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3,214,437

2-EQUIVALENT THIOCYANO COUPLERS
OF 5-PYRAZOLONES

Anthony Loria and Ilmari F. Salminen, Rochester, N.Y.,
assignors to Eastman Kodak Company, Rochester,
N.Y., a corporation of New Jersey
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This invention relates to photography and particularly
to compounds which form dyes on coupling with the ox-
idized developing agent to produce dye images.

The formation of colored photographic images by the
coupling of oxidized aromatic amino developing agents
with color-forming or coupling compounds is well known.
In these processes the subtractive process of color forma-
tion is ordinarily used and the image dyes are intended to
be cyan, magenta and yellow, the colors that are comple-
mentary to the primary colors. The couplers which pro-
duce the yellow dyes are ordinarily compounds contain-
ing a methylene group having two carbonyl groups at-
tached to it. Those producing the magenta dyes are ordi-
narily pyrazolones and the couplers which produce the
cyan dyes are usually phenols or naphthols. The dyes
produced by coupling are azomethines, indamines or in-
dophenols depending upon the composition of the coupler
and of the developer.

Conventional color-forming coupler compounds such
as the acetoacetanilides, 5-pyrazolones, phenols and nap-
ththols each have an active methylene group which reacts
with oxidized color developer during color development
to produce the dyes. These coupler compounds are 4-
equivalent couplers because they are characterized by re-
quiring the development of four exposed silver halide
molecules in order to produce one molecule of dye from
the coupling reaction between a coupler molecule and a
developer molecule.

It is, therefore, an object of the present invention to
provide a novel class of color-forming coupler compounds
for color photography which are 2-equivalent, that is, cou-
plers that require the development of only two exposed
molecules of silver halide to produce one molecule of dye.

A further object of the invention is to provide a novel
class of color-forming couplers which are not only 2-
equivalent but which are characterized by having all the
desirable features of prior art couplers from which they
are produced.

A still further object is to provide silver halide emul-
sions containing our novel 2-equivalent coupler com-
pounds.

Still further objects will become apparent from the fol-
lowing description.

These and other objects are accomplished by means of
our invention as described hereinafter.

We have discovered a novel class of color-forming cou-
pler compounds that are valuable for use in color pho-
tography. Our couplers are characterized by being 2-
equivalent couplers which require the development of
only two exposed silver halide molecules during color
development to form one molecule of dye from a molecule
of coupler and a molecule of developer.

2-equivalent couplers have several important and dis-
tinctive advantages over the conventional or 4-equivalent
couplers, for example, the amount of silver halide used
in an emulsion is reduced 50%. This not only reduces
the cost of producing the emulsions containing our color-
forming coupler but results in improved quality of pic-
tures made using these emulsions. The reduced silver
halide emulsion requirements make possible thinner emul-
sion layers. It is known that improved image definition
and resolution result from reducing the thickness of emul-

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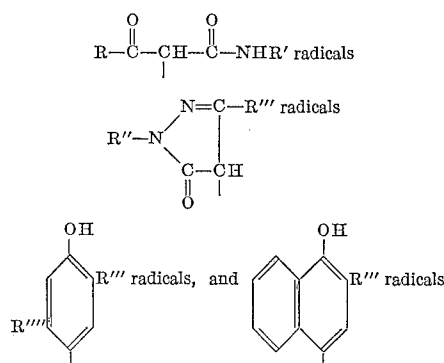
sion layers. Reductions of emulsion thickness have the
further advantage of decreasing the optical opacity of
the emulsion layer which allows more light to penetrate
into emulsion layers underneath the emulsion layer con-
taining our coupler.

Our couplers are further characterized by releasing
the thiocyanate ion upon color development. It is known
that the thiocyanate ion is a silver halide solvent so that
its release by the couplers of our invention may be used
to advantage in color development processes. It is pos-
sible to use blends of the couplers of our invention with
the corresponding parent coupler in order to predetermine
the amount of thiocyanate ion and thus the silver halide
solvent effect produced by color development.

