United States Patent

[11] **3,632,373**

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[54] METHOD FOR PREPARING SILVER HALIDE LAYERS HAVING SUBSTANTIALLY UNIFORM IMAGE CONTRAST

7 Claims, No Drawings

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96/22, 96/23, 96/74, 96/100
[51] **Int. Cl.** **G03c 1/00,**
G03c 1/76
[50] **Field of Search** 96/100, 9;
117/34

[56] **References Cited**

UNITED STATES PATENTS

2,761,791	9/1956	Russell	117/34
2,912,343	11/1959	Collins et al.	117/34
3,148,062	9/1964	Whitmore et al.	96/9

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ABSTRACT: Photographic elements are provided which comprise a support having thereon a layer containing silver halide and a photographic image forming coupler, the ratio of coupler to the silver halide varying from area-to-area in the layer, the layer also including a development inhibitor-releasing coupler which is maintained at a constant ratio to the image-forming coupler in all areas of the layer. The development inhibitor-releasing coupler functions to reduce variations in dye image contrast caused by the varying ratio of photographic image-forming coupler to silver halide in the layer. Methods for preparing photographic elements are also provided.

METHOD FOR PREPARING SILVER HALIDE LAYERS HAVING SUBSTANTIALLY UNIFORM IMAGE CONTRAST

This invention relates to novel photographic elements and novel methods for their preparation.

It is well known to provide photographic elements which comprise a support having coated thereon a photographic silver halide emulsion layer which contains color former. When certain methods of coating such emulsions are employed, there tend to be differences in the ratio of silver halide to color coupler in various areas of the photographic element. Such differences in the ratio of silver halide to image-forming coupler results in undesirable variations in the contrast of the photographic element. Variations in contrast can appear within a narrow area of the element, causing undesirable changes in the color balance in a single print prepared therefrom. The variations in ratio of coupler to silver halide can also appear slowly over the length of an emulsion layer. In such cases, differences in contrast are apparent, for example, when different samples are exposed and developed under standard development conditions and compared. Differences in contrast are also apparent when such films are utilized in movies. Such differences in contrast are highly undesirable since they result in photographic materials which are not reproducible and have different characteristics upon development. It therefore appears highly desirable to provide photographic elements and methods for their preparation which are characterized by essentially uniform contrast throughout.

One object of this invention is to provide novel photographic elements and processes.

Another object of this invention is to provide photographic silver halide emulsion layers which have essentially uniform contrast throughout.

A further object of this invention is to provide a novel method for preparing photographic silver halide emulsions containing color former, which emulsions provide substantially uniform contrast.

Still other objects of this invention will be apparent from the disclosure herein and the appended claims.

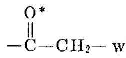
In accordance with one embodiment of this invention, a photographic element is provided comprising a support having coated thereon a photographic silver halide emulsion layer containing photographic image-forming coupler, the ratio of silver halide to photographic image-forming coupler varying in different areas of said layer, said emulsion layer containing a development inhibitor-releasing coupler, the ratio of development inhibitor-releasing coupler to photographic image-forming coupler being essentially constant throughout the layer. It has been found that such photographic layers exhibit substantially uniform contrast throughout. Similar photographic elements, which do not contain development inhibitor-releasing coupler, exhibit objectionably high variations in contrast from area to area in the layer.

In accordance with another embodiment of this invention, in the method of preparing light-sensitive photographic coatings wherein a photographic image-forming coupler and a photographic silver halide emulsion are separately introduced into a mixing zone, admixed and coated onto a support, and the ratio of photographic image-forming coupler to silver halide varies during the coating operation, the improvement is provided which comprises introducing into said mixing zone a development inhibitor-releasing coupler and maintaining an essentially constant ratio of development inhibitor-releasing coupler to photographic image-forming coupler throughout the coating operation. Such processes result in photographic layers which exhibit substantially uniform contrast throughout.

The process of this invention is conveniently carried out by separately metering a photographic emulsion (which can be separately sensitized) and the combination of photographic image-forming coupler and development inhibitor-releasing coupler (which can be incorporated in a hydrophilic colloid that can also contain other emulsion addenda); mixing the emulsion and coupler combination; and coating the mixture on a support, preferably substantially immediately after mixing as described by Collins et al., in U.S. Pat. No. 2,912,343. A plurality of such emulsions can have the coupler combination incorporated therein and the resulting emulsion can be coated simultaneously, as described by Russell in U.S. Pat. No. 2,761,791, issued Sept. 4, 1956, which disclosure is incorporated herein by reference.

