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3,551,157

ULTRASONICS FOR DISSOLVING COLOR COUPLERS

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24 Claims

ABSTRACT OF THE DISCLOSURE

Photographic color formers are dissolved by subjecting a mixture of color former and coupler solvent to ultrasonic vibrations.

This application is a continuation-in-part of my co-pending U.S. patent application Ser. No. 544,818 filed Apr. 25, 1966, now abandoned.

This invention relates to color formers, and more particularly to improved methods for dissolving color formers, incorporating color formers in photographic emulsions, and dispersing color formers in hydrophilic colloids.

Previously, photographic color formers have been dissolved by adding the color former to an organic solvent and heating the mixture until solution is obtained. This is a rather slow process, and the elevated temperatures necessary to obtain solution frequently involves the danger of damaging the color former. It therefore appears desirable to provide an improved process for dissolving photographic color formers rapidly at lower temperatures.

One object of this invention is to provide a novel method for dissolving photographic color formers. Another object of this invention is to provide a novel method for incorporating color formers in photographic emulsions. A further object of this invention is to provide a novel method for preparing dispersions of color formers in hydrophilic colloids. Still another object of this invention is to provide a novel method for dissolving development inhibitor-releasing photographic couplers. Other objects of this invention will be apparent from the following disclosure and the appended claims.

In one embodiment of this invention, color former is added to a solvent therefor, and the mixture is subjected to ultrasonic agitation until solution is obtained. It has been found that this method for dissolving color formers is more rapid than prior art techniques and may be conducted at low temperatures. In some instances, less solvent is required to dissolve color formers using the process of this invention.

In another embodiment of this invention a novel method is provided for incorporating color former in photographic emulsions which features the step of ultrasonically agitating a mixture of color former in a solvent therefor, and then combining the dissolved color former, in solvent, with a photographic emulsion. In a variation of this embodiment of the invention, a solution of color former in solvent is combined with a hydrophilic colloid substantially free from light sensitive material, such as silver halide,

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and the mixture is ultrasonically agitated to disperse the color former in the hydrophilic colloid. It is frequently desirable to use, in this procedure, a mixture of low and high boiling solvents as described in U.S. Pat. 2,801,171. The temperature of the mixture may be elevated to remove any low boiling solvent, the dispersion of color former in hydrophilic colloid thus obtained may then be added to photographic emulsions. Typical useful hydrophilic colloids are those described and referred to in column 13 of U.S. Pat. 3,039,873, such as gelatin and polyvinyl alcohol, or polymerized vinyl compounds such as those disclosed in U.S. Pats. 3,142,568, 3,193,386, 3,062,674 and 3,022,844, and includes the water insoluble polymers of alkylacrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

The temperature at which the mixture of color former and solvent are held during the ultrasonic agitation may be varied over a considerable range, depending on the particular color former and solvent and the ratio of color former to solvent used. Generally, the most useful temperature range is below 100° C., such as from 45 to 65° C., or up to 70° C., or higher if the color former is not damaged at the higher temperatures. The time required to dissolve the color former depends on the solvent and temperature. Usually, from one to five minutes is sufficient.

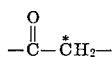
Conventional ratios of color former to solvent may be employed in this invention. Especially useful weight ratios of color former to high boiling crystalloidal solvent are from 1:0 to 1:3, and preferably 1/2:1 to 1:1. The most useful range of low boiling auxiliary solvent is 3 to 6 parts by weight to 1 part by weight color former.

The ultrasonic equipment employed in the practice of this invention is commercially available. Good results are achieved with Blackstone Model SG-2. Frequency ranges of from about 20 to 100 kc. produce good results. Preferably, frequency ranges of about 20-25 kc. are used.

It is frequently desirable to place the mixture of color former and solvent in a container the walls of which are good heat conductors and transmit ultrasonic vibrations, and place the container in a liquid maintained at the desired temperature. The liquid may be recycled to provide a constant temperature. Using this arrangement, the liquid is ultrasonically agitated, and the ultrasonic vibrations are transmitted through the wall of the container thereby ultrasonically agitating the color former and solvent.

The term "color formers" as used herein and in the appended claims refers to compounds which react with a primary aromatic amino developing agent on photographic development to form a dye (i.e., photographic couplers), and also to dye developers which include, in one molecule, a dye moiety and a photographic developer moiety, such as the dye developers referred to in U.S. Pat. 3,146,102. Useful photographic couplers, which may be colored, include the phenolic, 5-pyrazolone, open chain with reactive methylene group and polymeric types. Other couplers which may be used according to this invention are those disclosed in U.S. Pats. 2,322,027; 2,423,730; 3,062,653; 3,148,062; 3,227,554; French Pat. 1,291,110 and those listed in column 2 of U.S. Pat. 2,801,171.

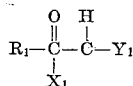
The term "photographic coupler" is used herein as a word of art and includes organic compounds which react with oxidized primary aromatic amine developing agents to form dye images. The photographic couplers utilized in the practice of this invention can embody any photographic coupler radical. Typical useful photographic coupler radicals include the 5-pyrazolone coupler radicals, the phenolic (including α -naphthol) coupler radicals, and the open-chain ketomethylene coupler radicals. As is well known in the art, 5-pyrazolone coupler radicals are customarily utilized for the formation of magenta dyes; phenolic coupler radicals are generally utilized for the formation of cyan color dyes; and, open-chain ketomethylene coupler radicals are generally utilized in the formation of yellow dyes. The coupling position of such coupler radicals is also well known in the art. The 5-pyrazolone coupler radicals couple at the carbon atom in the 4-position thereof; the phenolic coupler radicals couple at the carbon atom in the 4-position (relative to the hydroxyl group); and, the open-chain ketomethylene coupler radicals couple at the carbon atom forming the methylene moiety (e.g.,



wherein * denotes the coupling position).

An especially useful class of open-chain ketomethylene coupler radicals are described in Formula I below:

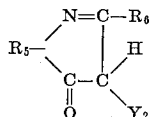
Formula I



wherein R_1 , X_1 and Y_1 represent substituents of the type used in open-chain ketomethylene couplers. For example, R_1 can represent an alkyl group (which can be substituted and preferably has from about 6 to 22 carbon atoms); an aryl group (preferably a phenyl or naphthyl group); or, a heterocyclic group (preferably a carbon containing heterocyclic radical which contains from 5 to 6 atoms in the heterocyclic ring, which ring contains at least one hetero oxygen, sulfur or nitrogen atom); X_1 can represent a member selected from the group consisting of cyano and carbamyl (which can be substituted); and, Y_1 can have a meaning given below.

