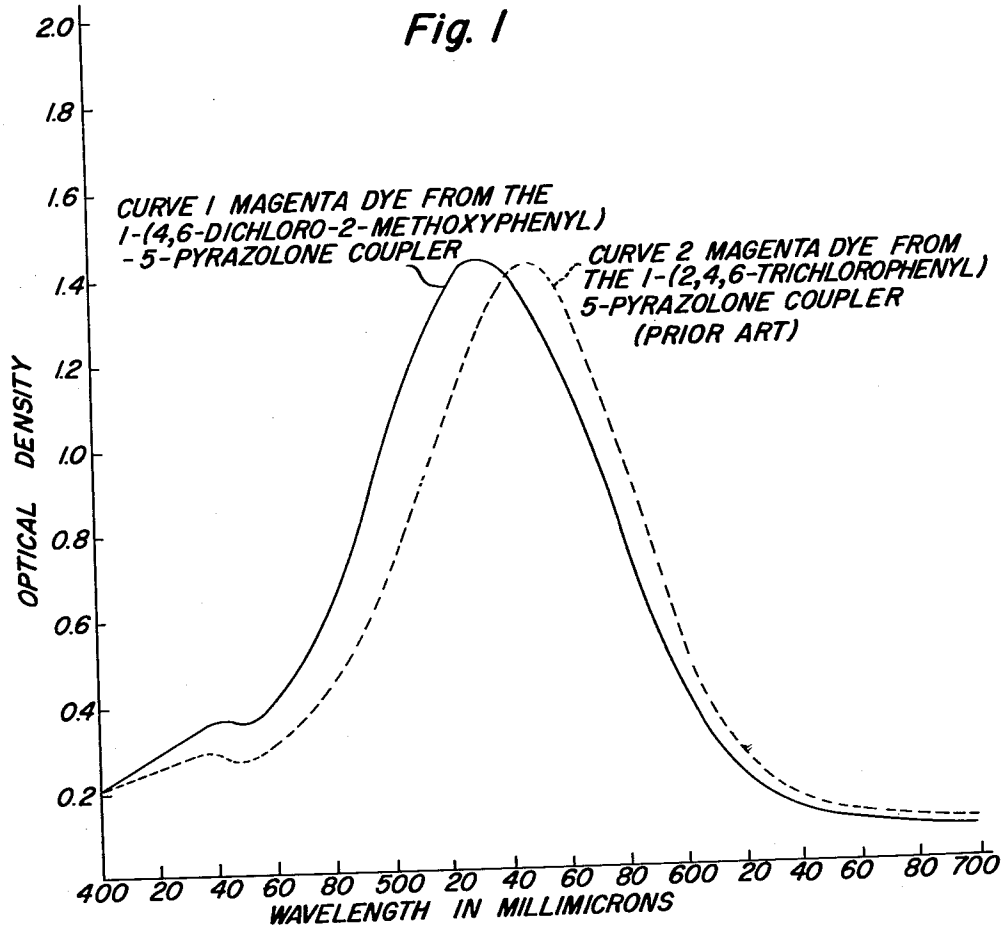
Nov. 6, 1962 A. WEISSBERGER ETAL 3,062,653

PHOTOGRAPHIC EMULSION CONTAINING PYRAZOLONE MAGENTA-FORMING COUPLERS

Filed Feb. 18, 1960 2 Sheets-Sheet 1

Fig. 1



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Fig. 2

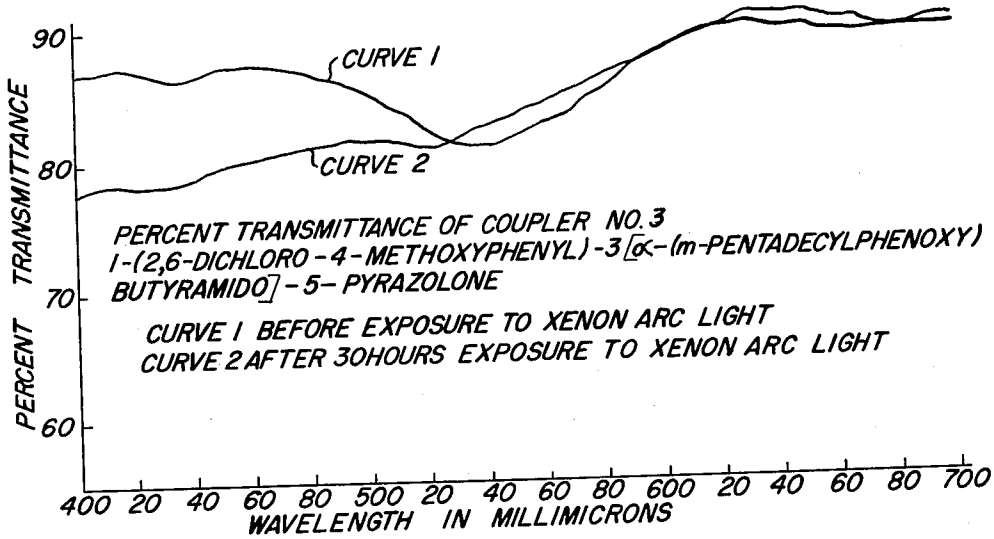
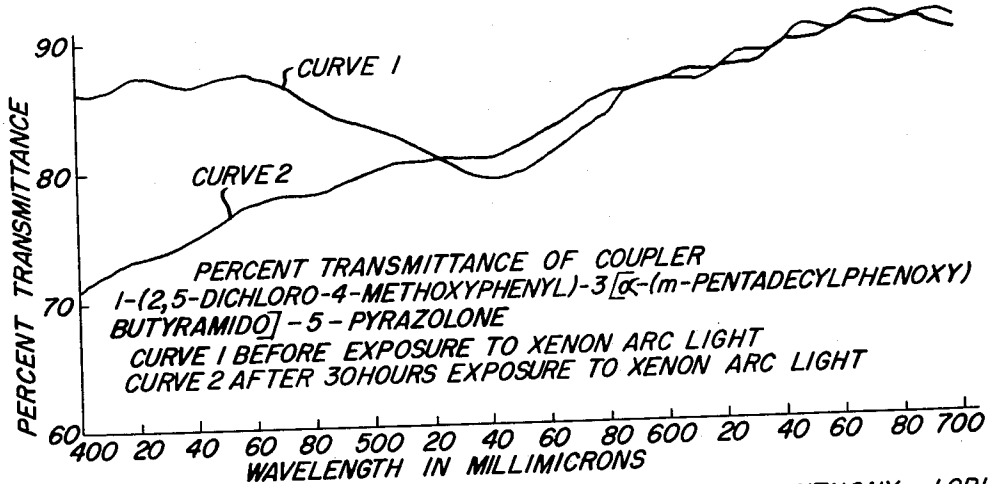


Fig. 3



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3,062,653

PHOTOGRAPHIC EMULSION CONTAINING PYRAZOLONE MAGENTA-FORMING COUPLERS

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9 Claims. (Cl. 96—100)

This invention relates to color photography and particularly to substituted 1-phenyl-3-amido-5-pyrazolone magenta-forming couplers and photographic silver halide emulsions containing these couplers.

Formation of colored photographic images by coupling the development product of primary aromatic amino developing agents with color forming or coupling compounds is well known. In these processes the subtractive process of color formation is ordinarily used and the image dyes are of the complementary primary colors, cyan, magenta and yellow. The couplers used to produce these dyes generally contain color-forming groups of the phenolic, hydroxyl, pyrazolone or benzoyl acetanilide classes. These groups render the coupler capable of coupling with the oxidation product of the primary aromatic amino developing agent formed during photographic development.

The use of various pyrazolone derivatives for the production of the magenta image in three-color photography is well known, and the use of 1-phenyl-3-acylamino-5-pyrazolones for this purpose is described in Porter and Weissberger U.S. Patent 2,369,489.