The present invention can be practiced with any photographic emulsion-coating process which tends to result in photographic silver halide emulsion layers having varying ratios of silver (or silver halide) to image-forming coupler in various areas of the element. The invention is particularly useful in coating processes of the type wherein a silver halide emulsion (which silver halide emulsion can be spectrally sensitized) has photographic image-forming coupler admixed therewith just before the emulsion is coated onto a support. Such processes are described in detail by Collins et al., in U.S. Pat. No. 2,912,343, issued Nov. 10, 1959, the disclosure of which is incorporated herein by reference. When such coating processes are utilized, there is a tendency for the emulsion layer resulting therefrom to contain variations in the ratio of silver halide to photographic image-forming coupler. Such variations in the ratio of silver to image-forming coupler occur despite elaborate and sophisticated controls on the flow rates of the silver halide emulsion and the photographic image-forming coupler.

The term "photographic image-forming 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 image-forming couplers, as well as the development inhibitor-releasing couplers which are 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.,

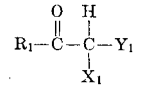


$$-\overset{\overset{\displaystyle O^*}{\|}}{C}-CH_2-$$

wherein* denotes the coupling position).

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

Formula I

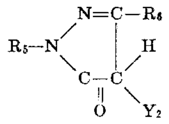


$$R_1-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle X_1}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-Y_1$$

wherein R_1, X_1 and V_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 six 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 five to six 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 for the image-forming and development inhibitor-releasing couplers utilized herein.

The image-forming and the development inhibitor-releasing couplers utilized in this invention can feature a 5-pyrazolone coupler radical having the following general formula:

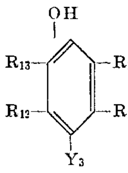
Formula II



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 for the image forming and the development inhibitor-releasing couplers utilized herein.

The photographic image-forming and development inhibitor-releasing couplers employed in the practice of this invention can utilize any suitable phenolic (including alphanaphtholic) coupler radicals, including those described in the structural formula below:

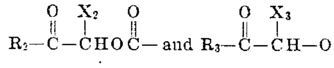
Formula III



22. 3-(4-ter-amyl-3'-phenoxybenzoylamino)phenol

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 for the image-forming and development inhibitor-releasing couplers utilized herein.

The image-forming couplers which can be utilized in the practice of this invention include the nondiffusible, open-chain, 5-pyrazolone and phenolic couplers referred to above, such as those couplers represented by Formula 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 thiocyano group; an acyloxy group, for example, an alkolyloxy group which can be substituted, or an aryloxy group which can be substituted, or a heterocycloyloxy group which can be substituted; a cyclooxy group including an aryloxy group, e.g., phenoxy, naphthoxy, or a heterocyclooxy group, such as a pyridinyloxy group, a tetrahydropyranyloxy group, a tetrahydroquinolyloxy 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:



$$R_2-\overset{O}{\overset{\|}{C}}-\overset{X_2}{\overset{|}{C}}HO\overset{O}{\overset{\|}{C}}- \text{ and } R_3-\overset{O}{\overset{\|}{C}}-\overset{X_3}{\overset{|}{C}}H-O-$$

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. It will be understood that the "image-forming coupler" does not release a development inhibitor.

The useful image-forming couplers include both the 4-equivalent and 2-equivalent nondiffusing couplers. Typical useful 4-equivalent yellow dye-forming couplers which can be utilized in this invention include the following:

1. N-amyl-p-benzoylacetaminobenzenesulfonate
2. N-(4-anisolyacetaminobenzenesulfonyl)-N-benzyl-m-toluidine
3. N-(4-benzoylacetaminobenzenesulfonyl)-N-benzylaniline
4. ω-(p-benzoylbenzoyl)acetaniline
5. ω-benzoyl-p-sec-amylacetaniline
6. N,N'-di(ω-benzoylacetyl)-p-phenylenediamine
7. α-{3[α-(2,4-di-tert-amylphenoxy)butyramido]-benzoyl}-2-methoxyacetaniline
8. 4,4'-di-(acetoacetamino)-3,3'-dimethyldiphenyl
9. p,p'-di-(acetoacetamino)diphenylmethane
10. nonyl-p-benzoylacetaminobenzenesulfonate
11. N-phenyl-N'-(p-acetoacetaminophenyl)urea
12. n-propyl-p-benzoylacetaminobenzenesulfonate acetoacetpiperidide
13. N-(ω-benzoylacetyl)-1,2,3,5-tetrahydroquinoline
14. N-(ω-benzoylacetyl)morpholine

The 2-equivalent yellow dye-forming couplers can be derived from corresponding parent 4-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 al., atom, the chlorine atom, an acyloxy group, a cyclooxy group and a thiocyano group. Typically useful 2-equivalent couplers include the alpha-fluoro couplers of U.S. Pat. No. 3,277,155, the alpha-chloro couplers of U.S. Pat. No. 2,778,658, the alpha-thiocyano couplers of U.S. Pat. No. 3,253,924, the alpha-acyloxy couplers of Loria U.S. patent application Ser. No. 477,353, filed July 26, 1965, the alpha-cyclooxy couplers of Loria U.S. patent application Ser. No. 469,887, filed July 6, 1965, and the alpha-alkoxy couplers of the type shown in Whitmore et al. U.S. Pat. No. 3,227,550.