The couplers of our invention have the general formula:



wherein W represents a coupler radical such as those
having the formula:



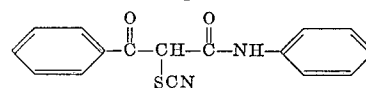
in which R represents an alkyl radical having from 1 to
32 carbon atoms which may be a normal alkyl radical
having from 1 to 18 carbon atoms, e.g., methyl, propyl,
hexyl, octyl, dodecyl, pentadecyl, octadecyl, etc., a sec-
ondary alkyl radical in which the secondary carbon atom
is preferably attached directly to the carbonyl radical and
has attached to it two alkyl radicals each of which may
have from 1 to 18 carbon atoms, as defined above, pro-
vided that the R group does not have more than a total
of 32 carbon atoms, a tertiary alkyl radical in which the
tertiary carbon atom is preferably attached directly to the
carbonyl radical and has attached to it three alkyl radicals
each of which may have from 1 to 18 carbon atoms, as
defined above, provided that the R group does not have
more than a total of 32 carbon atoms and in which one
or two of these alkyl radicals attached to the tertiary car-
bon may themselves be secondary or tertiary alkyl radi-
cals having from 1 to 18 carbon atoms, a tertiary alkyl
radical in which one, two, or three of the alkyl groups
defined above that are attached to the tertiary carbon
atom, are replaced by alkoxy radicals having from 1 to
18 carbon atoms such as methoxy, ethoxy, propoxy,
butoxy, pentoxy, hexoxy, octoxy, nonoxy, decoxy, do-
decoxy, tridecoxy, tetradecoxy, pentadecoxy, hexadecoxy,
octadecoxy, etc., or alkoxyalkyl having from 1 to 18 car-
bon atoms in which the alkoxy and alkyl radicals are
among those defined above such as methoxymethyl, eth-
oxymethyl, propoxymethyl, butoxymethyl, hexoxymethyl,
decoxymethyl, pentadecoxymethyl, methoxypropyl, meth-
oxyhexyl, methoxyoctyl, methoxydecyl, methoxydo-
decyl, methoxypentadecyl, nonoxynonyl, etc., or R repre-
sents a cyclohexyl radical substituted with an alkyl radi-
cal, an alkoxy radical, an alkoxyalkyl radical, each having
from 1 to 18 carbon atoms as described above or an aryl
radical such as phenyl, tolyl, etc., for example, 1-methyl-
cyclohexyl, 1-ethylcyclohexyl, 1-propylcyclohexyl, 1-octyl-
cyclohexyl, 1-dodecylcyclohexyl, 1-pentadecylcyclohexyl,

1-octadecylcyclohexyl, 2-methylcyclohexyl, 3-ethylcyclohexyl, 4-octylcyclohexyl, etc., 1-methoxycyclohexyl, 1-ethoxycyclohexyl, 1-propoxycyclohexyl, 1-nonoxycyclohexyl, 1-octadecoxycyclohexyl, 2-butoxycyclohexyl, etc., 1-methoxymethylcyclohexyl, 1-propoxymethylcyclohexyl, 1-decoxymethylcyclohexyl, 1-pentoxymethylcyclohexyl, 1-methoxydecylcyclohexyl, 1-nonoxynonylcyclohexyl, 2-nonoxynonylcyclohexyl, 3-nonoxydecylcyclohexyl, etc., 1-phenylcyclohexyl, 1-tolylcyclohexyl, etc., or R represents a bicycloalkyl radical such as a terpenyl radical, e.g., 7,7-dimethylnorbornyl, a 2-alkyl 7,7-dimethylnorbornyl, a 2-alkoxy-7,7-dimethylnorbornyl, a 2-alkoxyalkyl-7,7-dimethylnorbornyl, preferably although not necessarily attached to the carbonyl group through the bridgehead carbon, and in which the alkyl, alkoxy and alkoxyalkyl substituents may each have from 1 to 18 carbon atoms as defined above, such as 2-methyl-7,7-dimethylnorbornyl, 2-octyl-7,7-dimethylnorbornyl, 2-octadecyl-7,7-dimethylnorbornyl, etc., 2-ethoxy-7,7-dimethylnorbornyl, 2-nonoxy-7,7-dimethylnorbornyl, 2-octadecyloxy-7,7-dimethylnorbornyl, etc., a 2-aryl-7,7-dimethylnorbornyl such as 2-phenyl-7,7-dimethylnorbornyl, 2-tolyl-7,7-dimethylnorbornyl, etc., an aryl radical, e.g., phenyl, an alkphenyl radical in which the alkyl radical has from 1 to 18 carbon atoms, e.g., 3-methylphenyl, 2-butylphenyl, 4-octylphenyl, 2-dodecylphenyl, 3-octadecylphenyl, etc., an alkoxyphenyl radical in which the alkyl group has from 1 to 18 carbon atoms, e.g., 2-methoxyphenyl, 2-propoxyphenyl, 2-hexoxyphenyl, 2-nonoxyphenyl, 2-decoxyphenyl, 2-octadecyloxyphenyl, etc., R' represents an aryl radical such as phenyl, alkoxyphenyl in