Some of the prior art couplers are not as stable to light and heat as is desired. The couplers are uncolored but upon decomposition form products that have some color. Thus, if couplers incorporated in emulsions do not have good stability, decomposition will occur producing a very undesirable yellowing or staining of the pictures. Another effect generally known as print-out will also result in pictures made with emulsions containing couplers which are unstable upon exposure to heat and light. Print-out is produced by the decomposition of residual coupler that was unused in the image dye formation, and results in stain in the areas containing residual coupler.

A further disadvantage of the couplers in current use is that they form dyes having an excess red absorption and an inadequate green absorption. Some of the couplers in use are not soluble enough in coupler solvents to make it possible to incorporate them in photographic emulsions at the desired coupler to coupler solvent ratios. Couplers in use are not always as free from wandering in the photographic emulsion layers in which they are incorporated as is desired.

It is, therefore, an object of our invention to provide a new class of magenta-forming couplers which have good stability to heat and light and which can be incorporated in photographic emulsions that will therefore not be subject to print-out or yellowing.

Another object of our invention is to provide a new class of magenta-forming couplers which are readily incorporated in photographic silver halide emulsion layers with standard coupler solvents over a broad span of coupler to coupler solvent ratios, and which react during development with the oxidized developing agent to produce a magenta dye having improved light absorption characteristics.

Another object is to provide couplers which upon development with oxidized developing agents produce dyes whose light absorption curves are shifted toward the shorter wavelengths in such a way as to enable one to

avoid excess red absorption and inadequate green absorption of the dyes in current use.

Another object is to provide a new class of magenta-forming couplers which are not only readily soluble in coupler solvents but give dispersions which are free from coupler crystallization at high coupler to coupler solvent ratios.

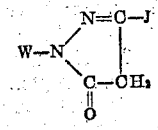
A further object is to provide a new class of magenta-forming couplers which give dyes of good light and heat-stability.

Another object is to provide magenta couplers which are not only readily incorporated in photographic emulsion layers but are free from wandering from the layer in which they are incorporated.

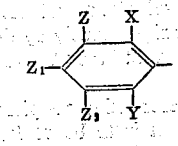
A still further object is to provide photographic emulsions containing our couplers which not only produce dyes having superior light absorption characteristics, dyes that have good stability to light and heat, and dyes that are free from wandering, but emulsions which when processed and stored have low print-out and yellowing from residual coupler.

Still further objects will become apparent from the following specification.

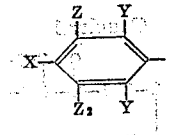
We have discovered that the above objects and other objects can be accomplished by using the new classes of magenta-forming couplers of our invention. Our couplers can advantageously be represented by the following formula:



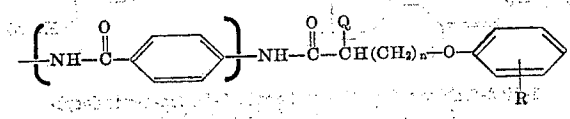
wherein W represents either



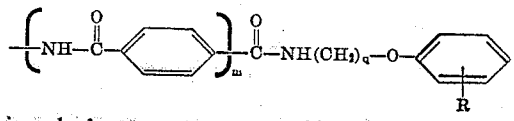
or



X is a halogen atom; Y is an alkyl group having from 1 to 18 carbon atoms such as methyl, ethyl, propyl, butyl, pentyl or hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tridecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, an alkoxy group, e.g., methoxy, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, tridecoxy, hexadecoxy, etc., an alkthio group, e.g., methylthio, ethylthio, butylthio, hexylthio, octylthio, decylthio, tridecylthio, etc., an alkseleno group e.g., methylseleno, ethylseleno, propylseleno, hexylseleno, etc., all of which may have from 1 to 18 carbon atoms in the alkyl part of these groups and in which the alkyl group may be secondary or tertiary as well as primary, an aryl group e.g., phenyl, tolyl, etc., aryloxy group e.g., phenoxy, etc., an arylthio group e.g., phenylthio or an arylseleno group, e.g., phenylseleno, etc.; Z, Z_1, and Z_2 each represents a hydrogen atom, a halogen atom or a Y group; J is an aromatic acyl amino group such as those of the Porter and Weissberger Patent 2,369,489 including for example such groups as

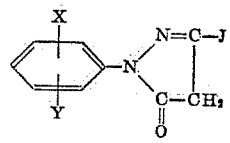


and the group



Q is a hydrogen atom or a lower alkyl group having from 1 to 6 carbon atoms; *n* is from 0 to 2; *m* is 0 or 1; R is an alkyl group having from 1 to 20 carbon atoms; and *q* is 1 to 3.

The preferred couplers of our invention can be represented by the formula:

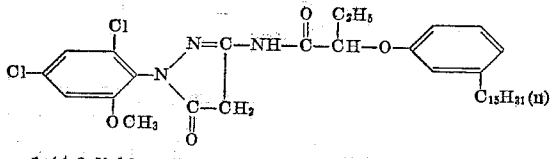


in which X, Y and J are as defined above and where X and Y occupy the 2, 4 and 6-positions of the 1-phenyl ring.

Although the preferred couplers have a ballasting group as defined by J, our couplers can have any of the ballasting groups attached to the 3-position on the 5-pyrazolone ring that are used in prior art couplers. Our couplers are distinguished from the prior art couplers by having the substituents X and Y attached to the 2, 4 and 6-positions of the 1-phenyl group. Our couplers are not only characterized by this novel structural arrangement but are charcterized far more significantly by the greatly improved print-out properties that result from this structural difference.

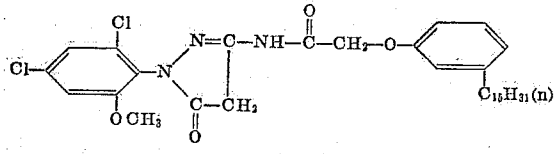
The following representative couplers will illustrate our invention. However, it is to be understood that our invention is not limited to these specific couplers.

Coupler 1



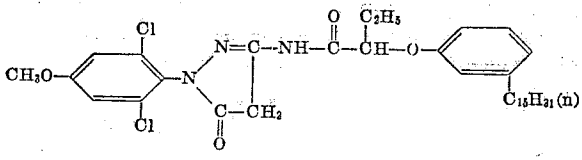
1-(4,6-dichloro-2-methoxyphenyl)-3-[α-(m-pentadecylphenoxy)butyramido]-5-pyrazolone

Coupler 2



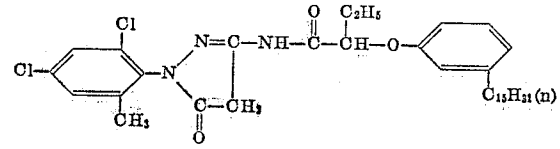
1-(4,6-dichloro-2-methoxyphenyl)-3-[α-(m-pentadecylphenoxy)acetamido]-5-pyrazolone

Coupler 3



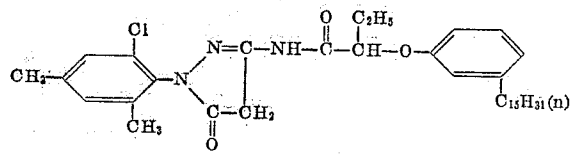
1-(2,6-dichloro-4-methoxyphenyl)-3-[α-(m-pentadecylphenoxy)butyramido]-5-pyrazolone

Coupler 4



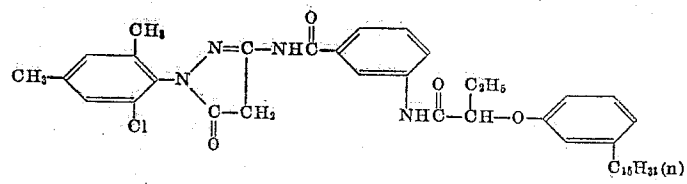
1-(4,6-dichloro-2-methylphenyl)-3-[α-(m-pentadecylphenoxy)butyramido]-5-pyrazolone

Coupler 5



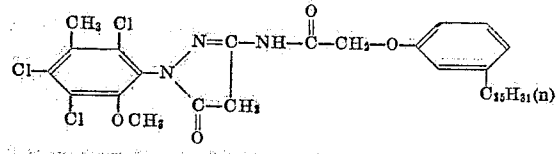
1-(6-chloro-2,4-dimethylphenyl)-3-[α-(m-pentadecylphenoxy)butyramido]-5-pyrazolone

Coupler 6



1-(2,4-dimethyl-6-chlorophenyl)-3-{[α-(m-pentadecylphenoxy)butyramido]m-benzamido}-5-pyrazolone

Coupler 7



1-(2-methoxy-5-methyl-3,4,6-trichlorophenyl)-3-[α-(m-pentadecylphenoxy)acetamido]-5-pyrazolone

Our coupler compounds are prepared by the halogenation of the appropriately substituted aniline hydrochloride, conversion of this compound to the corresponding phenylhydrazine, then reacting the phenylhydrazine with ethyl-β-ethoxy-β-iminopropionate to form the substituted 1-phenyl-3-amino-5-pyrazolone, followed by the reaction of this compound with the appropriate acylchloride.