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

1. 4-(α-2'-methoxybenzoyl-α-chloroacetamido)-3''-(4'''-tert-amylphenoxy)benzanilide
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-tert-amylphenoxy)butyramido]-2-chloroacetanilide
5. α-acetoxy-α-{3-[γ-(2,4-di-tert-amylphenoxy)butyramido]benzoyl}2-methoxyacetanilide
6. α-benzoyl-α-[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-methoxy-acetanilide
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]phenylcarbamyl methoxy]-diphenylsulfone
16. α-benzoyl-α-thiocyanoacetanilide

Specific representative 4-equivalent magenta dye-forming couplers include 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-valerylamino-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-phenylcarbamylamino-5-pyrazolone
24. 1-phenyl-3-palmitylamino-5-pyrazolone
25. 1-phenyl-3-benzenesulfonylamino-5-pyrazolone
26. 1-(p-phenoxyphenyl)-3-(p-tert-amyloxybenzoyl)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)benzamidoih-5-pyrazolone
30. 1-(2′, ,6′-trichlorophenyl)-3-[3″-(2‴, 4‴**-di-tert-amylphenoxyacetamido)benzamido-**5-pyrazolone
31. 1-(2′, ,6′-trichlorophenyl)-3-[β-b **2‴, ″-di-tert-amylphenoxy)-propionamido**]-5-pyrazolone
32. 1-(2′, **-dichloro)**-3-[3″-(4‴-tert-amylphenoxy)benzamido]-5-pyrazolone
33. 1-(2′, , **-tribromophenyl)**-3-[3″-(4‴-tert-amylphenoxy)-benzamido]-5-pyrazolone
34. 1-(2′, **-dichlorophenyl)**-3-[3″-(2‴, 4″-di-tert-amylphenoxyacetamido)benzamidoih-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 nonchromophoric coupling-off group. Examples of coupling-off groups which can be used in 2-equivalent magenta-forming 5-pyrazolone couplers are the thiocyano group illustrated by the couplers in Loria U.S. Pat. No. 3,252,924 and the acyloxy group containing 2-equivalent magenta-forming couplers of Loria U.S. Pat. No. 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. No. 3,227,550, the chlorine atom, the fluorine atom, and the sulfo group.

Typical 2equivalent 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-amylphenoxyacetaido)benzamido]-4-thiocyano-5-pyrazolone
5. 1-(p-tert-butylphenoxyphenyl)-3-α1-(p-tert-butylphenoxyphenyl)-3-α-(p-tert-butyl-phenoxy)-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-dimethoxylbenzamido)phenyl]-3-ethoxy-4-(3-octadecylcarbamylphenylthio)-5-pyrazolone

Typical 4-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-valerylamino)-1-naphthol
3. 5-caproylamino-1-naphthol
4. 2-chloro-5-(N-n-valeryl-N-p-isopropylbenzylamino)-1naphthol
5. 2-chloro-5-palmitylamino-1-naphthol
6. 5-diphenylethersulfonamido-
7. 1-hyroxy-2-(N-isoamyl-N-phenyl)naphthamide
8. 8-hydroxy-1-α-naphthoyl-1,2,3,4-tetrahydroquinoline
9. 1-naphthol-5-octyl-cyclomexylamide
10. 5-phenoxyacetamino-1-naphthol
11. Monochlor-5-(N-γ-phenylpropyl-N-p-sec-amylbenzoylamino)-1-nanphthol
12. 2-benzoylamino-3,5-dimethyphenol
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-[αα(-4′-tert.-butylphenoxy)propionylamino**4**]phenol
18. 2-[N-methyl-N-(4′-tert-amyl-3-phenoxybenzolyamino)]phenol
19. 2-**60** -(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-[αα-(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-(4bromodiphenyl-4-sulfonamido)1-napthol

Any of the 2-equivalent cyan-forming phenolic couplers can be used in the practice of this invention. The 2-equivalent phenolic couplers can be derived from the corresponding 4-equivalent phenolic couplers by substituting a nonchromophoric coupling-off group on the carbon in the 4-position of the phenolic or naphthoic ring. Included among the coupling-off groups are the acyloxy group illustrated by the 4-acyloxyphenols and 4-acyloxynaphthols of Loria U.S. Pat. No. 3,311,476, issued Mar. 28, 1967, the cyclooxy group illustrated by the 4-cyclooxy naphthols of Loria U.S. patent application Ser. No. 483,807, filed Aug. 30, 1965, the thiocyano group illustrated by the 4-thiophenols and 4-thionaphthols of Loria U.S. Pat. No. 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 Ser. No. 504,994, the chlorine atom as illustrated in the 4-chlorophenols of Weissberger U.S. Pat. No. 2,423,730, the alkoxy group as illustrated by the 4-alkoxynaphthols (and naphthols) of Whitmore et al. U.S. Pat. No. 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-acetxy-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-{-{-4[β-(2,4-di-tert-amylphenoxy)acetamido]phenyl}ethyl}-2-naphthamide
6. 1-hydroxy-4-(4-nitrophenoxy)-N-[αα-2,4-di-tert-amylphenoxy)butyl]-2-naphthamide
7. 1-hydroxy-4-(4-chlorophenoxy-2′-tetradecyloxy-2-naphthanilide

