporating in said layer a metallic salt of a coupler compound having the formula:



where X is selected from the class consisting of hydrogen and acetyl groups, and Y is selected from the class consisting of acyl and cyano groups, exposing said layer and developing it with a primary aromatic amino developing agent.

9. The method of producing a color-forming photographic emulsion which comprises forming a sensitive silver salt in a colloidal material and then incorporating in said material a metallic salt of a coupler compound having the following formula:



where R'' is selected from the class consisting of 2-hydroxy mononuclear aryl radicals, 5-hydroxynaphthyl radicals, 1-benzoyl acetanilido radicals, acetoacetylanilido radicals, omega-cyano acetophenone radicals, and 3-(1-phenyl-5-pyrazolone) radicals, R and R' are selected from the class consisting of hydrogen and alkyl groups, and X is selected from the class consisting of hydrogen and acetyl groups, exposing said layer and developing it with a primary aromatic amino developing agent, and forming a metallic salt of said coupler compound less soluble than said sensitive silver salt by replacement of the X substituent of said coupler compound with a metallic atom.

10. The method of producing a color-forming photographic emulsion which comprises forming a sensitive silver salt in gelatin and then incorporating in said gelatin a metallic salt of a coupler compound having the following formula:

$$R''—NHCOCH_2SX$$

where R'' is selected from the class consisting of

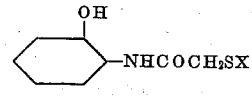
2-hydroxy mononuclear aryl radicals, 5-hydroxynaphthyl radicals, 1-benzoyl acetanilido radicals, acetoacetylanilido radicals, omega-cyano acetophenone radicals, and 3-(1-phenyl-5-pyrazolone) radicals, and X is selected from the class consisting of hydrogen and acetyl groups, and forming a silver salt of said coupler compound less soluble than said sensitive silver salt by replacement of the X substituent of said coupler compound with a silver atom.

11. The method of producing a color-forming photographic emulsion which comprises forming a sensitive silver salt in gelatin and then incorporating in said gelatin a metallic salt of a coupler compound having the following formula:

$$R''—NHCOCH_2SX$$

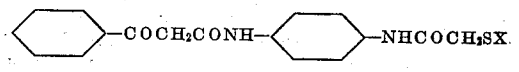
where R'' is a 2-hydroxy mononuclear aryl radical and X is selected from the class consisting of hydrogen and acetyl groups, and forming a silver salt of said coupler compound less soluble than said sensitive silver salt by replacement of the X substituent of said coupler compound with a silver atom.

12. The method of producing a color-forming photographic emulsion which comprises forming a sensitive silver salt in gelatin and then incorporating in said gelatin a metallic salt of a coupler compound having the following formula:



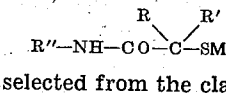
where X is selected from the class consisting of hydrogen and acetyl groups, and forming a silver salt of said coupler compound less soluble than said sensitive silver salt by replacement of the X substituent of said coupler compound with a silver atom.

13. The method of producing a color-forming photographic emulsion which comprises forming a sensitive silver salt in gelatin and then incorporating in said gelatin a metallic salt of a coupler compound having the following formula:



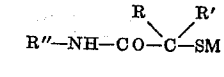
where X is selected from the class consisting of hydrogen and acetyl groups and forming a silver salt of said coupler compound less soluble than said sensitive silver salt by replacement of the X substituent of said coupler compound with a silver atom.

14. A gelatino-silver halide emulsion for color photography containing a non-diffusing color-forming compound having the following formula:



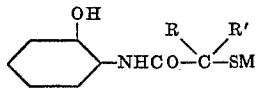
where R'' is selected from the class consisting of 2-hydroxy mononuclear aryl radicals, 5-hydroxynaphthyl radicals, 1-benzoyl acetanilido radicals, acetoacetylanilido radicals, omega-cyano acetophenone radicals, and 3-(1-phenyl-5-pyrazolone) radicals, R and R' are selected from the class consisting of hydrogen and alkyl groups, and M is a heavy metal radical.

15. A gelatino-silver halide emulsion for color photography containing a non-diffusing color-forming compound having the following formula:



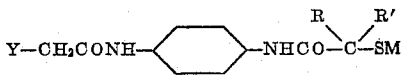
where R'' is a 2-hydroxy mononuclear aryl radical and where R and R' are selected from the class consisting of hydrogen and alkyl groups, and M is a heavy metal radical.

16. A gelatino-silver halide emulsion for color photography containing a non-diffusing color-forming compound having the following formula:



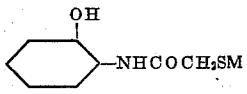
where R and R' are selected from the class consisting of hydrogen and alkyl groups, and M is a heavy metal radical.

17. A gelatino-silver halide emulsion for color photography containing a non-diffusing color-forming compound having the following formula:



where R and R' are selected from the class consisting of hydrogen and alkyl groups, and Y is selected from the class consisting of acyl and cyano groups, and M is a heavy metal radical.

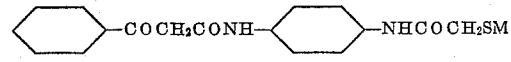
18. A gelatino-silver halide emulsion for color photography containing a non-diffusing color-forming compound having the following formula:



where M is a heavy metal radical.

19. A gelatino-silver halide emulsion for color photography containing a non-diffusing color-

forming compound having the following formula:



where M is a heavy metal radical.

ARNOLD WEISSBERGER.
CHARLES J. KIBLER.
RICHARD V. YOUNG.

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The following references are of record in the file of this patent:

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Certificate of Correction

Patent No. 2,448,939. September 7, 1948.

ARNOLD WEISSBERGER ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Column 11, line 25, claim 7, in the formula, for "NHHOCH$_2$SX" read *NHCOCH$_2$SX*; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 16th day of November, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.