The following examples will illustrate specific synthesis of representative couplers of our invention

EXAMPLE I

Coupler 1

STEP 1.—4,6-DICHLORO-2-METHOXYANILINE HYDROCHLORIDE

In a 3-liter flask, fitted with a stirrer, a condenser, a thermometer, and a dropping funnel was placed 160 g. (1.0 mole) of o-anisidine hydrochloride. The flask was cooled in an ice water bath and 500 cc. of sulfuryl chloride was added in one portion through the condenser with efficient stirring. A stirrable suspension was obtained which changed to a fluffy mass after a few minutes of stirring. After stirring from 15 to 20 minutes, a second 250 cc. portion of sulfuryl chloride was added and the mixture was stirred an additional 15 minutes. Anhydrous ether was then added and the suspended material collected on a Büchner funnel, washed well with dry ether, and dried giving 210 g. of a gray-white solid.

The crude product was dissolved in 1500 cc. of methanol by warming, stirred for 15 minutes with decolorizing carbon such as Nuchar, filtered and the clear filtrate concentrated to ½ its original volume. The solution was

diluted with 6 liters of cold water and the 4,6-dichloro-2-methoxyaniline which separated as an oil was extracted with ether.

The ether extract was dried over magnesium sulfate and then saturated with gaseous hydrogen chloride. 160 g. of product were obtained upon filtration and drying.

STEP 2.—4,6-DICHLORO-2-METHOXYPHENYL-HYDRAZINE

In a 12 liter flask fitted with a stirrer, and dropping funnel were placed 500 g. of 4,6-dichloro-2-methoxyaniline hydrochloride, 665 cc. of distilled water and 1330 cc. of concentrated hydrochloric acid. The mixture was vigorously stirred for 30 minutes at room temperature and then cooled to 0° C. to —2° C. by a Dry Ice bath. A solution of 160 g. of sodium nitrite in 500 cc. of water was introduced through a tube below the surface of the cold stirred suspension. Excess nitrous acid was destroyed with sulfamic acid. The diazonium solution was filtered and poured rapidly into a stirred solution of 1830 g. of stannous chloride dissolved in 20 liters of distilled water and 10 liters of concentrated hydrochloric acid contained in a 15-gallon crock. The reaction mixture was stirred for 1 hour and the supernatant liquid was removed by filtration. The solid was triturated with 20 gallons of distilled water and the supernatant liquid was again removed by filtration. The wet, solid residue was suspended in 15 liters of distilled water, stirred and made strongly basic with 40% sodium hydroxide. The mixture was extracted 4 times with 1-liter portions of ethyl ether and the combined extracts were dried over sodium sulfate. The dried ether solution was evaporated to dryness. The crude hydrazine was recrystallized from hexane to produce 348 g. of light orange crystals having a melting point of 90–92° C.

STEP 3.—1-(4,6-DICHLORO-2-METHOXY)PHENYL-3-AMINO-5-PYRAZOLONE

In a 3-liter, 3-neck flask were placed 139 g. (.67 mole) of 4,6-dichloro-2-methoxyphenylhydrazine and 107 g. (.67 mole) of ethyl β-ethoxy-β-iminopropionate. The two solids were mixed by rotating the flask manually for 2–3 minutes and then 3 ml. of glacial acetic acid was added and manual rotation was continued until the material completely dissolved. After 30 minutes to 1 hour, the material solidified and the temperature of the solution rose to 44° C. The flask was then placed in the temperature-controlled water bath at 35 to 45° C. and evacuated by means of an evaporator such as a Rinco evaporator for 1 hour. The flask was removed from the evaporator and a freshly prepared solution of 15 g. of sodium in 750 cc. of absolute ethyl alcohol was added. The reaction mixture was boiled under reflux for two hours, the excess alcohol was removed in vacuo and the remaining solid was dissolved in 1500 cc. of water. The solution was extracted 3 times with ethyl ether and the aqueous phase was filtered through a previously prepared cake of decolorizing carbon such as Nuchar. The filtrate was cooled to 20° C. and, with stirring, was acidified with glacial acetic acid. The precipitate was washed, filtered and dried. There was obtained 136 g. of dry product, with a melting point of 200–202° C. This was recrystallized from 10 parts of methyl alcohol to produce 84 g. of crystalline product having a melting point of 218–220° C.

STEP 4.—1-(4,6-DICHLORO-2-METHOXY)PHENYL-3[α-(3-PENTADECYLPHENOXY)BUTYRAMIDO] - 5 - PYRAZOLONE

1-(4,6-dichloro-2-methoxy)phenyl-3-amino - 5 - pyrazolone (171 g., 0.623 mole) was placed in a 5-liter, 3-neck flask equipped with a stirrer, a condenser, a thermometer, and a dropping funnel. The flask was placed in a 95% ethyl alcohol bath, 2500 cc. of acetonitrile was added and the temperature was raised to 40° C. to obtain a complete solution, and 260 g. (0.63 mole) of α-(meta-pentadecylphenoxy)butyryl chloride was added in 10 minutes. When the addition was complete, the reaction mixture was stirred under reflux overnight. The reaction mixture was cooled externally with water to 25° C. The supernatant liquor was poured off, and the crude product was heated in a water bath at 45–50° C. under vacuum to remove as much of the acetonitrile as possible. The residue was dissolved in a solution of 500 cc. of absolute alcohol, 30 g. of sodium hydroxide pellets, and 20 cc. of distilled water and stirred for 2 hours. The solution was poured into a stirred solution of 100 cc. of concentrated hydrochloric acid and 5 liters of ice water. The fine, white precipitate was suction-filtered, washed slightly with water, and dissolved in 500 cc. of ethyl ether. The ethereal solution was dried for 2 hours over sodium sulfate, filtered, and concentrated. The residue was dissolved in 3 liters of acetonitrile, the solution filtered through a filter cake composed of a mixture of filter aid and decolorizing carbon, and allowed to crystallize slowly overnight. There was obtained 260 g. of product having a melting point of 85 to 90° C.

The product was recrystallized from 3 liters of acetonitrile using decolorizing carbon such as Norite, and there was obtained 210 g. of crystals having a melting point of 87–90° C. A recrystallization from 2500 cc. of acetonitrile yielded 163 g. of white colored material having a melting point of 88–90° C.