The photographic image-forming coupler is used at a sufficient concentration to give a dye image of suitable density. The concentration employed will depend on the characteristics of the dye formed by the coupler, and on the nature of the photographic emulsion in which it is incorporated. The photographic image-forming coupler preferably is nondiffusible, and colorless. It can be a coupler of the type which forms a diffusible dye image (which can be transferred to a suitable receiving sheet) or a type which forms nondiffusible dye images. The invention is useful with all photographic incorporated image-forming couplers which form dye images by imagewise reaction with oxidized primary aromatic amine color-developing agent. "Incorporated" refers to silver halide emulsion layers containing photographic image-forming couplers at the time of exposure.

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 alpha-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 development 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 one to four heteronitrogen atoms) including heterocyclic radicals, such as, tetrazolyls, triazinyls, 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 alkylcarbamyl amino, etc., typical monothio groups representing the above include 2-aminophenyl, 2-nitrophenyl and a heterocyclic group (e.g., 2-benzo thiazolylthio, 1-phenyl-5-tetrazolythio, 1-(4-carbonmethoxyphenyl)-5-tetrazolythio, 5-phenyl-1,3,4-oxadiazolyl-2-thio, 2-phenyl-5-(1,3,4)-oxadiazolythio, 2-benzoxazolythio, etc.);
2. a 2-aminoarylazoxy group (e.g., 2-amino-4-methylphenylazoxy, 2-aminophenylazoxy, 2-amino-4-chlorophenylazoxy, etc.);
3. a 2-amidoarylazoxy group (e.g., 2-acetamidophenylazoxy, 2-acetamido-4-methylphenylazoxy, 2-acetamido-4-chlorophenylazoxy, 2-palmitamidophenylazoxy, 4-methoxy-2-palmitamidophenylazoxy, 4-chloro-2-palmitamidopehnylazoxy, etc.);
4. a 2-aryltriazolyl 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-4-sulfoethyl-2-benzotriazolyl, 2-naphthotriazolyl, 4-methyl-2-naphthotriazolyl, 5-chloro-2-naphthotriazoyl 5-hydroxy-2-naphthotriazolyl, 5-nitro-2-naphthotriazolyl 5-sulfoethyl-2-naphthotriazolyl, 4-amino-2-naphthotriazolyl, benzo[1,2-d:4,5-d′]-bristriazolyl, 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-2nitrophenylthio-2-methoxyacetanilide
4. α-{3γ-(2,4-di-tert-amylphenoxy)butyramido]-benzoyl}-α-(2-benzoxazolylthio)-2-methoxyacetanilide
5. α-Benzoyl-α-[1-(3-phenyl)-5-tetrazolythio]stearamido 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-chloro5-[-pivalyl-.**LOROb** 5 α(3-pentadecyl-4-sulfophenoxoy)-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-di-tert-amylphenoxy)butyramido]anilino}-4-(1-phenyl-5-tetrazolythio)-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-tetrazolythio)-
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-t-amylphenoxy)acetamido 3- α-(2,4-di-t-amylphenoxy)acetamido} benzamido]-5-pyrazolone
31. 4-(5-Methoxy-2-benzotriazolyl)-3-pentadecyl-1phenyl-5-pyrazolone
32. 4-(4-Carboxy-2-benzotriazolyl)-1-(2,4,6-trichlorophenyl)-3-pentacecyl-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-tetrazolythio)-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-tetrazolythio)-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)butramido]-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-t-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-benzotriazoly)phenol

Couplers **1** through **5**, **11** through **27**, **33** through **40** are described in Barr, U.S. Pat. No. 3,227,554. Couplers **6**, **7**, **28** and **41** are prepared by methods similar to those disclosed in U.S. Pat. No. 3,148,06. Couplers **8** through **10**, **29** through **32** and **42** through **45** are described by Sawdey, U.S. Pat. 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 five to six atoms and at least one hetero atom selected from oxygen, sulfur and nitrogen, such as a hetero ring, containing from one to four 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.

The development inhibitor-releasing coupler is utilized at a concentration sufficient to effectively provide substantially uniform contrast in the emulsion layer. The most useful concentration will depend upon how much variation there is in the ratio of silver halide to photographic image-forming coupler, as well as on the nature of the particular development inhibitor-releasing coupler selected. As a general guide, the most useful results are achieved using a ratio of from 2 to 25 parts by weight development inhibitor-releasing coupler per 100 parts by weight photographic image-forming coupler.