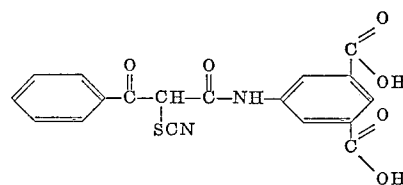
arylamino radical, e.g., anilino, toluidino, etc., amido radicals, e.g., acetamido, butyramido, etc., and R''' represents a halogen atom, e.g., chlorine, bromine, iodine or fluorine, a hydrogen atom, an alkyl radical having from 1 to 8 carbon atoms such as methyl, propyl, amyl, octyl, etc., or aryl, e.g., phenyl, etc.

The couplers of our invention are further illustrated by the following representative examples.

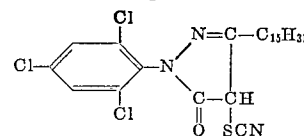
Coupler 1

 α -Benzoyl- α -thiocyanoacetanilide

Coupler 2

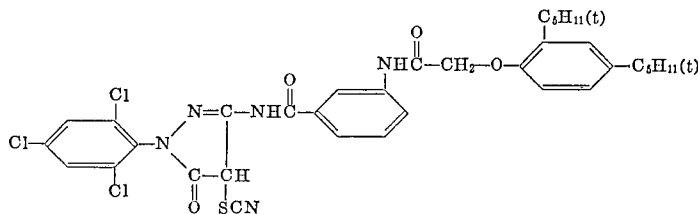
 α -Benzoyl- α -thiocyanoacet-3,5-dicarboxyanilide

Coupler 3



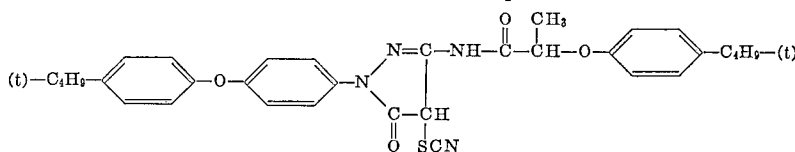
1-(2,4,6-trichlorophenyl)-3-pentadecyl-4-thiocyano-5-pyrazolone

Coupler 4

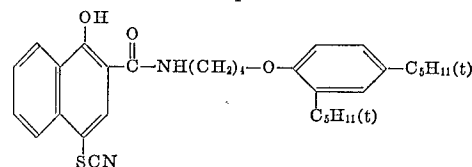


1-(2,4,6-trichlorophenyl)-3-[(2,4-di-tert-amylphenoxy)acetamido]benzamido-4-thiocyano-5-pyrazolone

Coupler 5

1-(p-tert-butylphenoxyphenyl)-3- α -(p-tert-butylphenoxy)propionamido-4-thiocyano-5-pyrazolone

Coupler 6

1-hydroxy-4-thiocyano-N-[δ -(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide

which the alkyl radical may have from 1 to 18 carbon atoms as defined above, for R, halophenyl radicals such as 2-chlorophenyl, 2,4-dichlorophenyl, 2,4,6-trichlorophenyl, the corresponding bromo- and corresponding fluoro-phenyl radicals, etc., sulfonamidophenyl radicals, e.g., benzenesulfonyl-N-(γ -phenyl-n-propyl)-p-toluidine, 2-chlorobenzenesulfonmethylanilide, 2-chlorobenzenesulfon-p-toluide, etc., amidophenyl e.g., 4-[α -(4'-tert-butylphenoxy)-propionamido]phenyl, 4-[α -(4'-tert-amylphenoxy)-butyramido]phenyl, etc., an aroyl radical, e.g., benzoyl, etc., R'' represents a phenyl radical, a halogen substituted phenyl radical, e.g., 2-chlorophenyl, 2,4-dichlorophenyl, 2,4,6-trichlorophenyl or the corresponding bromo- and fluoro-phenyl radicals, alkoxyphenyl and alkphenyl in which the alkyl radical may have from 1 to 18 carbon atoms as defined above, a phenoxyphenyl radical, a cyanophenyl radical, etc., R''' represents an amino radical, an alkamino radical in which the alkyl group may have from 1 to 18 carbon atoms, e.g., methylamino, butylamino, dodecylamino, octadecylamino, dimethylamino, dipropylamino, dioctylamino, didodecylamino, etc., an