The photographic couplers utilized in this invention can feature a 5-pyrazolone coupler radical having the following general formula:

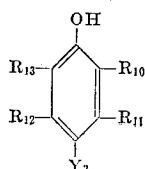
Formula II



wherein R_5 , R_6 and Y_2 represent substituents of the type used in 5-pyrazolone couplers, for example, R_5 can represent a value given for R_1 ; R_6 can represent a member selected from the group consisting of an alkyl group, a carbamyl group (which can be substituted), an amino group (which can be substituted with various groups such as one or two alkyl or aryl groups), an amido group, e.g., a benzamido group (which can be substituted), or an alkylamido group (which can be substituted), and, Y_2 can represent a value given below.

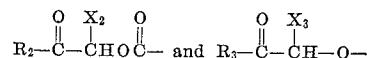
The photographic couplers employed in the practice of this invention can utilize any suitable phenolic (including α -naphtholic) coupler radicals, including those described in the structural formula below:

Formula III



wherein R_{10} , R_{11} , R_{12} , R_{13} and Y_3 can represent a substituent of the type used in phenolic couplers, for example, R_{10} and R_{11} each can represent a value given for R_1 , and in addition can represent a member selected from the group consisting of hydrogen, amino, carbonamido, sulfonamido, sulfamyl, carbamyl, halogen and alkoxy; R_{12} and R_{13} , when taken together, can represent the carbon atoms necessary to complete a benzo group, which benzo group can be substituted with any of the groups given for R_{10} and R_{11} and, when taken separately, R_{12} and R_{13} can each independently represent a value given for R_{10} and R_{11} ; and, Y_3 represents a value given below.

The photographic couplers which can be utilized in the practice of this invention include the non-diffusible, open-chain, 5-pyrazolone and phenolic couplers referred to above, such as those couplers represented by Formulas I, II and III above wherein Y_1 and Y_2 each represents a group of the type used in colorless image forming couplers, such as hydrogen or a coupling off group, e.g., halogen, such as a chlorine or a fluorine atom; a thiocyanate group; an acyloxy group, for example, an alkyl-acyloxy group which can be substituted, or an aryloxy group which can be substituted, or a heterocycloxyloxy group which can be substituted; a cyclooxy group including an aryloxy group, e.g., phenoxy, naphthoxy, or a heterocycloxyloxy group, such as a pyridinyloxy group, a tetrahydropyran-2-yl group, a tetrahydroquinol-2-yl group, etc.; and, an alkoxy group; and, Y_3 can represent any value given for Y_1 and Y_2 except an aryloxy group, and in addition Y_3 can also represent a cycloimido group (e.g., a maleimido group, a succinimido group, a 1,2-dicarboximido group, a phthalimido group, etc.) when R_{12} and R_{13} are taken together to form a benzo group. The various groups which Y_1 , Y_2 and Y_3 can represent may include groups such as:



wherein R_2 and R_3 have a meaning given for R_1 , and X_2 and X_3 each have a meaning given for X_1 .

Especially good results are obtained when the image forming coupler is colorless; it can, however, be colored if desired.

The useful photographic couplers include both the four-equivalent and two-equivalent non-diffusing couplers. Typical useful four-equivalent yellow dye-forming couplers which can be utilized in this invention include the following:

- (1) N- α -methyl-p-benzoylacetylaminobenzenesulfonate
- (2) N-(4-anisoylacetylaminobenzenesulfonyl)-N-benzyl-m-toluidine
- (3) N-(4-benzoylacetylaminobenzenesulfonyl)-N-benzyl-aniline
- (4) ω -(p-benzoylbenzoyl)acetanilide
- (5) ω -benzoyl-p-sec.-amylacetanilide
- (6) N,N'-di(ω -benzoylacetyl)-p-phenylenediamine
- (7) α -{3-[α -(2,4-di-tert-amylphenoxy)butyramido]-benzoyl}-2-methoxyacetanilide
- (8) 4,4'-di-(acetoacetamino)-3,3'-dimethyldiphenyl
- (9) p,p'-di-(acetoacetamino)diphenylmethane
- (10) nonyl-p-benzoylacetylaminobenzenesulfonate
- (11) N-phenyl-N'-(p-acetoacetaminophenyl)urea
- (12) n-propyl-p-benzoylacetylaminobenzenesulfonate
- (13) N-(ω -benzoylacetyl)-1,2,3,5-tetrahydroquinoline
- (14) N-(ω -benzoylacetyl)morpholine

The two-equivalent yellow dye-forming couplers can be derived from corresponding parent four-equivalent couplers by replacing one of the two hydrogens on the alpha-carbon (i.e., methylene) with any nonchromophoric coupling off group, including coupling off groups such as the fluorine atom, the chlorine atom, an acyloxy group, a cyclooxy group and a thiocyanate group. Typically useful 2-equivalent couplers include the alpha-

fluoro couplers of U.S. Pat. 3,277,155, the alpha-chloro couplers of U.S. Pat. 2,778,658, the alpha-thiocyano couplers of U.S. Pat. 3,253,924, the alpha-acyloxy couplers of Loria U.S. patent application 477,353, filed July 26, 1965, the alphacycloxy couplers of Loria U.S. patent application 469,887, filed July 6, 1965, and the alpha-alkoxy couplers of the type shown in Whitmore et al., U.S. Pat. 3,227,550.

Typical useful 2-equivalent yellow-forming open-chain ketomethylene couplers include the following:

- (1) 4-(α -2'-methoxybenzoyl- α -chloro-4-(α -(2,4-di-tert-amylphenoxy)-n-butyramido]-acetanilide
- (2) α -o-methoxybenzoyl- α -chloro-4-(α -(2,4-di-tert-amylphenoxy)-n-butyramido]-acetanilide
- (3) α -{3-[α -(2,4-di-tert-amylphenoxy)butyramido]benzoyl}- α -fluoro-2-methoxyacetanilide
- (4) α -fluoro- α -pivalyl-5-[γ -(2,4-di-tert-amylphenoxy)-butyramido]-2-chloroacetanilide
- (5) α -acetoxy- α -{3-[γ -(2,4-di-tert-amylphenoxy)butyramido]benzoyl}-2-methoxyacetanilide
- (6) α -benzoyl- α -[2,4-di-n-amylphenoxy]acetoxy]-2-methoxyacetanilide
- (7) α -pivalyl- α -stearoyloxy-4-sulfamylacetanilide
- (8) α -pivalyl- α -[α -(3-pentadecylphenoxy)acetoxy]-3,5-diamyloxyacetanilide
- (9) α -acetoxy- α -{3-[α -(2,4-di-tert-amylphenoxy)butyramido]benzoyl}-2-methoxyacetanilide
- (10) α -(3-dodecanamidobenzoyl)- α -octanoyloxy-2-methoxyacetanilide
- (11) α -{3-[γ -(2,4-di-tert-amylphenoxy)butyramido]benzoyl}- α -(4-nitrophenoxy)-2-methoxyacetanilide
- (12) α -[4-(N-methyl-N-octadecylsulfamyl)phenoxy]- α -pivalyl-4-octylacetanilide potassium salt
- (13) α -pivalyl- α -(4-sulfophenoxy-4-N-methyl-N-octadecylsulfamyl)acetanilide potassium salt
- (14) α -[4-(4-hydroxyphenylsulfonyl)phenoxy]- α -pivalyl-2-chloro-5-[γ -(2,4-di-tert-amylphenoxy)butyramido]acetanilide
- (15) 4,4'-bis[α -pivalyl- α -(2-chloro-5-[γ -(2,4-di-tert-amylphenoxy)butyramido]phenylcarbonyl)methoxy]-diphenylsulfone
- (16) α -benzoyl- α -thiocyanoacetanilide