The photographic image-forming coupler and the development inhibitor-releasing coupler utilized in the photographic emulsions and processes of this invention preferably are nondiffusible. The term "nondiffusible" as used herein has the meaning commonly applied to that term in color photography, and denotes materials which for all practical purposes do not migrate or wander through photographic hydrophilic colloid layers, such as gelatin, particularly during processing in aqueous alkaline solutions. The term "diffusible" has the converse meaning.

Preferably, the image-forming and the development inhibitor-releasing couplers utilized herein are ballasted. That is, the coupler contains an organic radical of such molecular size and configuration as to render the coupler nondiffusible in the element and when the element is processed in alkaline-developing solutions. The organic ballasting radical is chosen so that it does not exercise any detrimental effects on the photographic material.

The image-forming and development inhibitor-releasing couplers utilized in this invention can be incorporated into the silver halide emulsion in any convenient manner. For example, the coupler can contain a solubilizing group, such as a sulfonic acid group or a carboxylic acid group, such the couplers soluble in alkaline solution. This enables incorporation of the coupler into the silver halide emulsion by preparing an aqueous alkaline solution of coupler and mixing that solution directly into the photographic silver halide emulsion. Preferably, the couplers are incorporated into the emulsion by dissolving them in a suitable coupler solvent, for example, one of the color coupler solvents and utilizing one of the processes described in U.S. Pat. Nos. 2,322,027 and 2,801,171.

In addition to image-forming couplers and development inhibitor-releasing couplers, the photographic emulsions of this invention can contain a competing coupler, which can be introduced prior to coating the emulsion or during development thereof. The competing coupler can be one which forms a leuco dye or a diffusible dye. Typical useful competing couplers are described by Loria, Williams and Barr in British Pat. No. 1.038,331; Wellar and Groet in U.S. Pat. No. 2,689,793, and U.S. Pat. No. 2,998,314.

Emulsion layers can be produced in accordance with this invention which contain colored couplers, e.g., those which contain an azo group in the coupling position. Such couplers are well known in the photographic art. Representative useful azo substituted couplers are described in the following U.S. Pat. Nos: 2,428,054, 2,449,966, 2,453,551 (open-chain ketomethylene couplers having an arylazo group in the coupling position; and couplers in which the arylazo group is replaced with an alkylazo or a heterocycloazo group in the coupling position are also useful); U.S. Pat. No. 2,455,169 (phenolic couplers having an arylazo group in the coupling position; couplers in which a heterocycloazo group replaces the arylazo group are also useful); U.S. Pat. Nos. 2,455,170, 2,521,908, 2,569,418 (5-pyrazolones having an arylazo or heterocycloazo group in the coupling position); U.S. Pat. Nos. 2,706,684, 2,725,292; 2,983,608; 3,005,712; 3,034,892; and, in British Pat. Nos. 800,262 and 1,043,044. Specific useful photographic couplers can be selected from the disclosure of the foregoing references which are incorporated herein by reference. Such couplers can be utilized in the manner known in the art to correct or mask unwanted absorption of the dye formed by the image-forming coupler.

As used herein, "blue radiation" refers to radiation of from about 400 to 500 nm.; "green" refers to radiation of from about 500 to 600 nm.; and, "red" refers to radiation of from about 600 to 700 nm. Preferably, the cyan dyes formed by the colorless coupler has its major absorption between about 600 and 680 nm.; the magenta dye between about 500 and 580 nm.; and the yellow dye between about 400 and 480 nm.

In preparing silver halide emulsions or dispersions used in the photographic elements of the invention a wide variety of organic hydrophilic-dispersing agents or substrates for the silver halide can be utilized. Gelatin is preferred although other colloidal materials such as colloidal albumin, cellulose derivatives or synthetic resins such as polyvinyl alcohol can also be utilized.

In preparing the photographic elements of the invention, silver halide emulsions can be coated on a wide variety of photographic supports. Typical supports include cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyterephthalate film, polyethylene film, polypropylene film, polyethylene-coated paper, paper, glass and others.

The photographic silver halide emulsions and other layers on the present photographic elements can contain the addenda generally utilized in such elements including optical sensitizers, speed-increasing materials, antifoggants, coating aids, gelatin hardeners, plasticizers, ultraviolet absorbers and the like.

The photographic elements of the invention are developed with photographic alkaline color developing solutions containing aromatic primary amino color-developing agents. Such developing agents are well known in the art and typically are p-phenylenediamines. Suitable color-developing agents include 3-acetamido-4-amino-N,N-diethylaniline, p-amino-N-ethyl-N-βhydroxyethylaniline sulfate, p-aminoethyl-β-hydroxyaniline, N,N-diethyl-p-phenylenediamine, 2-amino-5-diethylaminotoluene, N-ethyl-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline, 4-amino-N-ethyl-3-methyl-N-(β-sulfoethyl)aniline and the like. Reference is also made to Bent et al., JACS 73, 3100–3125 (1951) for additional typical suitable color developing agents.