The couplers of our invention are in general prepared by reacting the parent coupler with the product of the reaction of an alkali metal or ammonium thiocyanate with bromine.

Among the couplers of our invention are those prepared from parent prior art couplers such as the following:

(a) The yellow couplers of Weissberger et al. U.S. 2,407,210, issued September 3, 1946, and the yellow couplers of Weissberger et al. 2,439,352, issued April 6, 1948,

(b) The 5-pyrazolone magenta-forming couplers of Porter et al. U.S. 2,369,489, issued February 13, 1945,

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Weissberger et al. U.S. 2,511,231, issued June 13, 1950, Loria et al. U.S. 2,600,788, issued June 17, 1952, and Feniak et al. U.S. 2,865,748, issued December 23, 1958, and

(c) The cyan-forming phenol and naphthol couplers of Weissberger et al. U.S. 2,474,293, issued June 28, 1949, Salminen et al. U.S. 2,367,531, issued January 16, 1945, and Vittum et al. U.S. 2,369,929, issued February 20, 1945.

The preparation of specific coupler examples will further illustrate the synthesis used.

EXAMPLE I

α-Benzoyl-α-thiocyanacetanilide.—Ammonium thiocyanate 7.6 g. (0.1 mole) was dissolved in 150 ml. of 95% acetic acid and the solution cooled to 15–18° C. To this solution was added a solution of 4 ml. of bromine (0.082 mole) in 50 ml. of glacial acetic acid while stirring. After 15 minutes, the reaction mixture was diluted with 2 volumes of water and the oil which separated was washed several times with ice water by decantation and then taken up in 125 ml. of ethyl ether. The ether solution was dried with anhydrous sodium sulfide and filtered.

To the ether solution was added all at once, 14.3 g. (0.06 mole) of *α*-benzoylacetanilide. The reaction mixture was stirred for 3 hours at room temperature and left to stand overnight. The product obtained on evaporation of the ether was extracted with boiling methyl alcohol, from which the *α*-benzoyl-*α*-thiocyanacetanilide crystallized as pale yellow needles. After a second crystallization from methyl alcohol, the product melted at 148–150° C.

Analysis:

	C	H	N	S
Calculated for C ₁₅ H ₁₂ N ₂ O ₂ S.....	64.5	4.05	9.5	10.8
Found.....	64.4	4.00	9.4	10.7

EXAMPLE II

α-Benzoylacet-3,5-dicarboxymethoxyanilide.—A 5-liter flask fitted with a mechanical stirrer and a 6-inch Vigreux distillation column was charged with 840 g. (4.35 moles) of ethyl benzoylacetate, 2100 ml. of xylene and 41 g. of sodium acetate. The mixture was heated to reflux and 100 ml. of xylene was distilled out. The heating was temporarily stopped and 862 g. (4.15 moles) of dimethyl 5-aminoisophthalate (M.P. 178–180° C.) was added to the stirred, hot reaction mixture. The heating was then continued at such a rate that ethanol was distilled out through the column; the temperature at the head of the column was not allowed to go above 90° C. After about 8 hours, ethanol had essentially stopped distilling, and the temperature was slowly raised to 130° C. An additional 50 ml. of distillate was collected at this point. An additional 1000 ml. of xylene was added to the mixture. It was again brought to a boil, filtered through a heated funnel and the filtrate was allowed to stand at room temperature overnight. The solid which had separated was filtered off and washed with 1 liter of xylene followed by 1 liter of methanol. It was taken up in 20 liters of boiling 90% ethyl alcohol. The solution was filtered and allowed to stand overnight at room temperature. The product was filtered off, washed with 2 liters of 90% ethyl alcohol, and dried. Eight hundred thirty-eight grams (57%) of fluffy cream-colored solid, which melted at 163–165° C. was obtained.