This material gave the following analysis:

Analysis	C	H	N
Calculated	65.0	7.7	6.5
Found	65.4	7.8	6.8

EXAMPLE II

Coupler 2

This coupler was prepared by the same method used for preparing Coupler 1 excepting that α-(meta-pentadecylphenoxy) acetyl chloride was used in Step 4 in place of α-(meta-pentadecylphenoxy) butyryl chloride. The product obtained was off-white in color, having a melting point of 119–129° C. It had the following analysis:

Analysis	C	H	N
Calculated	64.0	7.4	6.8
Found	64.3	7.1	6.6

EXAMPLE III

Coupler 3

STEP 1.—2,6-DICHLORO-4-METHOXYANILINE

A saturated solution of HCl gas in methanol was prepared by bubbling dry HCl in methanol with cooling. To 2.4 liters of this saturated solution was slowly added 290 g. of p-nitrosophenol (M.P. 142–143° C.) over a one-hour period, maintaining the temperature at 15 to 20° C. with an ice water bath. Dry HCl was continually bubbled through the mixture during the addition. Stirring was continued an additional 30 minutes while HCl gas was bubbled into the suspension. The product was collected on a sintered glass funnel, washed with ether and dried, giving a yield of 420 g.

The crude hydrochloride was dissolved in 1.4 liters of refluxing methanol plus 100 cc. of water, treated with Nuchar and the filtrate drowned in 10 liters of cold water. The solid which formed was collected by filtration and crystallized from 700 ml. of methanol giving 192 g. of 2,6-dichloro-4-methoxyaniline as white needles with a melting point of 72–73° C. This amine was diazotized as in Step 2 of Example 1 to produce the corresponding phenylhydrazine which was then carried through Steps 3 and 4 of Example 1 to produce the white coupler (3)

having a melting point of 107 to 110° C. The analysis of this material was as follows:

Analysis	C	H	N
Calculated	65.0	7.6	6.5
Found	65.0	7.8	6.2

EXAMPLE IV

Coupler 4

STEP 1.—4,6-DICHLORO-2-METHYLACETANILIDE

In a 5-liter flask equipped with a mechanical stirrer, a reflux condenser and a gas-addition tube were placed 450 g. (3.0 moles) of o-acetotoluidide, 492 g. of anhydrous sodium acetate (6.0 moles), 1.5 liters of glacial acetic acid, and 10 g. of iron powder. The mixture was heated to 90° on a steam bath and chlorine gas bubbled through the suspension for 4½ hours with continued heating and stirring. The hot mixture was filtered through a sintered glass funnel and sulfur dioxide was slowly bubbled through the dark solution for 30 minutes. Water (approximately 750 cc.) was added to the warm solution and the product allowed to crystallize slowly. After overnight standing the product was collected on a Büchner funnel, washed well with water and dried giving 381 g. of material with a melting point of 177–180° C. The crude product was recrystallized from 1 liter of 95% ethyl alcohol, thus obtaining 172 g. of material as white flakes having a melting point of 185–187° C.

STEP 2.—4,6-DICHLORO-2-METHYLANILINE

A mixture of 352 g. (1.62 moles) of 4,6-dichloro-2-methylacetanilide, 1.9 liters of 95% ethyl alcohol (3A alcohol) and 2.1 liters of concentrated hydrochloric acid in a 12-liter flask were refluxed overnight. The alcohol was removed by distillation and the semi-solid residue stirred and cooled while being neutralized with 28% ammonium hydroxide. The mixture was extracted 3 times with ether, the combined extracts water washed, dried over magnesium sulfate, filtered, and the solvent distilled. The residual oil was distilled under reduced pressure (the main fraction boiling point was 128–130°/13 mm. Hg) giving 175 g. of a white crystalline material having a melting point of 48–49° C.

STEP 3.—4,6-DICHLORO-2-METHYLPHENYLHYDRAZINE

This compound was prepared by the same method given for the preparation of 4,6-dichloro-2-methoxyphenylhydrazine using 4,6-dichloro-2-methylaniline instead of 4,6-dichloro-2-methoxyaniline as starting material. Crystallized from 1400 cc. of methanol, it had a melting point of 120.5 to 122° C.

STEP 4.—1-(4,6-DICHLORO-2-METHYLPHENYL)-3-AMINO-5-PYRAZOLONE

This compound was prepared by the same method given for the preparation of 1-(4,6-dichloro-2-methoxyphenyl)-3-amino-5-pyrazolone, using an equivalent of 4,6-dichloro-2-methylphenylhydrazine instead of 4,6-dichloro-2-methoxyphenylhydrazine as starting material. The crude product was recrystallized from 7.5 parts of ethyl acetate using 1.5 parts of ethanol to obtain complete solution. A yield of 94 g. was obtained having a melting point of 195–196° C.

STEP 5.—1-(4,6-DICHLORO-2-METHYLPHENYL)-2-[α-(META-PENTADECYLPHENOXY)BUTYRAMIDO]-5-PYRAZOLONE

In a 3-liter flask equipped with a mechanical stirrer and reflux condenser were placed 70 g. (0.27 mole) of 1-(4,6-dichloro-2-methylphenyl)-3-amino-5-pyrazolone, 123 g. (0.3 mole) of α-(meta-pentadecylphenoxy)butyryl chloride and 1500 ml. of anhydrous acetonitrile. The mixture was stirred and refluxed for 4 hours. On slow cooling overnight, with stirring, a solid separated and was collected on a filter, washed with a small portion of cold acetonitrile and dried. The crude product weighed 163 g. and was recrystallized from 30 parts of n-hexane yielding 78 g. of coupler No. 4 as a white solid having a melting point of 90–92° C. The analysis of this material was as follows:

Analysis	C	H	N
Calculated	66.8	7.8	6.6
Found	67.1	8.1	6.6

EXAMPLE V

Coupler 5

STEP 1.—6-CHLORO-2,4-DIMETHYLACETANILIDE

A 5-liter flask equipped with a mechanical stirrer, reflux condenser and gas addition tube was charged with 489 g. (3.0 mole) of 2,4-dimethylacetanilide, 246 g. (3.0 moles) of anhydrous sodium acetate dissolved in 1.5 liters of glacial acetic acid, and 10 grams of iron powder. The mixture was heated to 90° C. on a steam bath and chlorine gas was bubbled through the mixture for 3 hours with continued heating and stirring. The hot mixture was filtered through a sintered glass funnel and sulfur dioxide was bubbled through the dark filtrate for 5 minutes. Water was added to the warm solution until a precipitate began to form (approximately 750 cc.). The mixture was allowed to stand overnight, filtered and the solid washed well with water and dried. The crude product was recrystallized from 1100 cc. of 95% ethyl alcohol as white flakes with a melting point of 201–202° C.

STEP 2.—6-CHLORO-2,4-DIMETHYLANILINE

In a 12-liter flask equipped with a reflux condenser was placed 361 g. (1.82 moles) of 6-chloro-2,4-dimethylacetanilide, 1900 cc. of 3A alcohol and 2100 cc. of concentrated hydrochloric acid. The mixture was heated under reflux for 24 hours. The alcohol was removed by distillation and the semi-solid residue stirred and cooled while being neutralized with 28% ammonium hydroxide. The mixture was ether extracted 3 times, the combined ether extracts dried over magnesium sulfate, filtered and the solvent distilled. The residual oil was distilled under reduced pressure (boiling point 116–119° C./15 mm. Hg) giving 223 g. of white crystalline material having a melting point of 40.5 to 42° C.

STEP 3.—6-CHLORO-2,4-DIMETHYLPHENYLHYDRAZINE

This hydrazine was prepared by the same method given for the preparation of 4,6-dichloro-2-methoxyphenylhydrazine, using an equivalent quantity of 6-chloro-2,4-dimethylaniline instead of 4,6-dichloro-2-methoxyaniline. The product was crystallized from hexane, from which it came out as tan colored needles having a melting point of 76.5–77.5° C.

STEP 4.—1-(6-CHLORO-2,4-DIMETHYLPHENYL)-3-AMINO-5-PYRAZOLONE

This pyrazolone was prepared by the method described for the preparation of 1-(4,6-dichloro-2-methoxyphenyl)-3-amino-5-pyrazolone, using an equivalent amount of 6-chloro-2,4-dimethylphenylhydrazine instead of 4,6-dichloro-2-methoxyphenylhydrazine. The crude product was crystallized from 95% ethyl alcohol, and had a melting point of 158–160° C.