Specific representative 4-equivalent magenta dye-forming couplers which can be used in this invention include the following:

- (1) 1-p-sec.-amylphenyl-3-n-amyl-5-pyrazolone
- (2) 2-cyanoacetyl-5-(p-sec.-amylbenzoylamino)coumarone
- (3) 2-cyanoacetylcoumarone-5-(N-n-amyl-p-tert.-amylsulfanilide).
- (4) 2-cyanoacetylcoumarone-5-sulfon-N-n-butylanilide
- (5) 2-cyanoacetyl-5-benzoylamino-coumarone
- (6) 2-cyanoacetylcoumarone-5-sulfondimethylamide
- (7) 2-cyanoacetylcoumarone-5-sulfon-N-methylanilide
- (8) 2-cyanoacetylcoumarone-5-(N- γ -phenylpropyl(-p-tert.-amylsulfonanilide
- (9) 1-p-laurylphenyl-3-methyl-5-pyrazolone
- (10) 1- β -naphthyl-3-amyl-5-pyrazolone
- (11) 1-p-nitrophenyl-3-n-amyl-5-pyrazolone
- (12) 1-p-phenoxyphenyl-3-n-amyl-5-pyrazolone
- (13) 1-phenyl-3-n-amyl-5-pyrazolone
- (14) 1,4-phenylene bis-3-(1-phenyl-5-pyrazolone)
- (15) 1-phenyl-3-acetylamino-5-pyrazolone
- (16) 1-phenyl-3-n-valeryl-amino-5-pyrazolone
- (17) 1-phenyl-3-chloroacetylamino-5-pyrazolone
- (18) 1-phenyl-3-benzoylamino-5-pyrazolone
- (19) 1-phenyl-3-(m-aminobenzoyl)amino-5-pyrazolone
- (20) 1-phenyl-3-(p-sec.-amylbenzoylamino)-5-pyrazolone
- (21) 1-phenyl-3-diamylbenzoylamino-5-pyrazolone
- (22) 1-phenyl-3- β -naphthoylamino-5-pyrazolone
- (23) 1-phenyl-3-phenylcarbonylamino-5-pyrazolone
- (24) 1-phenyl-3-palmitylamino-5-pyrazolone
- (25) 1-phenyl-3-benzenesulfonylamino-5-pyrazolone

(26) 1-(p-phenoxyphenyl)-3-(p-tert-amylloxybenzoyl)amino-5-pyrazolone

(27) 1-(2',4',6'-trichlorophenyl)-3-benzamido-5-pyrazolone

(28) 1-(2',4',6'-tribromophenyl)-3-phenylacetamido-5-pyrazolone

(29) 1-(2',4'-dichlorophenyl)-3-[3''-(2''',4'''-di-tert-amylphenoxyacetamido)benzamido]-5-pyrazolone

(30) 1-(2',4',6'-trichlorophenyl)-3-[3''-(2''',4'''-di-tert-amylphenoxyacetamido)benzamido]-5-pyrazolone

(31) 1-(2',4',6'-trichlorophenyl)-3-[β -2''',4'''-di-tert-amylphenoxy]-propionamido]-5-pyrazolone

(32) 1-(2',5'-dichloro)-3-[3''-(4'''-tert.-amylphenoxy)benzamido]-5-pyrazolone

(33) 1-(2',4',6'-tribromophenyl)-3-[3''-(4'''-tert.-amylphenoxy)-benzamido]-5-pyrazolone

(34) 1-(2',5'-dichlorophenyl)-3-[3''-(2''',4'''-di-tert-amylphenoxyacetamido)benzamido]-5-pyrazolone

The 2-equivalent 5-pyrazolone couplers can be derived from the parent 4-equivalent 5-pyrazolone couplers by replacing one of the hydrogens on the carbon in the 4-position of the pyrazolone ring with a non-chromophoric coupling off group. Examples of coupling off groups which can be used in 2-equivalent magenta-forming 5-pyrazolone couplers are the thiocyanate group illustrated by the couplers in Loria U.S. Pat. 3,252,924 and the acyloxy group containing 2-equivalent magenta-forming couplers of Loria U.S. Pat. 3,311,476. Other useful coupling off groups include acyloxy, aryloxy, alkoxy such as any of those shown in Whitmore et al. U.S. Pat. 3,227,550, the chlorine atom, the fluorine atom, and the sulfo group.

Typical 2-equivalent magenta dye-forming couplers which can be used in this invention include the following:

(1) 1-(2,4,6-trichlorophenyl)-3-(4-nitroanilino)-4-stearoyloxy-5-pyrazolone

(2) 1-(2,4,6-trichlorophenyl)-3-{3-[α -(2,4-di-tert-amylphenoxy)-acetamido]benzamido}-4-acetoxy-5-pyrazolone

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

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

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

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

(7) 1-(2,4,6-trichlorophenyl)-3-pentadecyl-4-chloro-5-pyrazolone

(8) 1-[4-(3,5-dimethoxybenzamido)phenyl]-3-ethoxy-4-(3-octadecylcarbonylphenylthio)-5-pyrazolone

Typical four-equivalent cyan-forming phenolic couplers which can be used in this invention include:

(1) 5-(p-amylphenoxybenzenesulfonamino)-1-naphthol

(2) 5-(n-benzyl-N-n-valeryl-amino)-1-naphthol

(3) 5-caproylamino-1-naphthol

(4) 2-chloro-5-(N-valeryl-N-p-isopropylbenzylamino)-1-naphthol

(5) 2-chloro-5-palmitylamino-1-naphthol

(6) 5-diphenylethersulfonamido-1-naphthol

(7) 1-hydroxy-2-(N-isoamyl-N-phenyl)naphthamide

(8) 8-hydroxy-1- α -naphthoyl-1,2,3,4-tetrahydroquinoline

(9) 1-naphthol-5-octyl-cyclohexylamide

(10) 5-phenoxyacetamino-1-naphthol

(11) Monochloro-5-(N- γ -phenylpropyl-N-p-sec.-amylbenzoylamino)-1-naphthol

(12) 2-benzoylamino-3,5-dimethylphenol

(13) 2- α -(p-tert-amylphenoxy)-n-butyrylamino-5-methylphenol

(14) 1-hydroxy-N-[σ -(2,4-di-tert.-amylphenoxy)butyl]-2-naphthamide

(15) 2-(4-tert.-amyl-3-phenoxybenzoylamino)-3,5-dimethylphenol

- (16) 2-(4-tert.-amyl-3-phenoxybenzoylamino)phenol
- (17) 2-[α -(4'-tert.-butylphenoxy)propionylamino]phenol
- (18) 2-[N-methyl-N-(4-tert.-amyl-3-phenoxybenzoylamino)]phenol
- (19) 2- α -(4-tert.-amylphenoxy)butyrylamino-1-phenol
- (20) 2-(4-tert.-amyl-3-phenoxybenzoylamino)-3,5-dimethylphenol
- (21) 2-[α -(4-tert.-amylphenoxy)-n-butyrylamino]-5-methylphenol
- (22) 3-(4-tert.-amyl-3'-phenoxybenzoylamino)phenol
- (23) 2-[α -(4-tert.-amylphenoxy)-n-butyrylamino]-6-chlorophenol
- (24) 3-[α -(4-tert.-amylphenoxy)-n-butyrylamino]-5-chlorophenol
- (25) 5-benzene sulfonamido-1-naphthol
- (26) 2-chloro-5-benzenesulfonamido-1-naphthol
- (27) 5-(1,2,3,4-tetrahydronaphthalene-6-sulfonamido)-1-naphthol
- (28) 2-chloro-5-(4-bromodiphenyl-4-sulfonamido)-1-naphthol

Any of the two-equivalent cyan-forming phenolic couplers can be used in the practice of this invention. The two-equivalent couplers can be derived from the corresponding four-equivalent phenolic couplers by substituting a nonchromophoric coupling off group on the carbon in the 4-position of the phenolic or naphtholic ring. Included among the coupling off groups are the acyloxy group illustrated by the 4-acyloxyphenols and 4-acylonaphthols of Loria U.S. Pat. 3,311,476, issued Mar. 28, 1967, the cycloxy group illustrated by the 4-cycloxy naphthols of Loria U.S. patent application 483,807, filed Aug. 30, 1965, the thiocyanate group illustrated by the 4-thiophenols and 4-thionaphthols of Loria U.S. Pat. 3,253,294, the cyclic imido groups as illustrated by the 4-cyclic imido derivatives of 1-hydrogen-2-naphthamides of Loria U.S. patent application 504,994, the chlorine atom as illustrated in the 4-chlorophenols of Weissberger U.S. Pat. 2,423,730, the alkoxy group as illustrated by the 4-alkoxynaphthols (and naphthols) of Whitmore et al. U.S. Pat. 3,227,550, the sulfo group as in 4-sulfophenols and 4-sulfonaphthols, etc.

Typical 2-equivalent cyan-forming couplers which can be used in this invention include the following:

- (1) 1-hydroxy-4-decyloxy-2-naphthamide
- (2) 1-hydroxy-4-acetoxy-N-[α -(2,4-di-tert.-amylphenoxy)butyl]-2-naphthamide
- (3) 1-hydroxy-4-methoxy-N-octadecyl-3',5'-dicarboxy-2-naphthanilide
- (4) 1-hydroxy-4-thiocyano-N-[α -2,4-di-tert.-amylphenoxy)-butyl]-2-naphthamide
- (5) 1-hydroxy-4-(pentafluorophenoxy)-N-[β -{4-[α -(2,4-di-tert.-amylphenoxy)acetamido]phenyl}ethyl]-2-naphthamide
- (6) 1-hydroxy-4-(4-nitrophenoxy)-N-[α -2,4-di-tert.-amylphenoxybutyl]-2-naphthamide
- (7) 1-hydroxy-4-(4-chlorophenoxy)-2'-tetradecyloxy-2-naphthanilide

The process of the present invention is particularly suitable in dissolving photographic development inhibitor-releasing couplers. The term "development inhibitor-releasing coupler" is used herein as a word of art to refer to those photographic couplers which, upon reaction with oxidized primary aromatic amine color developing agent, form dye and release a compound which inhibits development. Development inhibitor-releasing (DIR) couplers which can be utilized herein can be represented by the general formula: ZC_p wherein C_p represents a photographic coupler radical, preferably an open-chain ketomethylene, 5-pyrazolone or phenolic (including α -naphtholic) coupler radicals, having said Z substituted in the coupling position of the coupler radical, Z representing an organic group which does not contain a chromophore, does not couple with oxidized primary aromatic amine color developer to form dye, does not inhibit de-

velopment while attached to C_p , but is released from C_p , on reaction with oxidized primary aromatic amine color developing agent, and either is or forms a compound which inhibits development. Especially useful DIR couplers have Formula I, II or III above, wherein Y_1 , Y_2 and Y_3 each are selected from:

- (1) A monothio group, such as, ortho-nitro or ortho-amino substituted arylmonothio groups (such as, 2-nitrophenyl and 2-aminophenyl), a carbon containing heterocyclic monothio group (generally having a 5 to 6 membered ring containing at least one heteronitrogen, oxygen or sulfur atom and preferably 1 to 4 heteronitrogen atoms) including heterocyclic radicals, such as tetrazolyls, triazolyls, triazolyls, oxazolyls, oxadiazolyls, diazolyls, thiazyls, thiadiazolyls, benzoxazolyls, benzothiazolyls, pyrimidyls, pyridinyl, quinolinyls, etc., and in which the aryl-, hetero- cyclic-moieties of the monothio group are either unsubstituted or substituted with various groups, such as nitro, halogen (chlorine, bromine, iodine, fluorine), lower alkyl, lower alkylamido, lower alkoxy, lower alkylsulfonamido, α -chloroacetylthio, lower alkylcarbonylamino, etc., typical monothio groups representing the above include 2-aminophenyl, 2-nitrophenyl and a heterocyclic group (e.g., 2-benzothiazolylthio, 1-phenyl-5-tetrazolylthio, 1-(4-carbomethoxyphenyl)-5-tetrazolylthio, 5-phenyl-1,3,4-oxadiazolyl-2-thio, 2-phenyl-5-(1,3,4)-oxadiazolylthio, 2-benzoxazolylthio, etc.);

- (2) A 2-aminoaryloxy group (e.g., 2-amino-4-methylphenylazoxy, 2-aminophenylazoxy, 2-amino-4-chlorophenylazoxy, etc.);

- (3) A 2-amidoaryloxy group (e.g., 2-acetamidophenylazoxy, 2-acetamido-4-methylphenylazoxy, 2-acetamido-4-chlorophenylazoxy, 2-palmitamidophenylazoxy, 4-methoxy-2-palmitamidophenylazoxy, 4-chloro-2-palmitamidophenylazoxy, etc.);

- (4) A 2-aryltrialzyl group (e.g., 2-benzotriazolyl, 5-chloro-2-benzotriazolyl, 5-hydroxy-2-benzotriazolyl, 4,7-dinitro-2-benzotriazolyl, 5-methyl-2-benzotriazolyl, 6-methoxy-2-benzotriazolyl, 4-carboxyethyl-2-benzotriazolyl, 4-sulfoethyl-2-benzotriazolyl, 2-naphthotriazolyl, 4-methyl-2-naphthotriazolyl, 5-chloro-2-naphthotriazolyl, 5-hydroxy-2-naphthotriazolyl, 5-nitro-2-naphthotriazolyl, 5-sulfoethyl-2-naphthotriazolyl, 4-amino-2-naphthotriazolyl, benzo[1,2-d:4,5-d']bistriazolyl, etc.).