α-Benzoylacet-3,5-dicarboxyanilide.—Three equivalents of alcoholic KOH were added to an alcohol solution of the diester and the mixture was stirred at room temperature overnight. Acidification with dilute hydrochloric acid and crystallization of the product from dioxane gave material melting at 240–242° C.

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α-Benzoyl-α-thiocyanacet-3,5-dicarboxyanilide.—Ammonium thiocyanate (7.6 g.; 0.1 mole) in 250 ml. of 95% acetic acid was treated with 4 ml. (0.082 mole) of bromine in 50 ml. of glacial acetic acid with stirring and cooling to 12–15° C. After 5 minutes, 16.4 g. (0.05 mole) of *α*-benzoylacet-3,5-dicarboxyanilide was added all at once and stirring continued for 3 hours at room temperature.

The reaction mixture was poured into 2 liters of ice water; the solid which formed was filtered and washed free of acetic acid and dried in a steam cabinet. Crystallized twice from methyl alcohol, the product melted at 273–5° C. (dec.).

Analysis:

	C	H	N	S
Calculated for C ₁₈ H ₁₂ N ₂ O ₆ S.....	56.3	3.1	7.3	8.3
Found.....	56.0	3.0	6.9	8.0

EXAMPLE III

1-(2,4,6-trichlorophenyl)-3-pentadecyl-4-thiocyano-5-pyrazolone.—Ammonium thiocyanate (7.6 g.; 0.1 mole) in 200 ml. of 95% acetic acid was treated with 4 ml. (0.082 mole) of bromine in 50 ml. of acetic acid with stirring at 15–20° C. After 5 minutes, 9.46 g. (0.02 mole) of 1-(2,4,6-trichlorophenyl)-3-pentadecyl-5-pyrazolone (prepared as described in Feniak et al. U.S. Serial No. 608,310) was added during 10 minutes and stirring was continued for 3 hours longer at room temperature. The reaction mixture was left to stand overnight. The yellow-brown precipitate which had formed was collected, washed free of acetic acid, and air dried.

The dry product was extracted with 400 ml. of boiling methyl alcohol in 2 portions. The combined extracts were diluted with an equal volume of hot water and the solution was allowed to cool slowly with stirring. The pinkish solid which formed was collected, washed well with cold water, and dried. It was purified by recrystallizing it from acetonitrile (charcoal) and twice from methyl alcohol.

The white product melted at 105–106° C.

Analysis:

	C	H	Cl	N	S
Calculated for C ₂₅ H ₂₁ Cl ₃ N ₃ OS.....	56.7	6.4	20.0	7.9	6.0
Found.....	57.0	6.8	20.2	7.9	6.0

EXAMPLE IV

1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-tert-amylphenoxyacetamido)benzamido]-4-thiocyano-5-pyrazolone.—This coupler was prepared by a process similar to that used for Example III but in which a molecular equivalent amount of 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-tert-amylphenoxyacetamido)benzamido]-5-pyrazolone prepared as in Loria et al. U.S. 2,600,788, issued June 17, 1952, was used in place of 1-(2,4,6-trichlorophenyl)-3-pentadecyl-5-pyrazolone. The coupler produced by this process had a melting point of 110° C.

Analysis:

	C	H	N	S
Calculated for C ₁₈ H ₁₂ N ₂ O ₆ S.....	57.8	4.8	9.6	4.4
Found.....	57.0	4.7	9.5	4.8

EXAMPLE V

1-(p-tert-butylphenoxyphenyl)-3-α-(p-tert-butylphenoxy)propionamido-4-thiocyano-5-pyrazolone.—This coupler was prepared by a method similar to that described in Example III excepting that a molecular equivalent amount of the parent coupler 1-(p-tert-butylphenoxyphenyl)-3-α-(p-tert-butylphenoxy)propionami-

do-5-pyrazolone prepared as in Porter et al. U.S. 2,369,489, issued February 13, 1945, was used in place of 1-(2,4,6-trichlorophenyl)-3-pentadecyl-5-pyrazolone. This coupler had a melting point of 60° C.