STEP 5.—1-(6-CHLORO-2,4-DIMETHYLPHENYL)-[α-(3-n-PENTADECYLPHENOXY)-BUTYRYLAMIDO]-5-PYRAZOLONE

In a 1-liter flask equipped with a mechanical stirrer and a reflux condenser were placed 25.5 g. (0.107 mole) of 1-(6-chloro-2,4-dimethylphenyl)-3-amino-5-pyrazolone, 48.3 g. (0.118 mole) of α-(3-n-pentadecylphenoxy)-butyryl chloride and 600 cc. of anhydrous acetonitrile. The mixture was stirred and refluxed for 4¼ hours. On slow cooling overnight with stirring, a solid separated which was collected on a Büchner funnel, washed with

a small portion of cold acetonitrile, and dried. The crude product was recrystallized from 1100 cc. of n-octane yielding 50 g. of white powder having a melting point of 96–98° C. A recrystallization from 500 cc. of acetonitrile gave 43.5 g. of coupler No. 5 as fine white needles having a melting point of 99–101° C.

Analysis	C	H	N
Calculated	70.8	8.6	6.9
Found	70.9	8.8	6.8

EXAMPLE VI

Coupler 6

STEP 1.—1-(6-CHLORO-2,4-DIMETHYLPHENYL)-3-(3-NITROBENZAMIDO)-5-PYRAZOLONE

A solution of 23.8 g. (0.1 mole) of 1-(6-chloro-2,4-dimethylphenyl)-3-amino-5-pyrazolone prepared as in Step 4 of Example V, and 20.4 g. of recrystallized 3-nitrobenzoylchloride (0.11 mole) in 500 cc. of acetonitrile was refluxed for 16 hours. After 30 minutes of refluxing solid material separated. The solid was collected, washed with acetonitrile and dried. It was crystallized from methanol to give material having a melting point of 262–264° C.

STEP 2.—1-(6-CHLORO-2,4-DIMETHYLPHENYL)-3-[α-(3-n-PENTADECYLPHENOXY)BUTYRAMIDO]BENZAMIDO-5-PYRAZOLONE

A suspension of 6.5 (0.017 mole) of the purified 1-(6-chloro-2,4-dimethylphenyl)-3-[3-nitrobenzamido]-5-pyrazolone in 50 cc. of glacial acetic acid was treated with 0.5 g. of palladium on carbon and shaken under hydrogen. The required volume of hydrogen was absorbed in 15 minutes. The catalyst was filtered off and the filtrate heated to 65° C. 7.8 g. (0.019 mole) of α-(3-n-pentadecylphenoxy)butyryl chloride dissolved in 10 cc. of acetic acid were added followed by 2.5 g. (0.03 mole) of anhydrous sodium acetate in 15 cc. of acetic acid with stirring. Sodium chloride precipitated. The solution was poured into water with stirring. The yellow solid formed was collected, dried overnight, and crystallized from acetonitrile. The product had a melting point of 106–108° C.

Analysis	C	H	N
Calculated	71.0	7.8	7.7
Found	70.8	8.1	7.3

EXAMPLE VII

Coupler 7

STEP 1.—2-METHOXY-5-METHYLACETANILIDE

A solution of 326 g. (2.4 mole) of 2-methoxy-5-methyl aniline in 500 cc. of glacial acetic acid was treated with 240 g. (2.4 mole) of acetic anhydride. The temperature rose to 90° C. The mixture was stirred for 30 minutes at this temperature then cooled and poured into ice water. The white solid formed was collected, washed thoroughly in water and dried. The damp white solid was recrystallized directly from alcohol and water (about 48% ethyl alcohol). 340 g. of product were obtained having a melting point of 110–113° C.

STEP 2.—2-METHOXY-5-METHYL-3,4,6-TRICHLOROACETANILIDE

A solution of 195 g. (1 mole) of 2-methoxy-5-methylacetanilide in 1 liter of acetic acid was treated with 405 g. (3 mole) of sulfuryl chloride keeping the temperature at 35–40° C. The reaction mixture was stirred for 3 hours at room temperature and then poured into water. The solid product was collected and washed thoroughly with water. The damp solid was recrystallized from methanol (3 liters) producing 100 g. of material having a melting point of 206–208° C.

STEP 3.—2-METHOXY-5-METHYL-3,4,6-TRICHLOROANILINE

2-methoxy-5-methyl-3,4,6-trichloroacetanilide dissolved in 95% ethyl alcohol and concentrated hydrochloric acid, was hydrolyzed under reflux by the same procedure used in Step 2 of Example V to produce the corresponding aniline derivative.

STEP 4.—2-METHOXY-5-METHYL-3,4,6-TRICHLOROPHENYLHYDRAZINE

2-methoxy-5-methyl-3,4,6-trichloroaniline was converted into the corresponding phenylhydrazine by the same procedure used in Step 3 of Example V using equimolecular portions of the reactants.

STEP 5.—1-(2-METHOXY-5-METHYL-3,4,6-TRICHLOROPHENYL)-3-AMINO-5-PYRAZOLONE

2-methoxy-5-methyl-3,4,6-trichlorophenylhydrazine was reacted with ethyl-β-ethoxy-β-iminopropionate in acetic acid according to the procedure used in Step 4 of Example V.

STEP 6.—1-(2-METHOXY-5-METHYL-3,4,6-TRICHLOROPHENYL)-3-[α-(META-PENTADECYLPHENOXY)ACETAMIDO]-5-PYRAZOLONE

The 1-(2-methoxy-5-methyl-3,4,6-trichlorophenyl)-3-amino-5-pyrazolone was reacted with α-(meta-pentadecylphenoxy)acetylchloride in anhydrous acetonitrile under reflux by the procedure used in Step 5 of Example V.

The recrystallized product was off-white in color having a melting point of 139–140.5° C.

Analysis	C	H	N
Calculated	61.2	7.0	6.3
Found	61.4	7.0	6.6

The couplers of our invention are particularly adapted for incorporation in light sensitive emulsion layers for color photography. These emulsions are of the developing-out type.

The emulsions can be chemically sensitized by any of the accepted procedures. The emulsions can be digested with naturally active gelatin, or sulfur compounds can be added such as those described in Sheppard U.S. Patent 1,574,944, issued March 2, 1926, Sheppard et al. U.S. Patent 1,623,499, issued April 5, 1927, and Sheppard et al. U.S. Patent 2,410,689, issued November 5, 1946.

The emulsions can also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium, and platinum. Representative compounds are ammonium chloropalladate, potassium chloroplatinate, and sodium chloropalladite, which are used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in Smith and Trivelli U.S. Patent 2,448,060, issued August 31, 1948, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245, issued August 28, 1951, and 2,566,263, issued August 28, 1951.

The emulsions can also be chemically sensitized with gold salts as described in Waller et al. U.S. Patent 2,399,083, issued April 23, 1946, or stabilized with gold salts as described in Damschroder U.S. Patent 2,597,856, issued May 27, 1952, and Yutzy and Leermakers U.S. Patent 2,597,915, issued May 27, 1952. Suitable compounds are potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

The emulsions can also be chemically sensitized with reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850, issued November 15, 1949), polyamines, such as diethyl triamine (Lowe and Jones U.S. Patent 2,518,698, issued August 15, 1950), polyamines, such as

spermine (Lowe and Allen U.S. Patent 2,521,925, issued September 12, 1950), or bis(β-aminoethyl) sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926, issued September 12, 1950).