The Z group (or Y_1 , Y_2 and Y_3 in the above formulas) (1) forms a diffusible mercaptan and (2), (3) and (4) form a diffusible aryltriazole upon reaction with oxidized color developing agent.

Representative DIR couplers include the following:

- (1) α -Benzoyl- α -(2-nitrophenylthio)-4-[N-(γ -phenylpropyl)-N-(p-tolyl)-sulfamyl]acetanilide
- (2) α -Benzoyl- α -(2-benzothiazolylthio)-4-[N-(γ -phenylpropyl)-N-(p-tolyl)sulfamyl]acetanilide
- (3) α -{3-[α -(2,4-di-tert.-amylphenoxy)butyramido]benzoyl}- α -2-nitrophenylthio-2-methoxyacetanilide
- (4) α -{3-[γ -(2,4-di-tert.-amylphenoxy)butyramido]benzoyl}- α -(2-benzoxazolylthio)-2-methoxyacetanilide
- (5) α -Benzoyl- α -[1-(3-phenyl)-5-tetrazolylthio]stearamido acetanilide
- (6) α -{3-[α -(2,4-di-tert.-amylphenoxy)butyramido]benzoyl}- α -(2-aminophenylazoxy)-2-methoxyacetanilide
- (7) α -{3-[γ -(2,4-di-tert.-amylphenoxy)butyramido]benzoyl}- α -(2-amino-4-methylphenylazoxy)-2-methoxyacetanilide
- (8) α -(5-chloro-2-benzotriazolyl)- α -pivalyl-5-[α -(2,4-di-tert.-amylphenoxy)propylamido]-2-chloroacetanilide
- (9) α -(4,7-dinitro-2-benzotriazolyl)- α -pivalyl-3,6-dichloro-4-(N-methyl-N-octadecylsulfamyl)acetoacetanilide

- (10) α -(6-chloro-5-methoxy-2-benzotriazolyl)- α -pivalyl-2-chloro-5-[α -(3-pentadecyl-4-sulphenoxy)butyramido]acetanilide, sodium salt
- (11) 1-phenyl-3-octadecylamino-4-[2-phenyl-5-(1,3,4)-oxadiazolylthio]-5-pyrazolone
- (12) 1-[4-[γ -(2,4-di-tert-amylphenoxy)butyramido]phenyl]-3-ethoxy-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- (13) 1-[4-[α -(3-pentadecylphenoxy)butyramido]phenyl]-3-ethoxy-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- (14) 1-(2,4,6-trichlorophenyl)-3-[4-[α -(2,4,1-di-tert-amylphenoxy)butyramido]anilino]-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- (15) 1-phenyl-3-octadecylamino-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- (16) 1-[4-(4-tert-butylphenoxy)phenyl]-3-phenyl-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- (17) 1-[4-(4-tert-butylphenoxy)phenyl]-3-[α -(4-tert-butylphenoxy)propionamido]-4-(5-phenyl-1,3,4-oxadiazolyl-2-thio)-5-pyrazolone
- (18) 1-[4-(4-tert-butylphenoxy)phenyl]-3-[α -(4-tert-butylphenoxy)propionamido]-4-(2-nitrophenylthio)-5-pyrazolone
- (19) 1-[4-(4-tert-butylphenoxy)phenyl]-3-[α -(4-tert-butylphenoxy)propionamido]-4-[1-(4-methoxyphenyl)-5-tetrazolylthio]-5-pyrazolone
- (20) 1-[4-(4-tert-butylphenoxy)phenyl]-3-[α -(4-tert-butylphenoxy)propionamido]-4-(2-benzothiazolylthio)-5-pyrazolone
- (21) 1-[4-(4-tert-butylphenoxy)phenyl]-3-[α -(4-tert-butylphenoxy)propionamido]-4-(2-nitrophenylthio)-5-pyrazolone
- (22) 1-[4-(4-tert-butylphenoxy)phenyl]-3-[α -(tert-butylphenoxy)propionamido]-4-(2-benzoxazolylthio)-5-pyrazolone
- (23) 1-(2,4-dichloro-6-methoxyphenyl)-3-[α -(3-pentadecylphenoxy)acetamido]-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- (24) 1-phenyl-3-octadecyl-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- (25) 1-phenyl-3-[α -(2,4-di-tert-amylphenoxy)acetamido]-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- (26) 1-phenyl-3-[γ -(2,4-di-tert-amylphenoxy)butyramido]-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone
- (27) 1-phenyl-3-(3,5-didodecyloxybenzamido)-4-(2-nitrophenylthio)-5-pyrazolone
- (28) 1-phenyl-3-[α -(2,4-di-tert-amylphenoxy)acetamido]-4-(2-aminophenylazoxy)-5-pyrazolone
- (29) 4-benzotriazolyl-3-pentadecyl-1-phenyl-5-pyrazolone
- (30) 4-benzotriazolyl-1-(2,4,6-trichlorophenyl)-3-[3- α -(2,4-di-tert-amylphenoxy)acetamido]benzamido]-5-pyrazolone
- (31) 4-(5-methoxy-2-benzotriazolyl)-3-pentadecyl-1-phenyl-5-pyrazolone
- (32) 4-(4-carboxy-2-benzotriazolyl)-1-(2,4,6-trichlorophenyl)-3-pentadecyl-5-pyrazolone
- (33) 1-hydroxy-4-(2-nitrophenylthio)-N-[δ -(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide
- (34) 1-hydroxy-4-(2-benzothiazolylthio)-N-[δ -(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide
- (35) 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-N-[δ -(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide
- (36) 1-hydroxy-4-(2-benzothiazolylthio)-N-octadecyl-3',5'-dicarboxy-2-naphthanilide
- (37) 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-2'-tetradecyloxy-2-naphthanilide
- (38) 1-hydroxy-4-[1-(4-methoxyphenyl)-5-tetrazolylthio]-N-[δ -(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide
- (39) 1-hydroxy-4-(5-phenyl-1,3,4-oxadiazolyl-2-thio)-N-[δ -(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide
- (40) 5-methoxy-2-[α -(3-n-pentadecylphenoxy)butyramido]-4-(1-phenyl-5-tetrazolylthio)phenol

- (41) 1-hydroxy-4-(2-amino-4-methylphenylazoxy)-N-[δ -(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide
- (42) 4-(2-benzotriazolyl)-2-[δ -(2,4-diamylphenoxybutyl)]-1-hydroxynaphthamide
- (43) 1-hydroxy-4-(6-nitro-2-benzotriazolyl)-N-[δ -(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide
- (44) 5-methoxy-2-[α -(3-pentadecylphenoxy)butyramido]-4-(5-chloro-2-benzotriazolyl)phenol
- (45) 5-methoxy-2-[α -(3-pentadecylphenoxy)butyramido]-4-(6-chloro-5-methoxy-2-benzotriazolyl)phenol

Couplers 1 through 5, 11 through 27, 33 through 40 are described in Barr U.S. Pat. 3,227,554. Couplers 6, 7, 28 and 41 are prepared by methods similar to those disclosed in U.S. Pat. 3,148,062. Couplers 8 through 10, 29 through 32 and 42 through 45 are described by Sawdey U.S. patent application Ser. No. 674,090, filed Oct. 10, 1967. The couplers referred to in the immediate paragraph are the DIR couplers listed above.