The following examples are included for a further understanding of this invention. The layer arrangement given below is used in the examples:

Gelatin overcoat
Blue sensitive silver bromiodide gelatin emulsion containing coupler A+coupler B
Yellow filter layer
Green sensitive silver bromoiodide gelatin emulsion+coupler C+coupler D+coupler E
Gelatin interlayer
Red sensitive silver bromoiodide gelatin emulsion+coupler F+coupler G+coupler H
Cellulose ester film support

Two or more of the layers of the photographic element are coated simultaneously as described in Russell U.S. Pat. No. 2,761,791. The couplers are dissolved in organic solvents and dispersed in a gelatin solution as described in Fierke et al. U.S. Pat. No. 2,801,171.

Coupler A—A yellow dye-forming coupler of the type described in example XIV of McCrossen et al. U.S. Pat. No. 2,875,057

Coupler B—A yellow dye-forming DIR-coupler of the type described in Weissberger et al. U.S. Pat. No. 3,265,506 (Compound 13)

Coupler C—A magenta dye-forming coupler of the type described in Loria et al. U.S. Pat. No. 2,600,788 (Compound 7)

Coupler D—A blue-absorbing magenta dye-forming coupler of the type described in Beavers U.S. Pat. No. 2,983,608 (Coupler I)

Coupler E—A magenta dye-forming DIR-coupler of the type described in Barr et al. U.S. Pat. No. 3,227,554 (e.g., Compound XXXVII)

Coupler F—A cyan dye-forming coupler of the type described in Weissberger et al. U.S. Pat. No. 2,474,293 (Compound 1)

Coupler G—A blue-green-absorbing cyan dye-forming coupler of the type described in Gledhill et al. U.S. Pat. No. 3,034,892 (Compound II)

Coupler H—A cyan dye-forming DIR-coupler of the type described in Barr et al. U.S. Pat. No. 3,227,554 (example 14, Compound XI)

EXAMPLE 1

A photographic element of the type described above is prepared and coated in which the red sensitive emulsion and the cyan dye-forming coupler dispersion are mixed just prior to coating as described in Collins et al. U.S. Pat. No. 2,912,343. A series of coatings are prepared in which (1) the silver coverage/coupler coverage ratio is varied by varying the coupler dispersion flow rate and (2) the nonDIR-coupler/DIR-coupler ratio is varied by coating at a constant flow rate separate coupler dispersion having the appropriate ratios. Samples of each coating are exposed on an intensity scale sensitometer and processed through the Eastman Color Print Process, described in "Production of Motion Picture Film and Motion Pictures in Color Using Eastman Color Films," III-15 et seq., published by the Eastman Kodak Company, 1963, at 75° F. and a development time of 8 minutes, with the following results:

Coating Number	Ag, mg./ft.^{2}	Coupler/silver ratio, percent	Coupler			Percent variation in cyan contrast
			F, mg./ft.^{2}	G, mg./ft.^{2}	H, mg./ft.^{2}	
1	160	Control	55	14.8	12.5	Control
2	160	−10	49.5	13.3	11.2	−1.8
3	160	−20	44	11.9	10	−3.5
4	160	+10	60.5	16.2	13.7	+3.5
5	160	+20	66	17.8	15	+1.7
6	160	Control	55	14.8	12.5	Control
7	160	+20	66	17.8	12.5	+8.3
8	160	+40	77	21.7	12.5	+16
9	160	−20	44	11.8	12.5	−12

It can be seen from the above results that when the coverage of the DIR-coupler varies with the image coupler (No. 1–5), substantially uniform contrast is obtained in the layer, although the ratio of silver to coupler varies widely in the same layers.

EXAMPLE 2

A photographic element of the type described above is prepared and coated in which the green-sensitive emulsion and the magenta dye-forming coupler dispersion are mixed just prior to coating as described in Collins et al. U.S. Pat. No.

2,912,343. A series of coatings are prepared in which the silver coverage/coupler coverage ratio is varied by varying the coupler dispersion flow rate and the nonDIR-coupler/DIR-coupler ratio is varied by coating at a constant flow rate separate coupler dispersion having the appropriate ratios. Samples of each coating are exposed on an intensity scale sensitometer and processed through the Eastman Color Print Process, at 75° F. and a development time of 8 minutes with the following results.

Coating Number	Ag, mg./ft.^{2}	Coupler/ silver ratio, percent	Coupler C, mg./ft.^{2}	Coupler D, mg./ft.^{2}	Coupler E, mg./ft.^{2}	Percent variation in magenta contrast
4	200	Control	77	16.5	8.5	Control
5	200	−10	69	14.8	7.6	−2.1
6	200	−20	61.5	13.2	6.8	−4.3
7	200	+10	85	18.2	9.35	+2.1
8	200	+20	92.5	19.8	10.2	+2.1
1	200	Control	77	16.5	8.5	Control
2	200	−10	69	14.8	8.5	−9.0
3	200	+10	7	18.2	8.5	+5.9

Coatings 4–8 demonstrate the good uniformity in contrast obtained in accordance with this invention.