The emulsions can also be optically sensitized with cyanine and merocyanine dyes, such as those described in Brooker U.S. Patents 1,846,301, issued February 23, 1932; 1,846,302, issued February 23, 1932; and 1,942,854, issued January 9, 1934; White U.S. Patent 1,990,507, issued February 12, 1935; Brooker and White U.S. Patents 2,112,140, issued March 22, 1938; 2,165,338, issued July 11, 1939; 2,493,747, issued January 10, 1950 and 2,739,964, issued March 27, 1956; Brooker and Keyes U.S. Patent 2,493,748, issued January 10, 1950; Sprague U.S. Patents 2,503,776, issued April 11, 1950 and 2,519,001, issued August 15, 1950; Heseltine and Brooker U.S. Patent 2,666,761, issued January 19, 1954; Heseltine U.S. Patent 2,734,900, issued February 14, 1956; Van-Lare U.S. Patent 2,739,149, issued March 20, 1956; and Kodak Limited British Patent 450,958, accepted July 15, 1936.

The emulsions can also be stabilized with the mercury compounds of Allen, Byers and Murray U.S. Patent 2,728,663, issued December 27, 1955; Carroll and Murray U.S. Patent 2,728,664, issued December 27, 1955; and Leubner and Murray U.S. Patent 2,728,665, issued December 27, 1955; the triazoles of Heimbach and Kelley U.S. Patent 2,444,608, issued July 6, 1948; the azaindenes of Heimbach and Kelley U.S. Patents 2,444,605 and 2,444,606, issued July 6, 1948; Heimbach U.S. Patents 2,444,607, issued July 6, 1948 and 2,450,397, issued September 28, 1948; Heimbach and Clark U.S. Patent 2,444,609, issued July 6, 1948; Allen and Reynolds U.S. Patents 2,713,541, issued July 19, 1955, and 2,743,181, issued April 24, 1956; Carroll and Beach U.S. Patent 2,716,062, issued August 23, 1955; Allen and Beilfuss U.S. Patent 2,735,769, issued February 21, 1956; Reynolds and Sagal U.S. Patent 2,756,147, issued July 24, 1956; Allen and Sagura U.S. Patent 2,772,164, issued November 27, 1956, and those disclosed by Birr in "Z. wiss. Phot.," vol. 47, 1952, pages 2–28; the disulfides of Kodak Belgian Patent 569,317, issued July 31, 1958; the quaternary benzothiazolium compounds of Brooker and Staud U.S. Patent 2,131,038, issued September 27, 1938, or the polymethylene bis-benzothiazolium salts of Allen and Wilson U.S. Patent 2,694,716, issued November 16, 1954 (e.g., decamethylene-bis-benzothiazolium perchlorate); or the zinc and cadmium salts of Jones U.S. Patent 2,839,405, issued June 17, 1958; and the carboxymethylmercapto compounds of Murray, Reynolds and Van Allen U.S. Patent 2,819,965, issued January 14, 1958.

The emulsions may also contain speed increasing compounds of the quaternary ammonium type of Carroll U.S. Patent 2,271,623, issued February 3, 1942; Carroll and Allen U.S. Patent 2,288,226, issued June 30, 1942; and Carroll and Spence U.S. Patent 2,334,864, issued November 23, 1943; or the quaternary ammonium salts and polyethylene glycols of Piper U.S. Patent 2,886,437, issued May 12, 1959; and the polyethylene glycol type of Carroll and Beach U.S. Patent 2,708,162, issued May 10, 1955; or the thiopolymers of Graham and Sagal U.S. application Serial No. 779,839, filed December 12, 1958, or Dann and Chechak U.S. application Serial No. 779,874, filed December 12, 1958.

The emulsions may contain a suitable gelatin plasticizer such as glycerin; a dihydroxy alkane such as 1,5-pentane diol as described in Milton and Murray U.S. application Serial No. 588,951, filed June 4, 1956, now U.S. Patent 2,960,404, issued November 15, 1960; an ester of an ethylene bis-glycolic acid such as ethylene bis(methyl glycolate) as described in Milton U.S. application Serial No. 662,564, filed May 31, 1957, now U.S. Patent 2,904,424, issued September 15, 1959; bis(ethoxy diethylene glycol) succinate as described in Gray U.S. application Serial No. 604,333, filed August 16, 1956, now U.S. Patent 2,940,854, issued June 14, 1960, or a polymeric hydrosol as results from the emulsion polymerization of a mixture of an amide of an acid of the acrylic acid series, an acrylic acid ester and a styrene-type compound as described in Tong U.S. Patent 2,852,386, issued September 16, 1958. The plasticizer may be added to the emulsion before or after the addition of a sensitizing dye, if used.

The emulsions may be hardened with any suitable hardener for gelatin such as formaldehyde; a halogen-substituted aliphatic acid such as mucobromic acid as described in White U.S. Patent 2,080,019, issued May 11, 1937; a compound having a plurality of acid anhydride groups such as 7,8-diphenylbicyclo (2,2,2)-7-octene-2,3,5, 6-tetra-carboxylic dianhydride, or a dicarboxylic or a disulfonic acid chloride such as terephthaloyl chloride or naphthalene-1,5-disulfonyl chloride as described in Allen and Carroll U.S. Patents 2,725,294, and 2,725,295, both issued November 29, 1955; a cyclic 1,2-diketone such as cyclopentane-1,2-dione as described in Allen and Byers U.S. Patent 2,725,305, issued November 29, 1955; a bisester of methane-sulfonic acid such as 1,2-di-(methanesulfonoxy)-ethane as described in Allen and Laakso U.S. Patent 2,726,162, issued December 6, 1955; 1,3-dihydroxymethylbenzimidazol-2-one as described in July, Knott and Pollak U.S. Patent 2,732,316, issued January 24, 1956; a dialdehyde or a sodium bisulfite derivative thereof, the aldehyde groups of which are separated by 2–3 carbon atoms, such as β-methyl glutaraldehyde bis-sodium bisulfite as described in Allen and Burness U.S. Patent application Serial No. 556,031, filed December 29, 1955; a bis-aziridine carboxamide such as trimethylene bis(1-aziridine carboxamide) as described in Allen and Webster U.S. patent application Serial No. 599,891, filed July 25, 1956, now U.S. Patent 2,950,197, issued August 23,1960; or 2,3-dihydroxy dioxane as described in Jeffreys U.S. Patent 2,870,013, issued January 20, 1959.

The emulsions may contain a coating aid such as saponin; a lauryl or oleyl monoether of polyethylene glycol as described in Knox and Davis U.S. Patent 2,831,766, issued April 22, 1958; a salt of a sulfated and alkylated polyethylene glycol ether as described in Knox and Davis U.S. Patent 2,719,087, issued September 27, 1955; an acylated alkyl taurine such as the sodium salt of N-oleoyl-N-methyl taurine as described in Knox, Twardokus and Davis U.S. Patent 2,739,891, issued March 27, 1956; the reaction product of a dianhydride of tetracarboxybutane with an alcohol or an aliphatic amine containing from 8 to 18 carbon atoms which is treated with a base, for example, the sodium salt of the monoester of tetracarboxybutane as described in Knox, Stenberg and Wilson U.S. Patent 2,843,487, issued July 15, 1958; a water-soluble maleopimarate or a mixture of a water-soluble maleopimarate and a substituted glutamate salt as described in Knox and Fowler U.S. Patent 2,823,123, issued February 11, 1958; an alkali metal salt of a substituted amino acid such as disodium N-(carbo-p-tert. octylphenoxypentaethoxy)-glutamate as described in Knox and Wilson U.S. Patent application Serial No. 600,679, filed July 30, 1956; or a sulfosuccinamate such as tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate or N-lauryl disodium sulfosuccinamate as described in Knox and Stenberg U.S. Patent application Serial No. 691,125, filed October 21, 1957, now U.S. Patent 2,992,108, issued July 11, 1961.