The most useful DIR couplers are those which have a monothio group in the coupling position (e.g., Formula I, II and III above in which Y_1 , Y_2 and Y_3 represent a monothio group). Preferred DIR couplers have Formula I, II or III above wherein Y_1 , Y_2 and Y_3 each represents a heterocyclic monothio radical in which the heterocyclic ring has from 5 to 6 atoms and at least one hetero atom selected from oxygen, sulfur and nitrogen, such as a hetero ring, containing from 1 to 4 hetero nitrogen atoms, e.g., a 5-tetrazolylthio group. Preferably, a DIR coupler is selected which forms a dye of substantially the same color as the dye formed by the image forming coupler.

Development inhibitor-releasing couplers are particularly susceptible to degradation by heat. Such couplers tend to decompose thermally with the production of a compound which inhibits development. Hence, not only is coupler undesirably destroyed, but there can be an undesirable non-imagewise development inhibition caused by such thermal degradation. This problem is effectively overcome when development inhibitor-releasing couplers are dissolved by the use of ultrasonics.

Any solvent or solvent mixture for the color formers useful in conventional dissolving techniques may be used in this invention. Typical useful solvents are the high boiling crystalloidal materials or oil formers (generally a low molecular weight organic material having a boiling point above 175° C.) which have high solvent action for color formers and are permeable to photographic developer oxidation products, including all those described on pages 2 and 3 of U.S. Pat. 2,322,027. The invention is also useful in preparing dispersions of color formers in low boiling solvent, which are employed in the process of U.S. Pat. 2,861,170. The "auxiliary solvent" referred to above includes water soluble and water insoluble low-boiling (preferably under 100° C.) oily organic materials having high solvent action for color formers, such as any of those listed in U.S. Pat. 2,801,171, column 10, lines 33 to 51.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

A mixture of one part by weight of Coupler 1 of U.S. Pat. 3,062,653 (1-(4,6-dichloro-2-methoxyphenyl)-3-[α -(m-pentadecylphenoxy)butyramido]-5-pyrazolone), one part by weight tri-o-cresyl phosphate and 4 parts by weight cyclohexanol are added to a glass container, placed in the water tank of a Blackstone Model SG-2 ultrasonic generator, and the water is ultrasonically agitated at about 20 kc. The temperature of the water, and the mixture of color former and solvent, are maintained at 45° C. by recycling 45° C. water in the tank. The coupler goes into solution in one minute. Using prior art procedures, it takes several minutes to dissolve the coupler at 65 to 75° C. Excellent dye images are obtained when the solution prepared in this Example is added to a light sensitive gelatin silver halide emulsion, exposed and processed as in Example VIII of U.S. Pat. 3,062,653.

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EXAMPLE 2

The procedure of Example 1 is followed except that the mixture includes a total of one part by weight of the following couplers: Coupler 1 of U.S. Pat. 3,062,653; 1-{4-[α - (3 - pentadecylphenoxy)butyramido]phenyl}-3-ethoxy-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone; and 1-(6-chloro-2,4-dimethylphenyl)-3-[α - (m-pentadecylphenoxy)butyramido]-5-pyrazolone, and the temperature of the water are maintained at 50° C. It takes three minutes to dissolve the couplers. Using prior art procedures, it takes several minutes to dissolve the couplers by heating at 85 to 90° C.

EXAMPLE 3

A mixture is prepared consisting of 18.9 g. of Coupler 1 of U.S. Pat. 3,062,653; 4.1 g. of 1-(6-chloro-2,4-dimethylphenyl) - 2[α - (m - pentadecylphenoxy)butyramido]-5-pyrazolone; 23.0 ml. tri-o-cresyl phosphate and 92.0 ml. cyclohexanone, placed in a glass container and ultrasonically agitated as in Examples 1 at 45° C. until dissolved. Then, 2.7 g. of 1-{4-[α -(3-pentadecylphenoxy)butyramido]phenyl}-3-ethoxy-4-(1 - phenyl - 5 - tetrazolylthio)-5-pyrazolone are added to the mixture, which is ultrasonically agitated again as in Example 1 at 45° C. The time required is approximately five minutes. Using the same color former and solvents, at the same concentrations, approximately ten minutes are required to dissolve the couplers by heating as in prior art methods at 75° C.

Example 4 shows methods for preparing photographic color former dispersions as described in U.S. Pat. 2,801,171, and modifying that procedure in accordance with this invention.

EXAMPLE 4

Solutions of coupler in solvent prepared as in Example 1 are added, at the rate of about one part by volume to 2 parts by volume of a 10% aqueous gelatin solution containing a small amount of Alkanol B (sodium tri-isopropyl-naphthalene sulfonate) as dispersing agent. The dispersions are prepared by the following procedures:

(1) Passing the mixture through a colloid mill five times as described in U.S. Pat. 2,801,171.

(2) Ultrasonically agitating the gelatin-Alkanol B mixture by inserting the ultrasonic probe directly into the mixture, then adding the solution of coupler in solvent, and continuing agitation of the mixture with the ultrasonic probe.

(3) Placing the gelatin-Alkanol B mixture in a container with the solution of coupler in solvent, stirring and then inserting the ultrasonic probe and agitating.

Samples of dispersions made by methods 2 and 3 are taken every minute. Microscopic examination and photomicrographs show that after 5 minutes, dispersions made by methods 2 and 3 had the same particle size as those of method 1. Ultrasonic activation of from 5 to 10 minutes is usually sufficient to provide good dispersion.

The heat used in dissolving photographic color formers can result in lower speed, as shown in Examples 5 and 6.