Analysis:

	C	H	N	S
Calculated for C ₃₃ H ₃₅ N ₄ O ₄ S-----	68.0	6.17	9.6	5.49
Found-----	67.0	6.20	9.5	5.30

EXAMPLE VI

1-hydroxy-4-thiocyano-N-[δ-(2,4-di-tert-amyphenoxy)butyl]-2-naphthamide.—A cooled solution of 7.6 g. (0.1 mole) of ammonium thiocyanate and 23.8 g. (0.05 mole) of 1-hydroxy-N-[δ-(2,4-di-tert-amyphenoxy)butyl]-2-naphthamide (prepared as given in Weissberger et al. U.S. 2,474,293, issued June 28, 1949) in 300 ml. of 95% acetic acid was treated with 4 ml. (0.082 mole) of bromine in 25 ml. of glacial acetic acid. The bromine solution was added during 15 minutes at 10–12° C. while stirring vigorously. The stirring was continued for 3 hours and the reaction mixture was allowed to come to room temperature.

After standing overnight, the orange-yellow precipitate which had formed was filtered and discarded. The filtrate was diluted with 3 volumes of cold water and stirred for 2 hours. The precipitate which formed was filtered, washed free of acetic acid, and dried. The dried product was recrystallized twice from methyl alcohol using decolorizing carbon in the first recrystallization.

The white solid melted at 122–114° C.

Analysis:

	C	H	N	S
Calculated for C ₃₂ H ₄₀ N ₂ O ₃ S-----	72.4	7.5	5.3	6.0
Found-----	72.4	7.6	5.2	6.1

Some of our couplers which have lower alkyl groups as substituents are diffusible and are used advantageously in color developer solutions for developing dye images in photographic emulsions according to conventional processes.

The non-diffusing couplers of our invention are advantageously incorporated in emulsion layers of the developing-out type for color photography. Emulsions containing our couplers are coated on transparent supports such as glass, cellulose esters, etc., or on a non-transparent reflecting material such as paper, opaque cellulose esters, etc.

The emulsions of our invention are color developed with developer solutions containing any of the well known primary aromatic amino silver halide developing agents such as the phenylenediamines including the alkyl phenylenediamines and the alkyl toluenediamines. These are generally used in the salt form such as the hydrochloride or sulfate. The para-aminophenols and their substituted products may also be used where the amino group is unsubstituted. All of the developing agents have an unsubstituted amino group which enables the oxidation product of the developer to couple with the color-forming coupler compounds to form the dye image.

Typical developers containing these developing agents are illustrated by the following:

Developer 1

2-amino-5-diethylaminotoluene hydrochloride -----	2.5
Sodium sulfite (anhydrous) -----	5
Sodium carbonate (anhydrous) -----	20
Potassium bromide -----	2
Water to 1 liter.	

Developer 2

N-ethyl-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate -----	2
Sodium sulfite (anhydrous) -----	.5
Sodium carbonate (anhydrous) -----	30
Water to 1 liter.	

Our couplers are incorporated in light-sensitive silver halide emulsion layers as described in Mannes and Gadowsky U.S. Patent 2,304,940 or Jelley and Vittum U.S. Patent 2,322,027. A wide range of coupler to coupler-incorporating solvent ratios may be used. For example, this ratio may range from 1:3 to 1:0. The preferred range of coupler to coupler-solvent ratios is from 1:2 to 1:½.

Any of the standard emulsion addenda may be used in the emulsions containing our couplers such as the emulsion addenda disclosed in Dann and Gates, U.S. Serial No. 797,577, filed March 6, 1959.

The following specific examples illustrate typical ways in which representative members of our couplers are incorporated in emulsion layers and used to produce dye images.

EXAMPLE VII

25 ml. of a dispersion of 1 g. of coupler No. 3 in 2 g. of tri-o-cresylphosphate and 2.2 g. of gelatin was mixed with 2½ ml. of a conventional medium-speed silver halide emulsion and the mixture was coated on a suitably-subbed cellulose acetate support. After being dried, the coating was exposed under an image and developed in a developer solution having the formula of Developer No. 1 to form a negative silver and magenta dye image. The silver image and the residual silver halide were removed from the emulsion layer by treatment with a conventional alkali ferricyanide bleach followed by a conventional hypo fixing bath, leaving a magenta-colored negative image. This magenta image possessed not only very good absorption characteristics having a maximum absorption or λmax value at 538 mμ but showed improved image resolving power and image definition.