The couplers which we have described may be used in various kinds of photographic emulsions. They may be added to the emulsions before or after any sensitizing dyes which are used. Various silver salts may be used as the sensitive salt such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide or silver bromoiodide. The agents may be used in emulsions intended for color photography, for example, emulsions containing color-forming couplers or emulsions to be developed by solutions containing couplers or other

color-generating materials, emulsions of the mixed-packet type, such as described in Godowsky U.S. Patent 2,698,794, issued January 4, 1955; or emulsions of the mixed-grain type, such as described in Carroll and Hanson U.S. Patent 2,592,243, issued April 8, 1952. These agents can also be used in emulsions which form latent images predominantly on the surface of the silver halide crystal or in emulsions which form latent images predominantly inside the silver halide crystal, such as those described in Davey and Knott U.S. Patent 2,592,250, issued April 8, 1952.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions, there may be employed as the dispersing agent for the silver halide in its preparation, gelatin or some other colloidal material such as colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound. Some colloids which may be used are polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in Lowe U.S. Patent 2,286,215, issued June 16, 1942; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19–26% as described in U.S. Patent 2,327,808 of Lowe and Clark, issued August 24, 1943; a water-soluble ethanolamine cellulose acetate as described in Yutzy U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamide or an imidized polyacrylamide as described in Lowe, Minsk and Kenyon U.S. Patent 2,541,474, issued February 13, 1951; zein as described in Lowe U.S. Patent 2,563,791, issued August 7, 1951; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith U.S. Patent 2,768,154, issued October 23, 1956; or containing cyano-acetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in Unruh, Smith and Priest U.S. Patent 2,808,331, issued October 1, 1957; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in U.S. Patent 2,852,382 of Illingsworth, Dann and Gates, issued September 16, 1958.

If desired, compatible mixtures of two or more of these colloids may be employed for dispersing the silver halide in its preparation. Combinations of these antifoggants, sensitizers, hardeners, etc., may be used.

The coupler compounds of our invention may be dispersed in any water permeable hydrophilic material such as gelatin, albumin, gum acacia, etc. or synthetic materials such as organic esters of cellulose, synthetic resins, etc. that are used for making photographic emulsions. Photographic emulsions containing these couplers may be coated on transparent supports such as glass, cellulose esters or on a non-transparent reflecting material, such as paper or on opaque cellulose esters.

Our couplers are readily soluble in conventional types of coupler solvents such as those described in Jelley and Vittum U.S. Patent 2,322,027, and can be used over a range of coupler to coupler solvent ratios of from 1:0 to 1:2. Our couplers do not crystallize when used in dispersions of high coupler to coupler solvent ratios. The preferred ratio is 1:1½.

The preferred couplers of our invention are free from wandering from the layer in which they are incorporated. However, if it is desirable to make these couplers diffusible this can be readily done by changing the ballasting group substituted on the 3-position of the pyrazolone ring.

Photographic emulsions containing our couplers can be developed by any of the conventional primary amino developing compositions. Among the preferred developing agents are developers such as 2-amino-5-diethylaminotoluene hydrochloride, and N-ethyl-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate. Typical developers containing these developing agents are as follows:

Developer 1

	G.
2-amino-5-diethylaminotoluene hydrochloride	2.5
Sodium sulfite (anhydrous)	5
Sodium carbonate (anhydrous)	20
Potassium bromide	2

water to 1 liter.

Developer 2

	G.
N - ethyl - β - methanesulfonamidoethyl - 3 - methyl-4-aminoaniline sulfate	2
Sodium sulfite	.5
Sodium carbonate	30

Water to 1 liter.

The following examples will illustrate the use of our couplers in photographic emulsions.

EXAMPLE VIII

A gelatin dispersion containing 0.50 g. of coupler No. 1 in tri-o-cresyl phosphate was added to 5 ml. of a green-sensitized medium-speed silver bromoiodide emulsion, the mixture was coated on a suitably subbed cellulose acetate support and dried. The coating was exposed in a spectrograph to tungsten illumination and developed in Developer No. 1 to form a negative silver image and a magenta dye image. The silver image and the residual silver halide were then removed with ferricyanide bleach and a hypo fixer leaving a magenta dye image having a maximum absorption at 538 mu.

Another sample of the above emulsion coating treated in the same manner but developed with Developer No. 2 resulted in the formation of a magenta image having a maximum light absorption at a wave-length of 538 mu.

EXAMPLE IX

A photographic emulsion was made as in Example VIII but Coupler No. 2 was used in place of Coupler No. 1. This was exposed, developed with Developer No. 1, bleached and fixed as in Example VIII to produce a good magenta dye image having a maximum absorption at a wavelength of 535 mu.

Another sample of this emulsion was exposed, developed with Developer No. 2, bleached and fixed to produce good magenta dye image having a maximum absorption at 533 mu.

EXAMPLE X

A photographic emulsion was made as in Example VIII, but Coupler No. 3 was used instead of coupler No. 1. Two samples of this emulsion were exposed, one of them was developed in Developer No. 1 and the second in Developer No. 2. After bleaching and fixing, both samples had good magenta dye images having a maximum absorption at a wavelength of 543 mu.

EXAMPLE XI

A photographic emulsion was prepared as in Example VIII but in which Coupler No. 4 was used in place of Coupler No. 1. Two samples of this emulsion were exposed to an image. Good magenta dye images having a maximum light absorption at 542 mu were produced by developing one of these in Developer No. 1 and the other in Developer No. 2, bleaching and fixing.

EXAMPLE XII

Similarly, photographic emulsions containing Coupler No. 5 were prepared, exposed, developed, bleached and fixed to produce good magneta dye images. Developer No. 1 and Developer No. 2 produced magneta dye images having maximum light absorption at wavelengths of 538 mu and 539 mu, respectively.

EXAMPLE XIII

When Coupler No. 7 was incorporated in a photo-

graphic emulsion in place of Coupler No. 1 of Example VIII good magenta dye images were produced after exposure, development, bleaching and fixing, the dye images formed by Developer No. 1 and by Developer No. 2 had maximum light absorption at wavelengths of 544 mu and 542 mu, respectively.

The valuable characteristics of our couplers and the dyes formed from them are further illustrated by the accompanying drawings in FIGURES 1, 2 and 3.

FIGURE 1 shows the spectrophotometric curves for the dye images produced upon the development of our emulsion containing Coupler No. 2 in Example IX and for the dye image produced with an emulsion made, exposed and processed in the same way but containing the prior art coupler 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-amylphenoxyacetamido)]-5-pyrazolone in place of our Coupler No. 2. From these curves it is apparent that the dye from our coupler has less absorption in the red region of the spectrum and considerably more absorption in the green region of the spectrum. The maximum absorption of our dye occurs at a wavelength of 533 as compared to 550 for the prior art dye.

All of these characteristics mentioned above make our dye more desirable than the corresponding prior art dye.

FIGURES 2 and 3 are percent transmittance curves showing the effect produced upon the transmission characteristic of our Coupler No. 3, 1-(2,6-dichloro-4-methoxyphenyl) - 3 - [α-(meta-pentadecylphenoxy)-butyramido]-5-pyrazolone, and of the coupler 1-(2,5-dichloro-4-methoxyphenyl - 3 - [α-(meta-pentadecylphenoxy)-butyramido]-5-pyrazolone, respectively by 30 hours of exposure to a xenon arc light. Curve No. 1 in each figure shows the percent transmittance for the respective couplers at wavelengths of 400 to 700 mu before exposure to the xenon and curve No. 2 shows the corresponding percent transmittance after the 30 hours of exposure. A comparison of the differences between the curves 1 and 2 of the FIGURE 2 and of the differences between these two curves in FIGURE 3 shows that our Coupler No. 3 produces considerably less print out than the corresponding coupler of the prior art type. These two couplers have tructures which differ only in the position on the 1-phenyl ring at which a chlorine atom is substituted.

Our coupler has greater stability to print-out as evidenced by the 8.5% decrease in transmittance as compared to the 15% decrease in transmittance that occurs when the other coupler is used. This valuable improvement shown by our couplers is unexpected in view of the relatively small difference in structure between it and the coupler of the prior art type. FIGURES 2 and 3 illustrate the criticalness of the substituents in the 2,4,6-positions over those in the 2,4,5-positions on the 1-phenyl group of the pyrazolone coupler.