EXAMPLE 5

A first photographic coupler 1-(2,4,6-trichlorophenyl)-3-[3-{ α -(2,4-di-tert-amylphenoxy) - acetamido} - benzamide]-5-pyrazolone and a second photographic coupler 1-{4-[α - (3-pentadecylphenoxy)butyramido]phenyl} - 3-ethoxy-4-(1-phenyl-5-tetrazolylthio) - 5 - pyrazolone are mixed with tricresyl phosphate coupler solvent, the coupler-to-solvent ratio being 1:1, and the couplers are dissolved by heating the mixture at a temperature of 107° C. The solution of couplers is then added to an aqueous gelatin solution containing a wetting agent (Alkanol B) and dispersed by passing the mixture

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through a colloid mill five times. The dispersion obtained is added to a green sensitized gelatin silver bromiodide emulsion containing approximately 2.2 mol percent iodide, which is then coated on a cellulose acetate film support at 200 milligrams silver, 225 milligrams gelatin, 60 milligrams of the first coupler and 10 milligrams of the second coupler and 10 milligrams of the first coupler and 10 milligrams of the second coupler posed in a spectrograph to tungsten illumination and developed in the following developer:

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

to form a negative silver image and a magenta dye image. The silver image and the residual silver halide are removed with ferricyanide bleach and hypo fixer, leaving a magenta dye image. The relative speed of the emulsion is 67.

EXAMPLE 6

The procedure of Example 5 is repeated except that the couplers are dissolved in the tricresyl phosphate by ultrasonically at 25 kc agitating a mixture of the couplers in tricresyl phosphate at 63° C. The relative speed of the emulsion, when exposed and processed as described in Example 1, is 100;

The heat used to dissolve the couplers in Example 1 caused coupler alteration as demonstrated by a slower speed than in Example 2, which utilized ultrasonics to dissolve the coupler at low temperatures;

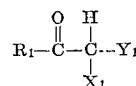
Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove, and as defined in the appended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

I claim:

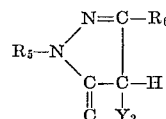
1. The method of dissolving a photographic color coupler selected from the group consisting of an open-chain ketomethylene coupler, a 5-pyrazolone coupler and a phenolic coupler which comprises adding the color coupler to a compound having a good solvent action for the color coupler, and subjecting the mixture of color coupler and said compound to ultrasonic vibrations, said ultrasonic vibrations being in a sufficiently low frequency range as not to alter or decompose significantly said color coupler, until the color coupler is dissolved in said compound.

2. The method of dissolving a photographic coupler in accordance with claim 1 wherein said photographic color coupler has one of the following general formulas:

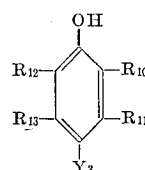
Formula I



Formula II



Formula III



wherein R_1 , X_1 , Y_1 , R_5 , R_6 , Y_2 , R_{10} , R_{11} , R_{12} , R_{13} and Y_3 each represents a group of the type employed in, respectively, open-chain ketomethylene couplers, 5-pyrazolone couplers and phenolic couplers.

3. The method of dissolving a photographic color coupler in accordance with claim 2 wherein the ultrasonic vibrations are in the frequency range of about 20 to 100 kc., and the temperature of the color coupler and said compound is maintained below about 100° C. during the dissolving operation.

4. The process of claim 3 wherein said compound is selected from the group consisting of:

- (a) low molecular weight materials which have high solvent action for the color former, have a boiling point above about 175° C. and are permeable to photographic developer oxidation products; and,
- (b) low boiling, oily, organic materials having high solvent action for the color former.

5. The process of claim 4 wherein the ratio, by weight, of color coupler to said compound (a) is from 1:0 to 1:3 and the ratio, by weight, of color coupler to said compound (b) is from 1:3 to 1:6.

6. The process of claim 4 wherein the ratio, by weight, of color coupler to said compound (a) is from 1/2:1 to 1:1 and the ratio, by weight, of color coupler to said compound (b) is from 1:3 to 1:6.

7. The method of adding a photographic color coupler to a light-sensitive dispersion of silver halide in hydrophilic colloid which comprises dissolving color coupler in a solvent in accordance with claim 1, and combining said solution of color coupler in said light-sensitive dispersion.

8. The method of adding a photographic color coupler to a light-sensitive dispersion of silver halide in hydrophilic colloid which comprises dissolving the color coupler in a solvent in accordance with claim 5, and combining said solution of color coupler in said light-sensitive dispersion.

9. The method of dispersing a photographic color coupler in a hydrophilic colloid which comprises dissolving said color coupler in accordance with claim 5, combining said solution of color coupler with a hydrophilic colloid, and ultrasonically agitating the resulting mixture to disperse the solution of color coupler in solvent in the hydrophilic colloid.

10. The method of dispersing a solution of photographic color coupler selected from the group consisting of an open-chain ketomethylene coupler, a 5-pyrazolone coupler and a phenolic coupler in solvent in a hydrophilic colloid which comprises combining said solution and hydrophilic colloid, and ultrasonically agitating the solution until the coupler solution is dispersed in the hydrophilic colloid, said ultrasonic agitation being in a sufficiently low frequency range as not to alter or decompose significantly said color coupler.

11. The method of dissolving a photographic development inhibitor-releasing coupler selected from the group consisting of an open-chain ketomethylene coupler, a 5-pyrazolone coupler and a phenolic coupler, which comprises adding the coupler to a compound having a good solvent action for the coupler and subjecting the mixture of coupler and said compound to ultrasonic vibrations, said ultrasonic vibrations being in a sufficiently low frequency range as not to alter or decompose significantly said color coupler, until the coupler is dissolved in said compound.

12. The method of dissolving a photographic development inhibitor-releasing coupler selected from the group consisting of an open-chain ketomethylene coupler, a 5-pyrazolone coupler and a phenolic coupler, which comprises adding the coupler to a compound having good solvent action for the coupler and subjecting the mixture of coupler and said compound to ultrasonic vibrations until the coupler is dissolved in said compound, said ultrasonic vibrations being in the frequency range of

from about 20 to 100 kc. and the temperature of the coupler and said compound being maintained below about 100° C. during the dissolving operation.

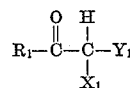
13. The process of dissolving a development inhibitor-releasing coupler as defined in claim 12 wherein said compound is selected from the group consisting of:

- (a) low molecular weight materials which have high solvent action for the coupler, having a boiling point above about 175° C. and are permeable to photographic oxidation products; and,
- (b) low boiling, oily, organic materials having high solvent action for the coupler.

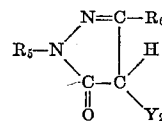
14. The method of dissolving a photographic development inhibitor-releasing coupler having a monothio group in its coupling position which, upon reaction with oxidized primary aromatic amino color-developing agent, forms a diffusible mercaptan which inhibits development, which comprises: adding the coupler to a compound having good solvent action for the coupler, and subjecting the mixture of coupler and said compound to ultrasonic vibrations, said ultrasonic vibrations being in a sufficiently low frequency range as not to alter or decompose significantly said color coupler, until the coupler is dissolved in said compound.