EXAMPLE VIII

A light-sensitive silver halide emulsion coating prepared as in Example VII was exposed under an image and developed in a developer composition having the formula of Developer No. 2 to form a negative silver and magenta dye image. After removal of the silver image and residual silver halide according to the method used in Example VII, a good magenta dye image was left having a λmax value of 536 mμ. This image also had excellent resolving power and definition.

EXAMPLE IX

A light-sensitive silver halide emulsion coating was prepared as in Example VII but containing 1 g. of coupler No. 4 and 0.5 g. of tri-o-cresylphosphate instead of 1 g. of coupler No. 3 and 2 g. of tri-o-cresylphosphate. This emulsion coating was exposed and processed as in Example VII to produce a magenta dye image having a λmax value of 538 mμ. This image also showed good resolving power and definition characteristics.

EXAMPLE X

A light-sensitive silver halide emulsion coating prepared as in Example VII was made containing coupler No. 5 in place of coupler No. 3. This was exposed and processed according to the method used in Example VII to produce a good magenta dye image having a λmax value of 549 mμ. This magenta image also had good definition and excellent resolving power.

EXAMPLE XI

A light-sensitive silver halide emulsion coating was prepared in a similar manner to the emulsion coating of Ex-

ample VII but in which 1 g. of coupler No. 6 and 0.5 g. of di-n-butylphthalate was used in place of coupler No. 3 and tri-o-cresylphosphate. After exposure to an image and processing according to the method of Example VII, a good cyan dye image was produced having a λ_{max} value of 700 m μ .

EXAMPLE XII

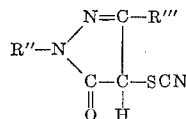
A photographic emulsion coating prepared as in Example XI was exposed and developed in a developer having the formula of Developer No. 2 then bleached and fixed as in Example VII to produce a cyan dye image having good definition and resolving power and a λ_{max} value of 690 m μ .

The novel 2-equivalent dye-forming thiocyanate couplers of our invention are valuable for use in color photography. Some of them are advantageously used in color developer solutions while the other couplers of our invention are advantageously incorporated in light-sensitive silver halide emulsion layers for color photography. In addition to having the advantages of the prior art parent couplers from which they are made, our couplers are characterized by requiring only one-half of the amount of silver halide that conventional couplers require in emulsion layers to produce equivalent dye images. Photographic emulsions containing our color-forming couplers or photographic emulsions developed in color developers containing our couplers are characterized by being considerably thinner than corresponding emulsions containing or used with prior art couplers. The thinner emulsion coatings which are made possible by use of our color-forming couplers are very effective in color photography since they make possible the production of images of improved resolving power and definition. In addition to these advantages, the reduced optical opacity of thinner emulsion layers allows more light to penetrate into emulsions coated under our emulsion which makes it possible to produce photographic products of higher speed.

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 magenta-dye-forming coupler having the formula:



wherein R'' represents a member selected from the class consisting of phenyl, cyanophenyl, halophenyl, alkylphenyl in which the alkyl group has from 1 to 18 carbon atoms, alkoxyphenyl in which the alkoxy group has from 1 to 18 carbon atoms, and phenoxyphenyl; and R''' represents a member selected from the class consisting of an alkyl having 15 carbon atoms, amino, alkamino in which the alkyl moiety has from 1 to 18 carbon atoms, anilino, toluidino, acetamido, propionamido, butyramido, 3-(2,4-di-tert-amylphenoxyacetamido)benzamido, and (p-tert-butylphenoxy)propionamido.

2. The magenta-forming coupler 1-(2,4,6-trichlorophenyl)-3-pentadecyl-4-thiocyano-5-pyrazolone.

3. The magenta-forming coupler 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-tert-amylphenoxyacetamido)benzamido]-4-thiocyano-5-pyrazolone.

4. The magenta-forming coupler 1-(p-tert-butylphenoxyphenyl)-3- α -(p-tert-butylphenoxy)propionamido-4-thiocyano-5-pyrazolone.

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WALTER A. MODANCE, *Primary Examiner*.

PHILIP E. MANGAN, HAROLD N. BURSTEIN,
NICHOLAS S. RIZZO, *Examiners*.