Not only do our couplers show good stability to light but they also have good heat stability. The dyes formed from them have good stability to heat and light.

Our couplers are not only valuable in their own right, but also as parent couplers for making valuable colored couplers and other types of couplers which are used in color photography. Colored couplers for example may be readily made by replacing one of the hydrogens on the 4-carbon of the 5-pyrazolone ring with a phenylazo group or any of the other splittable groups which are used in colored couplers.

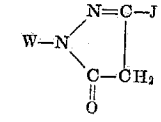
The valuable characteristics imparted by substituents on the 2,4,6-positions of the 1-phenyl ring of our couplers are also imparted to corresponding colored couplers.

The novel 2,4-6-substituted 1-phenyl pyrazolone couplers of our invention are valuable for use in color photography. They are distinguished from other couplers which have substituents in the 2,4,5-positions on the 1-phenyl ring by having unexpectedly greater stability to light and heat and thus have greatly improved print-out characteristics when used in photographic emulsions. For example, a photographic emulsion containing our Coupler No. 3 loses only 8.5% in its light transmission after being subject to 30 hours' exposure to xenon light as compared to a 15% loss in transmission shown by a photographic emulsion containing the 2,4,5-substituted 1-phenyl analogue of our coupler when subjected to the same treatment. Our couplers produce dyes having improved light absorption characteristics which avoid the excessive red absorption and the inadequate green absorption of the dyes in current use. These dyes have satisfactory light and heat stability and are well adapted for use in color photography. Our couplers are readily soluble in standard coupler solvents over a broad range of coupler to coupler solvent ratios and give dispersions which are free from crystallization at high coupler to coupler solvent ratios. Furthermore, our couplers are free from wandering from the emulsion layer they are incorporated in. Not only are our couplers valuable per se but also for use as parent couplers in making colored couplers which are also characterized by having all of the desirable properties of the parent coupler.

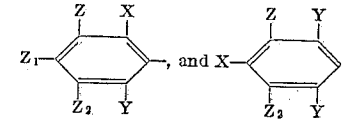
The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

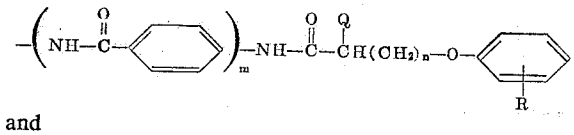
1. A photographic silver halide emulsion containing a magenta forming coupler having the formula:



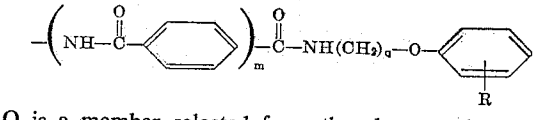
wherein W represents a member selected from the class consisting of groups having the formulas:



X is a halogen atom; Y is a member selected from the class consisting of an alkyl group, an alkoxy group, an alkthio group, an alkseleno group, an aryl group, an aryloxy group, an arylthio group, and an arylseleno group; Z, Z_1 and Z_2 each represent a member selected from the class consisting of a hydrogen atom, a halogen atom and a Y group; J is a member selected from the class having the formulas:

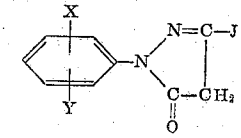


and

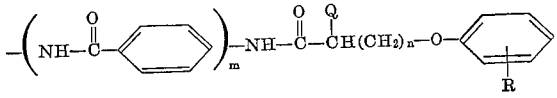


Q is a member selected from the class consisting of a hydrogen atom, and a lower alkyl group having from 1 to 6 carbon atoms; *n* is from 0 to 2; *m* is from 0 to 1; R is an alkyl group having from 1 to 20 carbon atoms, and *q* is from 1 to 3.

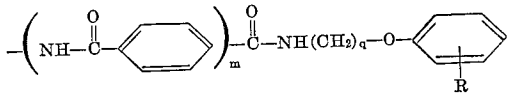
2. A photographic silver halide emulsion containing a magenta forming coupler having the formula:



wherein X is a halogen atom; Y is a member selected from the class consisting of an alkyl group, an alkoxy group, an alkthio group, an alkseleno group, an aryl group, an aryloxy group, an arylthio group and an arylseleno group, where said X and said Y groups are substituted on the carbon atoms in the 2, 4 and 6-positions of the 1-phenyl group; J is a member selected from the class having the formulas:

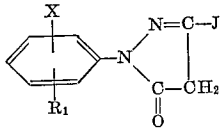


and

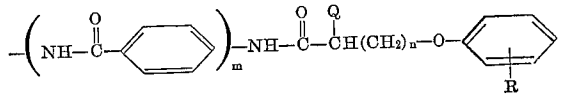


Q is a member selected from the class consisting of a hydrogen atom, and a lower alkyl group having from 1 to 6 carbon atoms; *n* is from 0 to 2; *m* is from 0 to 1; R is an alkyl group having from 1 to 20 carbon atoms, and *q* is from 1 to 3.

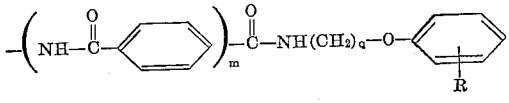
3. A photographic silver halide emulsion containing a magenta forming coupler having the formula:



wherein X is a halogen atom; R_1 is selected from the class consisting of alkyl groups having from 1 to 6 carbon atoms; where said X and said R_1 groups are substituted on the carbon atoms in the 2, 4 and 6-positions of the 1-phenyl group; J is a member selected from the class having the formulas:

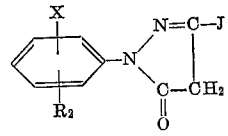


and

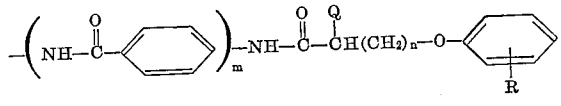


Q is a member selected from the class consisting of a hydrogen atom, and a lower alkyl group having from 1 to 6 carbon atoms; *n* is from 0 to 2; *m* is from 0 to 1; R is an alkyl group having from 1 to 20 carbon atoms, and *q* is from 1 to 3.

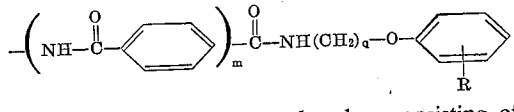
4. A photographic silver halide emulsion containing a magenta forming coupler having the formula:



wherein X is a halogen atom; R_2 is an alkoxy group having from 1 to 6 carbon atoms, where said X group and said R_2 group are substituted on the carbon atoms in the 2, 4 and 6-positions of the 1-phenyl group; J is a member selected from the class having the formulas:



and



Q is a member selected from the class consisting of a hydrogen atom, and a lower alkyl group having from 1 to 6 carbon atoms; *n* is from 0 to 2; *m* is from 0 to 1; R is an alkyl group having from 1 to 20 carbon atoms, and *q* is from 1 to 3.

5. A photographic silver halide emulsion containing the magenta forming coupler 1-(4,6-dichloro-2-methoxyphenyl) - 3 - [α-(m-pentadecylphenoxy)butyramido]-5-pyrazolone.

6. A photographic silver halide emulsion containing the magenta forming coupler 1-(4,6-dichloro-2-methoxyphenyl) - 3 - [α - (m-pentadecylphenoxy)acetamido]-5-pyrazolone.

7. A photographic silver halide emulsion containing the magenta forming coupler 1-(2,6-dichloro-4-methoxyphenyl) - 3 - [α - (m-pentadecylphenoxy)butyramido]-5-pyrazolone.

8. A photographic silver halide emulsion containing the magenta forming coupler 1-(4,6-dichloro-2-methylphenyl) - 3 - [α - (m-pentadecylphenoxy)butyramido]-5-pyrazolone.

9. A photographic silver halide emulsion containing the magenta forming coupler 1-(6-chloro-2,4-dimethylphenyl) - 3 - [α - (m-pentadecylphenoxy)butyramido]-5-pyrazolone.

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