15. The method of dissolving a photographic development inhibitor-releasing coupler having one of the following structural formulas:

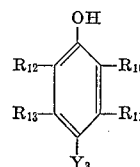
Formula I



Formula II



Formula III



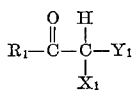
wherein R_1 , X_1 , R_5 , R_6 , R_{10} , R_{11} , R_{12} and R_{13} each represents a group of the type employed in, respectively, open-chain ketomethylene couplers, 5-pyrazolone couplers and phenolic couplers; and Y_1 , Y_2 and Y_3 each represents a colorless monothio group to complete said development inhibitor-releasing coupler, which comprises: adding said coupler to a compound having good solvent action for the coupler, and subjecting the mixture of coupler and said compound to ultrasonic vibrations, said ultrasonic vibrations being in a sufficiently low frequency range as not to alter or decompose significantly said color coupler.

16. The method of dissolving a photographic develop-

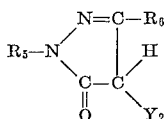
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ment inhibitor-releasing coupler having one of the following structure formulas:

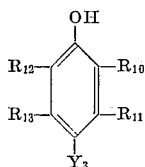
Formula I



Formula II



Formula III



wherein R_1 and R_5 each represents a member selected from the group consisting of alkyl, aryl and a heterocyclic group containing at least one hetero atom selected from oxygen, sulfur and nitrogen; X_1 represents a member selected from the group consisting of cyano and carbamyl; R_6 represents a member selected from the group consisting of alkyl, carbamyl, amino, amido, benzamido and alkamido; R_{10} and R_{11} each represents a member selected from the group consisting of hydrogen, alkyl, aryl, a heterocyclic group containing at least one hetero atom selected from oxygen, sulfur and nitrogen, amino, carbonamido sulfonamido, sulfamyl, carbamyl, halogen and alkoxy; R_{12} and R_{13} , when taken together, represent the atoms required to complete a benzo group and, when taken separately, each represents a value selected from those given for R_{10} and R_{11} ; and said Y_1 , Y_2 and Y_3 each represents a monothio group selected from an ortho-amino-substituted arylmonothio group, an orthonitro-substituted arylmonothio group and a heterocyclic radical containing at least one hetero atom selected from oxygen, sulfur and nitrogen, to complete said coupler, which process comprises: adding the coupler to a compound having good solvent action for the coupler, and subjecting the mixture of coupler and said compound to ultrasonic vibrations, said ultrasonic vibrations being in a sufficiently low frequency range as not to alter or decompose significantly said color coupler, until the coupler is dissolved in said compound.

17. The method as defined in claim 16 wherein the ultrasonic vibrations are in the frequency range of about 20 to 100 kc., and the temperature of the coupler, and said compound is maintained below about 100° C. during the dissolving operation.

18. The method of dissolving the photographic couplers 1 - (2,4,6 - trichlorophenyl)-3-[3-{ α -(2,4-di-tert-amyphenoxy) - acetamido} - benzamido]-5-pyrazolone and 1 - {4-[α -(3-pentadecylphenoxy)butyramido]phenyl}-3 - ethoxy - 4 - (1-phenyl-5-tetrazolythio)-5-pyrazolone which comprises mixing said couplers with tricresyl phosphate coupler solvent, the coupler-to-solvent ratio being 1:1, and ultrasonically agitating the mixture of couplers and coupler solvent at 25 kc. at about 63° C. until the couplers are dissolved.

19. The method of incorporating a photographic development inhibitor-releasing coupler selected from the group consisting of an open-chain ketomethylene coupler, a 5-pyrazolone coupler and a phenolic coupler in a photographic silver halide emulsion which comprises:

- mixing said coupler with a compound having good solvent action for the coupler;
- subjecting the mixture of coupler and said compound to ultrasonic vibrations, said ultrasonic vibrations being in a sufficiently low frequency range as

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not to alter or decompose significantly said color coupler, until the coupler is dissolved in said compound; and

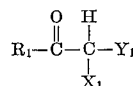
- dispersing the solution of coupler in said compound in a photographic silver halide emulsion.

20. The method of incorporating a photographic development inhibitor-releasing coupler in a photographic silver halide emulsion as defined in claim 19 wherein said ultrasonic vibrations are in the frequency range of from about 20 to 100 kc. and the temperature of the coupler and said compound are maintained below about 100° C. during the dissolving operation.

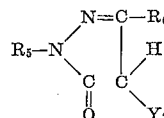
21. The method of incorporating a photographic development inhibitor-releasing coupler in a photographic silver halide emulsion as defined in claim 20 wherein said development inhibitor-releasing coupler has a monothio group in its coupling position which, upon reaction with oxidized primary aromatic amino color developing agent, forms a diffusible mercaptan which inhibits development.

22. The method of incorporating a photographic development inhibitor-releasing coupler in a photographic silver halide emulsion as defined in claim 21 wherein said development inhibitor-releasing coupler has one of the following structural formulas:

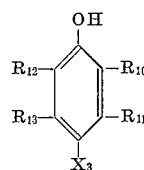
Formula I



Formula II



Formula III



wherein R_1 and R_5 each represents a member selected from the group consisting of alkyl, aryl, and a heterocyclic group containing at least one hetero atom selected from oxygen, sulfur and nitrogen; X_1 represents a member selected from the group consisting of cyano and carbamyl; R_6 represents a member selected from the group consisting of alkyl, carbamyl, amino, amido, benzamido, and alkamido; R_{10} and R_{11} each represents a member selected from the group consisting of hydrogen, alkyl, aryl, a heterocyclic group containing at least one hetero atom selected from oxygen, sulfur and nitrogen, amino, carbonamido sulfonamido, sulfamyl, carbamyl, halogen and alkoxy; R_{12} and R_{13} when taken together, represent the atoms required to complete a benzo group, and when taken separately, each represents a value selected from those given for R_{10} and R_{11} ; and, said Y_1 , Y_2 and Y_3 each represents a monothio group selected from an ortho-amino-substituted arylmonothio group, an orthonitro-substituted arylmonothio group, and, a heterocyclic radical containing at least one hetero atom selected from oxygen, sulfur and nitrogen.

23. The method of incorporating the development inhibitor-releasing coupler 1 - {4 - [α -(3-pentadecylphenoxy)-butyramido]phenyl} - 3 - ethoxy-4-(1-phenyl-5-tetrazolythio)-5-pyrazolone in a photographic silver halide emulsion which comprises mixing said coupler in tricresyl phosphate, ultrasonically agitating a mixture of said coupler in tricresyl phosphate at about 25 kc. and at a temperature of about 63° C. until the coupler is dissolved in

the tricresyl phosphate, and dispersing the solution of coupler in tricresyl phosphate into a gelatin photographic silver halide emulsion.

24. The method of dissolving the photographic color coupler 1 - (4,6 - dichloro - 2 - methoxyphenyl)3- α -pentadecylphenoxy) - butyramido] - 5-pyrazolone, which comprises adding one part of said color coupler to about one part tri-o-cresyl phosphate and about four parts cyclohexanol, subjecting the resulting mixture to ultrasonic vibration in the frequency range of about 20 to 25 kc. for about 5 to 10 minutes while maintaining the temperature of the mixture at about 45 to 60° C.

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J. TRAVIS BROWN, Primary Examiner