EXAMPLE 3

A photographic element of the type described above is prepared and coated in which the blue-sensitive emulsion and the yellow dye-forming coupler dispersion are mixed just prior to coating as described in Collins et al. U.S. Pat. No. 2,912,343. A series of coatings is prepared in which the silver coverage/coupler coverage ratio is varied by varying the coupler dispersion flow rate and the nonDIR-coupler/DIR-coupler ratio is varied by coating at a constant flow rate separate coupler dispersion having the appropriate ratios. Samples of each coating were exposed on an intensity scale sensitometer and processed through the Eastman Color Print Process, at 75° F. and a development time of 8 minutes with the following results.

Coating Number	Ag, mg./ft.^{2}	Coupler/ silver ratio, percent	Coupler A, mg./ft.^{2}	Coupler B, mg./ft.^{2}	Percent variation in yellow contrast
4	80	Control	90	2.0	Control
5	80	−10	81	1.8	−1.9
6	80	−20	72	1.6	−1.9
1	80	Control	90	2.0	Control
2	80	−10	81	2.5	−4.5

High-contrast uniformity is apparent in coatings 4, 5 and 6 which maintain constant ratios of image coupler to DIR-coupler.

When colored couplers D and G are omitted from examples 1 and 2, similar results are obtained with highly uniform contrast being exhibited throughout the emulsion layers.

The invention has been described in detail with particular reference to certain 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:

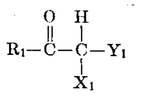
1. A method for avoiding substantial differences in image contrast within a photographic element, said differences being attributable to uncontrolled variations in the ratio of incorporated image-forming coupler-to-silver halide in a photographic emulsion layer of said element, the improvement comprising introducing a development inhibitor-releasing coupler and at least one other coupler separately or in admixture at a controlled rate to effect an essentially constant ratio of development inhibitor-releasing coupler-to-other coupler into a silver halide emulsion, admixing and coating the resulting composition onto a support.

2. The method of claim 1 wherein said photographic image-forming coupler, upon reaction with oxidized primary aromatic amine color developing agent, forms nondiffusible image dye; and, said development inhibitor-releasing coupler has a monothio group in its coupling position which, upon reaction with oxidized primary aromatic amine color-developing agent, forms a diffusible mercaptan which inhibits development.

3. The method of claim 1 wherein each of said couplers are selected from the group consisting of an open-chain ketomethylene coupler radical; a 5-pyrazolone coupler radical; and, a phenolic coupler radical.

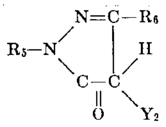
4. The method of in claim 3 wherein each of said couplers has one of the following structural formulas:

Formula I

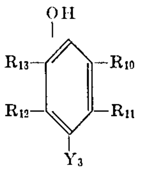


$$R_1-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle X_1}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-Y_1$$

Formula II



Formula III



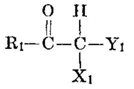
wherein R_1, X_1, R_5, R_{10}, R_{11}, R_{12} and R_{13} each represents a group of the type employed in, respectively, open-chain ketomethylene couplers, 5-pyrazolone couplers, and phenolic couplers; and Y_1, Y_2 and Y_3 each represents:

a. a member selected from the group consisting of hydrogen and a colorless coupling-off group to complete said image-forming coupler; and,

b. a colorless monothio group to complete said development inhibitor-releasing coupler.

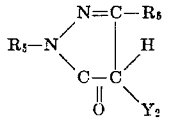
5. The method of claim 3 wherein each of said couplers has one of the following structural formulas:

Formula I

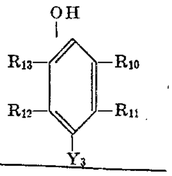


$$R_1-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle X_1}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-Y_1$$

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, represents 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. a member selected from the group consisting of hydrogen, halogen, a thiocyano group, an acyloxy group, an aryloxy group, a cyclooxy group, and, when said R_{12} and R_{13} represent the atoms to complete a benzo group, Y_3 represents any of the foregoing groups given for Y_1 and Y_2 except aryloxy, and can in addition represent a cycloimido group, to complete said photographic image forming coupler; and,

b. a monothio group selected from an orthoamino substituted arylmonothio group; and, a heterocyclic radical containing at least one hetero atom selected from oxygen, sulfur and nitrogen, to complete said third coupler.

6. The method of claim 5 wherein said Y_1, Y_2 and Y_3 each represents a heterocyclic monothio radical containing from one to four hetero nitrogen atoms, to complete said development inhibitor-releasing coupler.

7. The method of claim 6 wherein said Y_1, Y_2 and Y_3 each represents a member selected from the group consisting of: a 2-nitrophenylthio group; a 2-aminophenylthio group; a 5-tetrazolylthio group; 2-benzothiazolylthio group; and a 5-phenyl-1,3,4-oxadiazolylthio group, to complete said development inhibitor-releasing coupler.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No.: 3,632,373 Dated January 4, 1972

Inventor(s) Reid J. O'Connell and John H. VanCampen

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3 , line 35, delete entire line.

Column 4 , line 33, replace "al.," with --fluorine--.

Column 5 , line 1 , after "pivalyl-α-" insert --{--;
line 2 , after "phenylcarbamyl" insert --}--;
line 41, replace "benzamidoih" with --benzamido]--;
line 42, after "1-(2'," insert --4'--;
line 43, after "benzamido" insert a bracket --]--;
line 44, after "1-(2'," insert --4'--;
line 44, after "[β -" delete "b" and insert a hyphen -- - --;
line 44, after "2''''," insert --4'--;
line 46, after "1-(2'," insert --5'--;
line 48, after "1-(2'," insert --4',6'--;
line 50, after "1-(2'," insert --5'--;
line 50, replace "4''" with --4'''--;
line 51, replace "benzamidoih" with --benzamido]--.

Column 6 , line 3 , after "α" delete "l";
lines 4 and 5, replace both lines with --tylphenoxy)-propionamido-4-thiocyano-5-pyrazolone--;
line 6 , after "trichlorophenyl" insert a parenthesis --)--;

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,632,373 Dated January 4, 1972

Inventor(s) Reid J. O'Connell and John H. VanCampen

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6 , line 18, after "1" insert a hyphen -- - --;
line 20, after "diphenylethersulfonamido-" insert --1-naphthol--;
line 35, replace entire line with --2-[α-(4'-tert.-butylphenoxy)propionylamino]phenol--;
line 38, after "2-" delete "60" and insert --α--;
line 44, after "2-[α" delete "α" (second occurrence);
line 52, after "(4" insert a hyphen -- - --;
line 52, after "sulfonamido)" insert a hyphen -- - --;
line 55, delete "phenolic".

Column 7 , line 8 , after "-N-{" delete "-{-4[β -" and insert --β-{4-[α - --;
line 11, after "-N-[α" delete "α" (second occurrence).

Column 8 , line 9 , after "4-carboxyethyl-" delete "4-sulfoethyl-";
line 10, after "benzotriazolyl" insert --4-sulfoethyl-2-benzotriazolyl,--;
line 25, after "-α-2" insert a hyphen -- - --;
line 26, after "α-{3" insert a hyphen and then a bracket -- -[--;
line 29, delete "stearamido";
line 32, after "benzolyl" delete "}";
line 38, after "benzotriazolyl)" insert a hyphen -- - --;

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,632,373 **Dated** January 4, 1972

Inventor(s) Reid J. O'Connell and John H. VanCampen

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8 , line 39, replace entire line with --chloro-5-/α -
(3-pentadecyl-4-sul- --;
line 47, after "trichlorophenyl)-3" insert a hyphen -- - --;
line 64, after "propionamido/" insert a hyphen -- - --.

Column 9 , line 1 , after "tetrazolythio)-" insert --5-pyrazolone--;
lines 12 and 13, after "acetamido" (line 12) delete
"3-α(2,4-di-t-amylphenoxy)acetamido";
line 17, replace "pentacecyl" with --pentadecyl--.

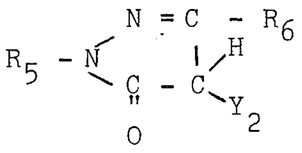
Column 10, line 23, after "group," insert --which render--.

Column 11, line 23, after "N-β" insert a hyphen -- - --.

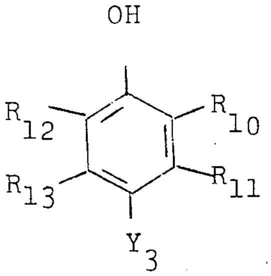
Column 13, Example 2, the table, replace the number "7" on last line of Col. 4 with --85--.

Column 14, Formulae II and III, replace both formulae with
--

Formula II



Formula III



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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

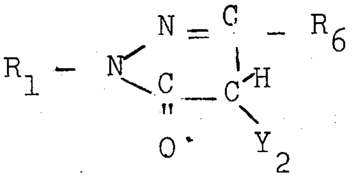
Patent No. 3,632,373 Dated January 4, 1972

Inventor(s) Reid J. O'Connell and John H. VanCampen PAGE - 4

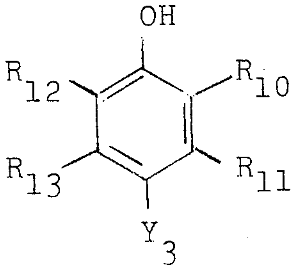
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 15, Formulae II and III, replace both formulae with

--Formula II



Formula III



--.

Column 16, line 15, after "group;" insert --an orthonitro-substituted arylmonothio group;--.

Signed and sealed this 20th day of June 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents