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SILVER HALIDE EMULSIONS CONTAINING A STABILIZER PYRAZOLONE COUPLER

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U.S. Cl. 96—100 12 Claims

ABSTRACT OF THE DISCLOSURE

Magneta-forming stabilizer couplers containing from one to two 5-pyrazolone coupler moieties in which each of aid 5-pyrazolone coupler moieties has from one to two stabilizer radicals substituted in the 1, 3 or 4 positions of the 5-pyrazolone ring are advantageously incorporated in light-sensitive hydrophilic colloid silver halide emulsion layers. The immediate couplers produce image dyes that exhibit substantially improved stability to prolonged exposure to light.

This invention relates to color photography and more particularly to new and improved pyrazolone couplers for use in image-forming systems and processes utilizing such compounds.

The formation of dye images by the chromogenic development of silver halide photographic materials, involving the coupling reaction of oxidized primary aromatic amino developing agents with coupling compounds to form indophenol, indoaniline, azomethine, phenoxazine, phenazine, and similar dyes, is well known. In this system, the subtractive color process of color formation is ordinarily used and the image dyes customarily formed are cyan, magenta and yellow, which are the colors that are complementary to the primary colors red, green, and blue, respectively. Usually phenolic couplers (i.e., phenols and naphthols) are used to form the cyan dye image; pyrazolone, cyanoacetyl, or indazolone couplers are used to form the magenta dye image; and α-acylacetamide or dibenzoylmethane couplers are used to form the yellow dye image.

In these color photographic systems, the color-forming coupler may be applied in a developer solution or incorporated in the light-sensitive photographic emulsion layer or in another dye-image-forming layer, so that, during development, it is available to react with oxidized color developing agent formed as the result of latent image development.

The dye images formed in such processes are not indefinitely stable to ultraviolet and visible radiation, so that under rigorous viewing or display conditions involving, for example, long periods of exposure to sunlight, or other ultraviolet-radiant illumination, the dyes may fade, resulting in deterioration in the quality of the picture.

Marked increases in the stability of indoaniline and azomethine dyes to ultraviolet radiation have been achieved by the use of a variety of agents which can be added to the emulsion in processing, or more conveniently, in manufacture. The need remains for further enhancement of the resistance of these dyes to actinic light, especially those dyes formed from pyrazolone couplers, and indeed this requirement is increasing as recent and continuing technological improvements in the durability of

the photographic layers and supports are making practical the use of prints in exposed locations, indoors and out, which would have been unthinkable a few years ago.

It is therefore an object of my invention to provide new and improved coupler compounds for use in color photography which form dyes having increased stability to ultraviolet and visible radiation.

It is a further object of my invention to provide new and improved coupler compounds containing stabilizing moieties, which compounds are compatible with and nondiffusing in the hydrophilic colloid layers in which they are incorporated.

It is a further object of my invention to provide new and improved coupler compounds containing stabilizing moieties, which compounds do not form highly colored oxidation products in the processing baths such as bleach baths, etc.

It is another object of my invention to provide novel color photographic image-forming layers comprising hydrophilic colloid film-forming binders containing finely particulate dispersions of solutions of my novel coupler compounds.

It is another object of my invention to provide novel color photographic image-forming layers comprising hydrophilic colloid film-forming binder containing my novel coupler compounds dispersed directly in said binders.

It is a further object of my invention to provide new and improved coupler compounds containing stabilizer moieties, which compounds can be incorporated into silver halide emulsions without adverse emulsion effects.

It is a still further object of my invention to provide processed color photographic layers containing dye images formed from my new and improved coupler compounds.

It is still a further object of my invention to provide new and improved coupler compounds which have a materially reduced tendency to produce unwanted color density in the non-image areas.

It is a still further object of my invention to provide simple, economical and reproducible processes for preparing my novel couplers in high yield.

These and other objects of my invention are achieved by the addition to layers intened for the preparation of color photographic dye images of my new and improved coupler compounds. My invention includes the preparation and use in photographic materials of any pyrazolone coupler compound which is substituted with at least one stabilizer group, i.e., a group containing an essentially non-coupling phenolic stabilizer moiety (i.e., the stabilizer moiety is either attached directly through a covelant bond or is connected through a connecting group). The pyrazolone couplers so stabilized include 5-pyrazolones which are substituted on at least one of the 1, 3 or 4 positions of the ring with a group containing an essentially non-coupling stabilizer moiety. By essentially non-coupling is meant that the phenolic stabilizer moiety does not couple enough to contaminate the image dye formed by the pyrazolone coupler or by other image-forming couplers in the photographic element.

My novel stabilizer couplers contain either one or two coupling functions for each stabilizer group. My couplers which contain only one pyrazolone ring (coupling function) have from one to three stabilizer groups attached thereto, and couplers having two pyrazolone rings have from one to two stabilizer groups attached to each pyrazolone ring. The stabilizer moieties are attached either

directly to or through divalent groups to non-coupling positions on the pyrazolone ring, while the stabilizer moiety is attached to the coupling position on a pyrazolone ring through a connecting group, e.g., alkylene having from 1 to 18 carbon atoms. My novel stabilizer couplers are represented by the following general Formula I:

(I) $[R]_n[—R^1]_m$

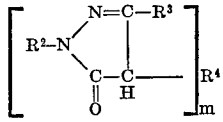
wherein n is an integer of from 1 to 4; m is an integer of from 1 to 2; R represents a phenolic stabilizer radical as represented by Formula III or Formula IV below, said stabilizer radical is attached to R^1, the coupler moiety, by a convalent bond or a photographically inert divalent organic radical such as, for example, alkylene either straight or branched chain having from 1 to 18 carbon atoms (e.g., methylene, ethylene, isopropylene, octadecylene, etc.), in arylene radical (e.g., phenylene, substituted phenylene, naphthylene, substituted naphthylene, etc.), an amide radical (e.g., —NHCO—,

—CONH—

—SO_2NH—, —$NHSO_2$—), an alkoxy radical (e.g., —CH_2CH_2O—, —OCH_2CH_2—, —C_4H_9O—, etc.) or an ether group, —O—, etc., which may or may not contain ballast for rendering the stabilizer coupler nondiffusible, R^1 represents a 5-pyrazolone coupler radical attached to said R stabilizer radical.

The effectiveness of my new and improved coupler compounds is not dependent on the specific composition of R and R^1, and it will be understood that these radicals may contain various substituent groups and that the character and degree of substitution may be modified according to such requirements as spectral, absorptivity, reactivity, solubility, and diffusibility as may be imposed by the photographic system in which the coupler is to be used.

According to the invention, my stabilizer couplers advantageously contain sufficient ballasting to render said couplers nondiffusable in conventional hydrophilic colloid photographic coatings. Typical examples of such pyrazolone couplers in accordance with my invention include those represented by the Formula II below:



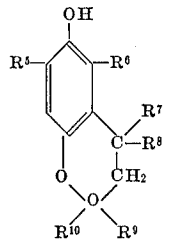
wherein R^2 represents an alkyl group including a straight or branched chain alkyl group of from about 1 to about 30 carbon atoms, preferably from 1 to 22 carbon atoms (e.g., methyl, isopropyl, tertiary butyl, hexyl, dodecyl, docosyl, etc.), a monocyclic alkyl group (e.g., cyclohexyl, etc.), a bicyclic alkyl group, such as, a terpenyl group especially a norbornyl group (e.g., norbornyl, 7,7-dialkylnorbornyl, 2-phenyl-7,7-dialkylnorbornyl, 2-pentadecyl-7,7-dialkylnorbornyl, etc.), a substituted alkyl group in which any of the described alkyl groups contain any of the substituted groups used in couplers, such as, a halogen, the nitro group, the hydroxyl group, the carboxyl group, an amino group (e.g., amino, N-alkylamino, N,N-dialkylamino, N-arylamino, N-alkyl-N-aryl-amino, etc.), a carboxy ester (e.g., carbomethoxy, carboethoxy, carbophenoxy, etc.), the sulfo group, a sulfo ester (e.g., methoxysulfonyl, butoxysulfonyl- phenoxysulfonyl, etc.) an amido group (e.g., acetamido, butyramido, [α-(2,4-di-t-amylphenoxy)acetamido]benzamido, α-(3-pentadecylphenoxy)butyramido, α-(4-t-butylphenoxy)propionamide, 3,5-dicarboxybenzamido, ethylsulfonamido, phenylsulfoamido, etc.), a carbamyl group (e.g., N-methylcarbamyl, N-phenylcarbamyl, etc.), a sulfonyl group (e.g., N-propylsulfamyl, N-tolylsulfamyl, etc.), an alkoxy group (e.g., methoxy, butoxy, etc.), an aryloxy group (e.g., phenoxy, tolyloxy, naphthoxy, etc.), including the substituents defined for substituted alkyl groups above, R^2 also represents an aryl group such as phenyl, naphthyl, etc.

in which the aryl groups include any of the substituents defined for substituted alkyl groups above, R^2 also represents a heterocyclic group having from 5 to 6 atoms in the ring including nitrogen, sulfur, oxygen, etc., as the heteroatoms and including heterocyclic groups such as furanyl, benzothiazolyl, oxazolyl, imidazolyl, quinolyl, etc., a substituted heterocyclic group in which any of the heterocyclic groups are substituted by any of the substituents described above as being on the substituted alkyl groups, R^2 also represents a carbamyl group (e.g., alkylcarbamyl, arylcarbamyl, heterocyclic carbamyl, etc.), and R^2 also represents a thiocarbamyl group (e.g., alkylthiocarbamyl, arylthiocarbamyl and heterocyclicthiocarbamyl), in which the alkyl, aryl and heterocyclic groups in the said carbamyl and thiocarbamyl groups may be substituted with any of the substituents described for R^2 when it represents an alkyl, aryl or heterocyclic group itself, and a stabilizer group containing a stabilizer moiety, e.g., a hydroxy chroman (see Formula III below) or a 4-substituted phenol (see Formula IV below); R^3 represents hydrogen, an alkyl group, an aryl group and a heterocyclic group (unsubstituted or substituted) as described previously for R^2, R^3 also represents a carboxy ester (e.g., carbopropoxy, carbobutoxy, carbophenoxy, etc.), a substituted oxy group (e.g., methoxy, ethoxy, decyloxy, phenoxy, tolyloxy, etc.), a substituted thio group (e.g., ethylthio, propylthio, phenylthio, tolylthio, etc.), an amino group (e.g., amino, N-alkylamino, N-arylamino, N,N-dialkylamino, N-alkyl, N-arylamino, etc), an amido group (e.g., acetamido, α-(2,4-di-t-amylphenoxy)acetamido, α-butylphenoxypropionamido, α-(3-pentadecyl-4-sulfophenoxyacetamido)benzamido, etc.), a carbamyl group (e.g., carbamyl, N-octodecylcarbamyl, N,N-dihexylcarbamyl, N-methyl-N-phenylcarbamyl, 3-pentadecylphenylcarbamyl, etc.), sulfamyl, a ureido group (e.g., an N-arylureido group, an N-alkylureido group, etc.), a thioureido group (e.g., an N-alkylthioureido group, an N-arylthioureido group, etc.), a guanidino group (e.g., guanidino, N-arylguanidino, N-alkylguanidino, etc.), such that the alkyl and aryl groups in R^3 may contain substituent groups as defined previously for such groups in R^2, and a stabilizer group containing a stabilizer moiety, e.g., (see Formula III) or a 4-substituted phenol (see Formula IV), such that at least one of R^2, R^3 and R^4 represents a stabilizer moiety attached to said coupler through a covalent bond or a photographically inert divalent organic radical as described previously; m prepresents an integer from 1 to 2; R^4 when m is the integer 1, represents hydrogen, an alkyl group preferably having from 1 to 22 carbon atoms (e.g., methyl, hexyl, docosyl, etc.), an aryloxy group (e.g., phenoxy, alkylsulfonylphenoxy, arylsulfonylphenoxy, N-alkylsulfamylphenoxy, N,N-dialkylsulfamylphenoxy, N-arylsulfamylphenoxy, N-alkyl-N-arylsulfamylphenoxy, sulfamylphenoxy, nitrophenoxy, acetamidophenoxy, halophenoxy, naphthoxy, methoxyphenoxy, octadecoxyphenoxy, hydroxyphenoxy, sulfophenylazophenoxy, carboxyphenoxy, sulfophenoxy, etc.), a heterocycloxy group (e.g., pyridinyloxy, etc.), an arylazo group (e.g., phenylazo, naphthylazo, etc.), a substituted arylazo group in which the substituent is any of the substituents described previously for the R^2 group excepting that the substituent cannot be a stabilizer moiety unless R^4 is alkyl, an arylthio group (e.g., phenylthio, an alkylcarbamylphenylthio group (preferably where the alkyl moiety has from 6 to 22 carbon atoms, such as octadecylcarbamylphenylthio), a 1-phenyl-5-tetrazolylthio group, a nitrophenylthio group (e.g., 2-nitrophenylthio, 4-nitrophenylthio, etc.), an aminophenylthio group, (e.g., 2-aminophenylthio, 4-aminophenylthio, etc.), a 2-benzothiazolylthio group, a 5-phenyl-1,3,4-oxadiazolyl-2-thio group etc., an acyloxy group (e.g., acetoxy, butyryloxy, dodecanoyloxy, benzoyloxy, naphthoyloxy, etc.) wherein the alkyl or aryl moiety of said acyloxy group is unsubstituted or substituted with any of the substituents described pre-

viously on the R^2 group excepting that the substituent can not be a stabilizer radical, R^4, when *m* is the integer 2, represents a divalent group, such as, an alkylidene group (e.g., ethylidene, propylidene, etc.), an arylidene group (e.g., benzylidene), an arylene group (e.g., phenylene, naphthylene, diphenylene, etc.) an arylenedioxy group (e.g., 1,4-phenylenedioxy, 4,4'-diphenylenedioxy, etc.), an arylenedithio group (e.g., 1,4-phenylenedithio, 4,4'-diphenylenedithio, etc.), a heterocyclene group (e.g., pyryidylene, quinalyene, etc.), diphenyl sulfone, ω,ω-phenylene alkyl, such that the said divalent groups are unsubstituted or are substituted with any of the substituents described previously as substituents for R^2 excepting that the substituent can not be a stabilizer moiety.

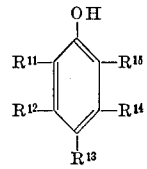
The phenolic stabilizer moieties which are attached to my novel couplers are further illustrated by the following general Formula III and IV:

(III)



wherein R^5, R^8 and R^9 each represents the same or a different member selected from the group comprising hydrogen, an alkyl group (either straight or branched chain preferably having from 1 to 18 carbon atoms, such as, methyl, t-butyl, t-octyl, n-octadecyl, etc.), and a radical containing a 5-pyrazolone coupler moiety such that from 1 to 2 of R^5, R^8 and R^9 represents a radical containing a 5-pyrazolone coupler moiety, R^6, R^7 and R^{10} represent any combination of hydrogen and an alkyl group having preferably from 1 to 18 carbon atoms as the alkyl group defined for R^5, providing that one of R^5 and R^6 represents hydrogen.

(IV)



wherein R^{11}, R^{12}, R^{14} and R^{15} each represent the same or a different member selected from hydrogen, halogen, an alkyl group (either straight or branched chain preferably having from 1 to 18 carbon atoms), an alkoxy group (in which the alkyl group is either straight or branched chain preferably having 1 to 18 carbon atoms, an aryl group (e.g., phenyl, tolyl, naphthyl, etc.), an aryloxy group (e.g., phenoxy, tolyloxy, naphthyloxy, etc.), carboxyl (including the alkali metal salts thereof), the sulfo group, an alkoxycarbonyl group, an alkoxysulfonyl group, an amido group (e.g., acetamido, carbamyl, alkylcarbamyl, arylcarbamyl, sulfamyl, alkylsulfamyl, arylsulfamyl, etc.), an alkylsufonyl group, an arylsulfonyl group, such that the alkyl and aryl moieties of the said R^{11}, R^{12}, R^{14}, and R^{15} groups are unsubstituted or substituted as described in detail for the alkyl groups of R^2 (of Formula II) and a radical containing a 5-pyrazolone coupler moiety attached as described above to said stabilizer group such that, at least one but not more than two of R^{11}, R^{12}, R^{14} and R^{15} represents said 5-pyrazolone coupler radical, and R^{13} represents the groups defined for R^{11}, R^{12}, R^{14} and R^{15} above except that it is not hydrogen, halogen, sulfo or carboxy (or alkali metal salt thereof) and is not a 5-pyrazolone coupler radical when two of R^{11}, R^{12}, R^{14} and R^{15} represent a 5-pyrazolone coupler radical.

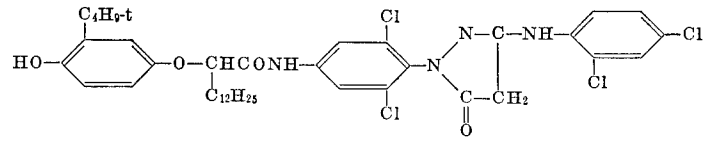
My novel couplers may be used either alone or in combinations of two or more. They may also be used in combination with other couplers or other addenda such as antistain agents, stabilizing agents, ultraviolet absorbers, brighteners, etc.

My novel couplers are characterized by having at least one stabilizer group attached to the coupler which gives them improved stability to ultraviolet and visible light radiation and other valuable properties.

The use of separate compounds as addenda together with prior art couplers in emulsion layers of color photographic elements for the purpose of improving the quality of the image dyes formed in said elements is well known. One of the disadvantages in the use of separate ballasted stabilizer compounds in such layers is the increased bulk which is added to the layer due to such ballasted compounds. One advantage of my new and improved coupler compounds over the prior art practice of adding separate stabilizer compounds is that common ballasting groups are used for both coupler and stabilizer compound. Consequently, less bulk is added to the emulsion layers; this results in thinner layers giving rise to sharper images (i.e., less light scattering due to thinner layers). Further, when such phenolic moieties are attached to the coupler, as in the compounds of my invention, a greater increase in the light stability of the dyes is obtained than when a separate phenolic compound was incorporated with a nonstabilized control coupler. A comparison of coatings containing the control couplers (i.e., containing no stabilizer moiety) together with separate stabilizer compounds with coatings containing my novel coupler compounds containing the stabilizer moiety shows clearly that an unexpected increase in the light stability of the dyes was obtained with my novel stabilizer couplers.

Included among my novel couplers which are used to illustrate but not limit the invention are the following:

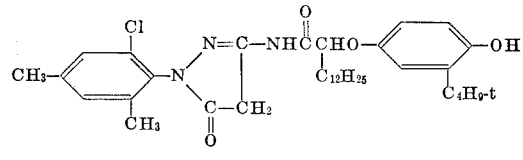
(1) 1-{4-{α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]-2,6-dichlorophenyl}-3-(2,4-dichloroanilino)-5-pyrazolone, M.P. 90–91° C.



(2) 1-(2-chloro-4,6-dimethylphenyl)-3-{3-{α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]benzamido}-5-pyrazolone

(3) 1-(2,4,6-trichlorophenyl)-3-{3-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]benzamido}-5-pyrazolone, M.P. 157–158° C.

(4) 1-(2-chloro-4,6-dimethylphenyl)-3-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]-5-pyrazolone, M.P. 142–143° C.



(5) 1-{4-[α-(3-t-butyl-4-hydroxyphenoxy)tetra-

decanamido]-2,6-dichlorophenyl}-3-(4-cyanoanilino)-5-pyrazolone, M.P. 140–142° C.

(6) 1-{4-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]-2,6-dichlorophenyl}-3-(2-bromo-4-cyanoanilino)-5-pyrazolone, M.P. 100–101° C.

(7) 1-{4-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]-2,6-dichlorophenyl}-3-(2,4-difluoroanilino)-5-pyrazolone, M.P. 81–82° C.

(8) 1-(2,4,6-trichlorophenyl)-3-{4-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]-2-chloroanilino}-5-pyrazolone

(9) 1-(2,4-dichloro-6-methoxyphenyl)-3-{3-[α,(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]benzamido}-5-pyrazolone, M.P. 126–128° C.

(10) 1-(2,4,6-trichlorophenyl)-3-{4-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]anilino}-5-pyrazolone, M.P. 125–126° C.

(11) 1-(2,4,6-trichlorophenyl)-3-{5-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]-2-chloroanilino}-5-pyrazolone, M.P. 175–177° C.

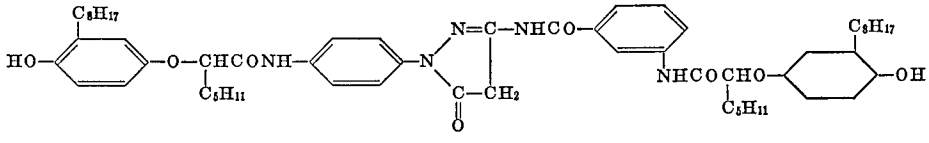
(12) 1-(2,4,6-trichlorophenyl)-3-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]-5-pyrazolone

(13) 1-(2,4-dichloro-6-methoxyphenyl)-3-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]-5-pyrazolone

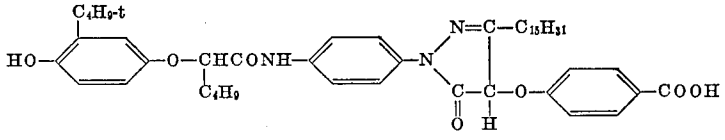
(14) 1-{4-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]-2,6-dichlorophenyl}-3-(2,6-dichloroanilino)-5-pyrazolone

(15) 1-{4-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]-phenol}-3-ethoxy-5-pyrazolone

(16) 1-{4-[α-(4-hydroxy-3-octylphenoxy)heptanamido]phenyl}-3-{3-[α-(4-hydroxy-3-octylphenoxy)heptanamido]benzamido}-5-pyrazolone



(17) 1-{4-[α-(3-t-butyl-4-hydroxyphenoxy)hexanamido]phenyl}-3-pentadecyl-4-(4-carboxyphenoxy-5-pyrazolone

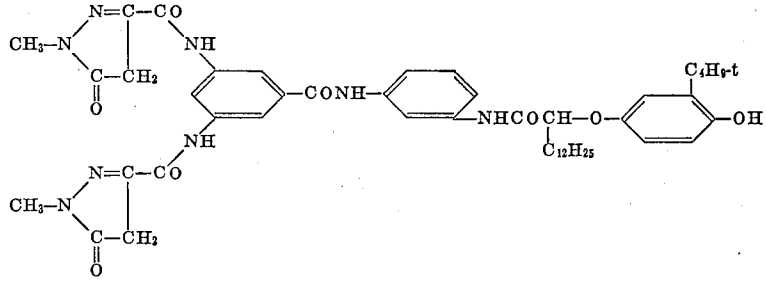


(18) 1-phenyl-3-{3-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]benzamido}-4-methyl-5-pyrazolone

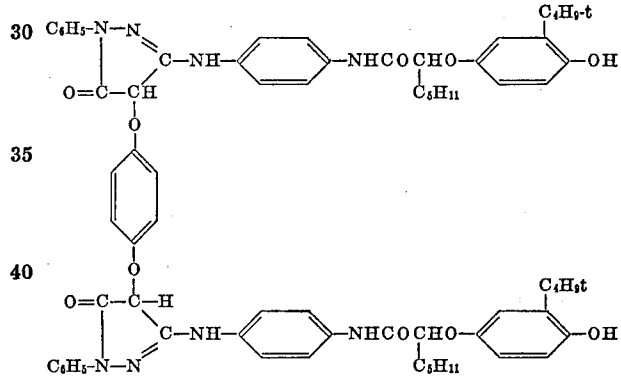
(19) 1-(2,4,6-trichlorophenyl)-3-{3-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]benzamido}-4-phenylazo-5-pyrazolone

(20) 1-[4-(3,5-disulfobenzamido)phenyl]-3-{3-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]phenylcarbamyl}-5-pyrazolone disodium salt

(21) 2-t-butyl-4-{α-{3-[3,5-bis-(1-methyl-3-pyrazol-5-onylcarbonamido)benzamido]phenylcarbamyl}tridecyloxy}phenol

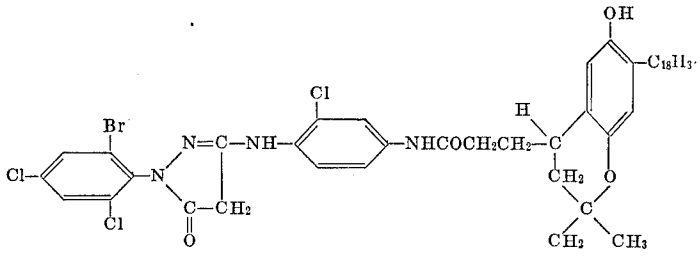


(22) 1,4-bis-{1-phenyl-3-{4-[α-(3-t-butyl-4-hydroxyphenoxy)heptanamido]anilino}-4-pyrazol-5-onyloxy}benzene



(23) 1-(2-benzothiazolyl)-3-{3-[γ-(2,4-dioctyl-2-methyl-6-hydroxy-7-chromanyl)butyramido]benzamido}-5-pyrazolone

(24) 1-(2-bromo-4,6-dichlorophenyl)-3-{2-chloro-4-[β-(2,2-dimethyl-6-hydroxy-7-octadecyl-4-chromanyl)propionamido]anilino}-5-pyrazolone



(25) 1-(2,4,6-trichlorophenyl)-3-{3-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]benzamido}-4-phenylthio-5-pyrazolone

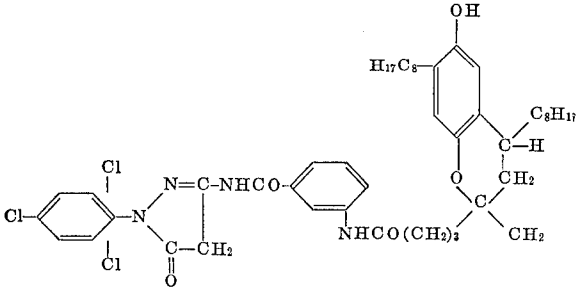
(26) 4,4'-thiobis{{1-(2,4,6-trichlorophenyl)-3-{3-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]benzamido}-5-pyrazolone}}

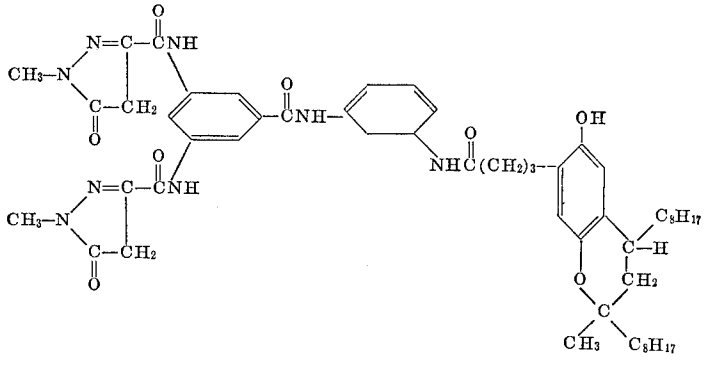
(27) 4,4'-methylenebis{{1-{4-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]-2,6-dichlorophenyl}-3-(2,4-dichloroanilino)-5-pyrazolone}}

(28) 1-{4-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]-2,6-dichlorophenyl}-3-(2,4-dichloroanilino)-4-(4-methoxyphenylazo)-5-pyrazolone

(29) 1-{4-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]2,6-dichlorophenyl}-3-(2,4-dichloroanilino)-4-(2-hydroxyphenylazo)-5-pyrazolone

(30) 1-(2,4,6-trichlorophenyl)-3-{3-[γ-(4,7-dioctyl-6-hydroxy-2-methyl-2-chromanyl)butyramido]-benzamido}-5-pyrazolone





(31) 7-{{γ-{3-[3,5-bis-(1-methyl-3-pyrazol-5-onylcarbonamido)benzamido]phenylcarbamyl}propyl}}-2,4-dioctyl-2-methyl-6-hydroxychroman

(32) 1-{4-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]-2,6-dichlorophenyl}-3-(2,4-dimethylanilino)-5-pyrazolone

(33) 1-phenyl-3-pentadecyl-4-[γ-(3-t-butyl-2-hydroxy-5-methylphenyl)propyl]-5-pyrazolone

The couplers of my invention are nondiffusible and are used to advantage in photographic emulsion layers. They can be incorporated into such layers by methods such as those described by Mannes et al., U.S. Pat. 2,304,939, issued Dec. 15, 1942, Jelley et al., U.S. Pat. 2,322,027, issued June 15, 1943, etc., in which high-boiling organic solvents are used to dissolve the coupler, and by methods described in Vittum et al., U.S. Pat. 2,801,170 and Fierke et al., U.S. Pat. 2,801,171, both issued July 30, 1957, and Julian U.S. Pat. 2,949,360, issued Aug. 16, 1960, in which low-boiling or water-soluble solvents are used with or in place of the high-boiling solvent. Not only can emulsion layers containing my couplers be made thinner because they require no additional dye-stabilizer compound, but some of my couplers are sufficiently reactive so that they do not require any high-boiling coupler solvent that is usually required by couplers. The thin image-forming layers are very desirable because they cause less light scattering and produce sharper images.

Any of the well known primary aromatic amino color-forming silver halide developing agents such as the phenylenediamines, e.g., diethyl-p-phenylenediamine hydrochloride, monomethyl-p-phenylenediamine hydrochloride, dimethyl-p-phenylenediamine hydrochloride, 2-amino-5-diethylaminotoluene hydrochloride, 2-amino-5-(N-ethyl-N-lauryl)toluene, N-ethyl-β-methanesulfonamidoethyl - 3 - methyl - 4-aminoaniline sulfate, N-ethyl-β-methanesulfonamidoethyl-4-aminoaniline, 4-N-ethyl-N-β-hydroxyethylaminoaniline, etc., the p-aminophenols and their substitution products where the amino group is unsubstituted may be used to develop photographic coatings containing my couplers. Various other materials may be included in the developer solutions depending upon the particular requirements, for example, an alkali metal sulfite, carbonate, bisulfite, bromide, iodide, etc., and the thickening agents such as carboxymethyl cellulose, hydroxyethyl cellulose, etc. used in viscous developer compositions. Typical developer solutions are given in Examples 1 and 3, but do not limit the invention.

My couplers are used in the photographic hydrophilic colloid-silver halide emulsion layers of the developing-out type. The emulsions may contain silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide, etc. as the light-sensitive material.

Hydrophilic colloids used to advantage include gelatin, colloidal albumin, a cellulose derivative, a synthetic resin, for instance, a polyvinyl compound, or any of the other hydrophilic colloids used in photographic emulsions.

The emulsions used in the photographic element of my invention can be chemically or optically sensitized by any of the accepted procedures.

The couplers of my invention may also be used to advantage in image-forming layers, either alone or with image-forming compounds other than silver halide such as ZnO, ZnS, CdS, CdSe, NiS, etc., either with or without binders such as gelatin, polyvinyl alcohol, etc.

Usualy my couplers are incorporated in silver halide emulsions which are coated on photographic supports in the form of multilayer color photographic elements wherein at least three differently sensitized emulsion layers are coated over one another on the support. Usually the support is coated in succession with a red-sensitive layer, a green-sensitive layer, and a blue-sensitive layer either with or without a Carey Lea filter layer between the blue-sensitive and green-sensitive layers. The three differently color sensitized layers may be arranged in any other order over one another that is desirable; however, the Carey Lea filter layer obviously would not be put over the blue-sensitive layer. Preferably, these light-sensitive layers are arranged on the same side of the support.

My invention is further illustrated by the following typical examples.

EXAMPLE 1

Single layer gelatin silver bromoiodide coatings were prepared, one containing coupler 2 and a second coating containing as control coupler, the Intermediate 1-(2-chloro-4,6-dimethylphenyl)-3-{3-[α-(4-acetoxy-3-t-butylphenoxy)tetradecanamido] - benzamido} - 5 - pyrazolone from which coupler 2 was derived. Each of these couplers were disposed in the said coatings in the form of a finely dispersed solution of coupler and coupler solvent di-n-butylphthalate. In addition to the coupler in the control coating, an equimolar quantity of phenolic stabilizer compound, 2-t-butyl-4-(α-carbethoxytridecyloxy)phenol, was also incorporated into the coupler dispersion. This is the same stabilizer as that which is attached to stabilizer coupler No. 2. These coatings contained 10 parts of gelatin, 4 parts of silver, 2 parts of coupler, and 1 part of coupler solvent. Samples of said coatings were given 1/25 second exposure on a model 1B intensity scale sensitometer and processed to color negatives as described later in Example 3 but using the following developer solution:

	G.
Sodium sulfite (anhydrous)	2.0
2-amino-5-diethylaminotoluene HCl	2.0
Sodium carbonate monohydrate	20.0
Potassium bromide	2.0

Water to 1.0 liter.
pH adjusted to 10.86.

Samples of each of the processed strips taken from an area having a magenta image dye density of 1 were subjected to 4 days of exposure to a xenon arc. After this fading tests, the magenta dye density was again measured for each of the respective samples using a color densitometer. The magenta image dye formed from the control coupler (i.e., in the control coating) faded more than the magenta image dye formed from the corresponding stabilizer coupler No. 2.

When tested in the above manner, the image dyes formed in coatings containing couplers 3–14, respectively, exhibited similar improvements in stability relative to that of the respective controls.

EXAMPLE 2

Single layer gelatin silver bromoiodide coatings were prepared containing couplers 1, 2, 3 and 4,, respectively. Control coatings for each of the above mentioned coatings were prepared using Intermediate 5 (1-{4-[α-(4-acetoxy-3-t-butylphenoxy)tetradecanamido]-2,6-dichlorophenyl}-3-(2,4-dichloroanilino)-5-pyrazolone of coupler 1, and the intermediate couplers of couplers 2, 3 and 4, respectively, i.e., 1-(2-chloro-4,6-dimethylphenyl) - 3 - {3-[α-(4-acetoxy-3-t-butylphenoxy)tetradecanamido] - benzamido}-5-pyrazolone, 1-(2,4,6-trichlorophenyl)-3-{3 - [α-(4-acetoxy - 3 - t-butylphenoxy)tetradecanamido]benzamido}-5-pyrazolone) and 1-(2-chloro-4,6-dimethylphenyl)-3-[α-(4-acetoxy-3-t - butylphenoxy)tetradecanamido] - 5-pyrazolone)respectively. Each of these eight couplers were dispersed in said coatings in the form of a finely dispersed solution of coupler in coupler solvent, di-n-butylphthalate. These coatings contained 10 parts of gelatin, 4 parts of silver, 2 parts of coupler, and 1 part of coupler solvent. Samples of said coatings were given 1/25 second exposure on a model 1B intensity scale sensitometer and processed as described in Example 1 to color negatives, respectively, using the developer solution given in Example 1 above.

Samples of each of the processed strips taken from an area having a magenta image dye density of 1 were subjected to 10 days of simulated average north skylight exposure. After this fading test the magenta dye density was again measured for each of the respective samples using a color densitometer. The magenta image dyes formed from the control couplers in each of the respective control coatings faded an average of 4 times more than the magenta image dyes formed from the correspond stabilizer couplers.

Similar results were also obtained in coatings containing couplers 5–14, respectively, relative to coatings containing the corresponding control couplers.

EXAMPLE 3

Multilayer color films were prepared as described in Example 16, Part 1, of Carroll et al., U.S. Pat. 2,944,900, issued July 12, 1960, except that in place of the magenta dye-forming coupler used in the green-sensitive layer of said film, couplers 1–5 were used, respectively. Control coatings containing the corresponding control couplers as mentioned in Example 2 above were also prepared. The intermediate of coupler 5 (control for stabilizer coupler 5) was 1-{4-[α-(4-acetoxy-3-t-butylphenoxy)tetradecanamido] - 2,6 - dichlorophenyl} - 3 - (4-cyanoanilino)-5-pyrazolone. Samples of the above described color films were exposed on a model IB sensitometer using a standard intensity scale color chart and processed through the following steps:

(1) Color developer—12 minutes
(2) Rinse—10 seconds
(3) Kodak F–5 fixing bath—4 minutes
(4) Wash—4 minutes
(5) Bleach (ferricyanide)—8 minutes
(6) Wash—4 minutes
(7) Kodak F–5 fixing bath—4 minutes
(8) Wash—8 minutes

The various processing solutions had essentially the compositions set out below:

Color developer:
- Benzyl alcohol—5.5 ml.
- Sodium hexametaphosphate—2.5 g.
- Sodium sulfite desiccated—1.95 g.
- Sodium bromide—1.18 g.
- Sodium hydroxide—13.3 g.
- Borax—44.9 g.
- 4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-m-toluidine sesquisulfate monohydrate—5.0 g.
- Water to make 1 liter

Ferricyanide bleach:
- Potassium ferricyanide—50.0 g.
- Sodium bromide—20.0 g.
- Borax—7.3 g.
- Boric acid—15.0 g.
- Water to make 1 liter

Samples of the above mentioned processed coatings from an area of said film containing the magenta image dyes were subjected to 10 days of simulated average north skylight exposure. As in Example 2 above, the image dyes formed from the stabilizer couplers exhibited considerable improvement in light stability relative to those from the respective controls.

Similarly, other couplers of my invention are used to advantage in color photography as illustrated above

with representative couplers. Further, the couplers of my invention are valuable as magenta image-forming couplers in multilayer photographic color films containing other classes of couplers in the other layers of said film. Such other couplers are, for example, yellow image-forming couplers containing a methylene or substituted methylene group having two carbonyl groups directly attached thereto; and cyan couplers such as naphthols and phenols.

In general my couplers are prepared by the various methods used for preparing conventional prior art 5-pyrazolone couplers except that a stabilizer radical is incorporated into the coupler molecule in a non-coupling position. The following preparations will serve to illustrate the methods which are used to prepare my stabilizer couplers.

Preparation of Compound 1

Intermediate 1: 2-t-butyl-4-(α-carbethoxytridecyloxy)-phenol.—A mixture of 41 g. of t-butyl hydroquinone, 86 g. of ethyl α-bromotetradecanoate, and 40 g. of potassium carbonate in 500 ml. of acetone was refluxed for 3 days, after which time the solution was poured into a mixture of 1 liter of diethyl ether and 500 ml. of water. The ether layer was separated from the water, dried and concentrated in vacuo. The residue was distilled under reduced pressure and the fraction which boiled at 225° C. at a pressure of 0.4 mm. was collected. This solid was recrystallized from acetonitrile to yield the product.

Intermediate 2: 2 - t-butyl-4-(α-carboxytetradecyloxy) phenol.—A mixture of 21 g. of Intermediate 1 above and 11 g. of potassium hydroxide in 250 ml. of methyl alcohol was refluxed for ½ hour, after which time the clear solution was neutralized by the addition of dilute hydrochloric acid. The solid which separated was collected and recrystallized from hexane to yield the product.

Intermediate 3: α - (4 - acetoxy - 3-t-butylphenoxy) tetradecanoic acid.—A mixture of 10 g. of Intermediate 2 above and 2 drops of concentrated sulfuric acid in 40 ml. of acetic anhydride was heated on the steam bath under a drying tube for 2 hours. To the resultant solution was added 250 ml. of water. The oil-water mixture was heated for 10 minutes at 60° C. with stirring, after which time the clear solution was cooled in an ice bath; whereupon a solid separated, was collected, dried, and recrystallized from petroleum ether to yield the product.

Intermediate 4: α - (4 - acetoxy - 3-t-butylphenoxy) tetradecanoyl chloride.—A mixture of 41 g. of Intermediate 3 above and 20 g. of phosphorous pentachloride in 200 ml. of dry petroleum ether was refluxed for 2 hours, after which time the clear solution was concentrated in vacuo. The residual solid was recrystallized twice from acetonitrile to yield the product.

Intermediate 5: 1 - {4 - [α - (4 - acetoxy-3-t-butylphenoxy)tetradecanamido]2,6 - dichlorophenyl} - 3 - (2,4-dichloroanilino) - 5 - pyrazolone.—To a mixture of 45 g. of 1 - (4 - amino - 2,6-dichlorophenyl)-3-(2,4-dichloroanilino)-5-pyrazolone and 9 g. of anhydrous sodium acetate in 250 ml. of acetic acid was added at room temperature with stirring a solution of 51 g. of Intermediate 4 above in 100 ml. of acetic acid. The reaction mixture was stirred at room temperature for 1 hour, after which time it was poured into 1 liter of water and the solid which separated was recrystallized from acetonitrile to yield the product.

Compound 1: 1 - {4 - [α - (3-t-butyl-4-hydroxyphenoxy)tetradecanamido] - 2,6 - dichlorophenyl} - 3 - (2,4-dichloroanilino)-5-pyrazolone.—A solution of 10 g. of Intermediate 5 above and 2.8 g. of sodium hydroxide in 100 ml. of methyl alcohol was stirred at room temperature under nitrogen for 1 hour, after which time the reaction mixture was acidified with concentrated hydrochloric acid and poured into 1 liter of water. The white solid which separated was collected and recrystallized from acetonitrile to yield the product.

Preparation of Compound 2

Compound 2: 1 - (2 - chloro - 4,6-dimethylphenyl)3-{3 - [α - (3 - t-butyl-4-hydroxyphenoxy)tetradecanamido]-benzamido}-5-pyrazolone.—A solution of 10 g. of the intermediate below and 3 g. of sodium hydroxide in 150 ml. of methanol was stirred at room temperature under nitrogen for 1 hour, after which time the clear solution was poured into an ether-water mixture. The ether layer was separated, washed again with water, dried and concentrated in vacuo. The residual solid was recrystallized from acetonitrile to yield the product.

Intermediate: 1 - (2 - chloro - 4,6-dimethylphenyl)-3-{3 - [α - (4 - acetoxy-3-t-butylphenoxy)tetradecanamido]-benzamido}-5-pyrazolone.—To a mixture of 8 g. of 1 - (2 - chloro - 4,6-dimethylphenyl)-3-(3-aminobenzamido)-5-pyrazolone and 2 g. of anhydrous sodium acetate in 100 ml. of acetic acid under a nitrogen atmosphere was added at room temperature with stirring a solution of 9 g. of Intermediate 4 of Compound 1 above in 50 ml. of acetic acid. The reaction mixture was stirred at room temperature for ½ hour, after which time it was poured into 500 ml. of water with stirring. The solid which separated was collected, and dissolved in 500 ml. of ether. The ether solution was washed with 3% aqueous sodium carbonate, dried and concentrated in vacuo to yield the product.

Preparation of Compound 3

Compound 3: 1 - (2,4,6 - trichlorophenyl) - 3-{3-[α-(3 - t - butyl - 4-hydroxyphenoxy)tetradecanamido]benzamido}-5-pyrazolone.—A solution of 8 g. of the intermediate below and a mixture of 1.2 g. of sodium hydroxide in 3 ml. of water in 100 ml. of methyl alcohol was stirred at room temperature under nitrogen for 1 hour, after which time the clear solution was poured into 500 ml. of water. The solid which separated was collected and recrystallized from acetonitrile to yield the product.

Intermediate: 1 - (2,4,6 - trichlorophenyl)-3-{3-[α-(4-acetoxy - 3-t-butylphenoxy)tetradecanamido]benzamido}-5-pyrazolone.—To a solution of 6 g. of 1-(2,4,6-trichlorophenyl)-3-(3-aminobenzamido)-5-pyrazolone and 1.3 g. of anhydrous sodium acetate in 60 ml. of acetic acid was added at room temperature with stirring a solution of 7 g. of Intermediate 4 of Compound 1 above in 25 ml. of acetic acid. The reaction mixture was stirred at room temperature for 1 hour, after which time it was poured into 500 ml. of water. The solid which separated was collected, dissolved in chloroform and dried over magnesium sulfate. This dried liquid was passed through a chromatographic column and the lower ⅔ of said column was then extracted with methyl alcohol. The methyl alcohol extracts were combined and concentrated in vacuo to yield the product.

Preparation of Compound 4

Compound 4: 1-(2-chloro-4,6-dimethylphenyl)-3-[α-(3-t-butyl - 4 - hydroxyphenoxy)tetradecanamido]-5-pyrazolone.—A solution of 8 g. of the intermediate below and a mixture of 3 g. of sodium hydroxide in 5 ml. of water in 150 ml. of methyl alcohol was stirred at room temperature under nitrogen for 1 hour, after which time it was poured into 500 ml. of water. The solid which separated was collected and recrystallized from acetonitrile to yield the product.

Intermediate: 1-(2-chloro-4,6-dimethylphenyl)-3-[α-(4-acetoxy-3-t-butylphenoxy)tetradecanamido] - 5 - pyrazolone.—To a solution of 12 g. of 1-(2-chloro-4,6-dimethylphenyl)-3-amino-5-pyrazolone and 4 g. of anhydrous sodium acetate in 125 ml. of acetic acid was added at room temperature with stirring a solution of 23 g. of Intermediate 4 of Compound 1 above in 50 ml. of acetic acid. The reaction was stirred at room temperature for 1 hour, after which time it was poured into 500 ml. of

water. The gummy solid which separated was dissolved in 200 ml. of chloroform. This solution was dried and then passed through a chromatographic column. The lower ⅔ of the column was then extracted with methyl alcohol. The methyl alcohol extracts were combined and concentrated in vacuo to yield the product.

Similarly, the other couplers of my invention are readily prepared by the illustrative methods described above.

Compounds 5, 6 and 7 were prepared by the method described for Compound 1, but substituting for 1-(4-amino - 2,6 - dichlorophenyl)-3-(2,4-dichloroanilino)-5-pyrazolone, an equimolar amount of the appropriate intermediate, i.e., for Compound 5, 1-(4-amino-2,6-dichlorophenyl)-3-(4-cyanoanilino)-5-pyrazolone, for Compound 6, 1-(4-amino-2,6-dichlorophenyl)-3-(2-bromo - 4 - cyanoanilino)-5-pyrazolone and for Compound 7, 1-(4-amino-2,6-dichlorophenyl)-3-(2,4-difluoroanilino)-5-pyrazolone.

Compounds 8, 9, 10 and 11 were prepared by the method described for Compound 3, but in which the 1-(2,4,6 - trichlorophenyl)-3-(3-aminobenzamido)-5-pyrazolone was replaced by an equimolar amount of the appropriate intermedite, i.e., for Compound 8 1-(2,4,6-trichlorophenyl)-3-(4-amino-2 - chloroanilino) - 5 - pyrazolone, for Compound 9 1-(2,4-dichloro-6-methoxyphenyl)-3-(3-aminobenzamido)-5-pyrazolone, for Compound 10 1-(2,4,6-trichlorophenyl)-3-(4-aminoanilino) - 5 - pyrazolone, and for Compound 11 1-(2,4,6-trichlorophenyl)-3-(3-amino-6-chloroanilino)-5-pyrazolone.

Compounds 12 and 13 are prepared to advantage like Compound 4, but by substituting for 1-(2-chloro-4,6-dimethylphenyl) - 3 - amino-5 - pyrazolone, an equimolar amount of the appropriate intermediate, i.e., for Compound 12 1-(2,4,6-trichlorophenyl)-3-amino-5-pyrazolone, and for Compound 13 1-(2,4-dichloro-6-methoxyphenyl)-3-amino-5-pyrazolone.

Compounds 14, 15 and 32 are prepared to advantage by the method described for Compound 1 using in place of 1-(4-amino-2,6-dichlorophenyl)-3 - (2,4 - dichloroanilino)-5-5-pyrazolone, an equimolar amount of the appropriate intermediate, i.e., for Compound 14 1-(4-amino-2,6-dichlorophenyl)-3-(2,6 - dichloroanilino) - 5 - pyrazolone and for Compound 15 1-(4-aminophenyl)-3-ethoxy-5-pyrazolone and for Compound 32 1-(4-amino-2,6-dichlorophenyl)-3-(2,4-dimethylanilino)-5-pyrazolone.

Compounds 16 and 17 are made advantageously by the method used for Compound 1, but by using the appropriate intermediates, i.e., for Compound 16, 1 mole of 1-(4-amino-phenyl)-3-(3-aminobenzamido)-5-pyrazolone with 2 moles of α-(4-acetoxy-3-octylphenoxy)heptanoyl chloride, and Compound 17 was made by reacting equimolar amounts of 1-(4-aminophenyl)-3-pentadecyl - 4 - (4 - carboxyphenoxy)-5-pyrazolone with α-(4-acetoxy-3-t-butylphenoxy)hexanoyl chloride.

Compounds 18, 19 and 25 were prepared to advantage by syntheses similar to that used for making Compound 2, but in which the 1-(2-chloro-4,6-dimethylphenyl)-3-(3-aminobenzamido)-5-pyrazolone is replaced by the appropriate intermediate, i.e., for Compound 18, 1-phenyl-3-(3-aminobenzamido)-4-methyl-5-pyrazolone, for Compound 19, 1-(2,4,6 - trichlorophenyl - 3 - (3 - aminobenzamido)-4-phenylazo-5-pyrazolone, and for Compound 25, 1-(2,4,6-trichlorophenyl) - 3 - (3 - aminobenzamido) - 4-phenylthio-5-pyrazolone. Compound 20 is made to advantage by reacting meta-nitroaniline with Intermediate 4 of Compound 1 to yield 3[α-(3-t-butyl-4-acetoxyphenoxy) tetradecanamido]nitrobenzene (Intermediate 1). This nitro compound is then reduced catalytically to yield the corresponding aniline (Intermediate 2). This aniline derivative is reacted with 1-(4-nitrophenyl)-3-chlorocarbonyl-5-pyrazolone to yield 1-(4-nitrophenyl)-3-{3-[α-(3-t-butyl-4-acetoxy phenoxy)tetradecanamido]phenyl carbamyl}-5-pyrazolone (Intermediate 3). This nitro pyrazolone is catalytically reduced and the corresponding amine (Intermediate 4) acylated with 3,5-dichloro sulfonyl benzoyl chloride. The product (Intermediate 5) is then converted to Compound 20 by alkaline hydrolysis (i.e., by a method similar to that used for Compound 1).

Compound 21 is prepared by acylating 3-[α-(3-t-butyl-4-acetoxyphenoxy)tetradecanamido]aniline (i.e. Intermediate 2 of Compound 20) with 3,5-dinitrobenzoylchloride. The resulting dinitro compound (Intermediate 1) is catalytically reduced. The diamine (Intermediate 2) is then acylated with 2 moles of 1-methyl-3-chlorocarbonyl-5-pyrazolone. The resulting bis pyrazolone (Intermediate 3) is then converted to Compound 21 by alkaline hydrolysis of the acetoxy group (i.e., using a method similar to that used for Compound 1).

Compound 22 is prepared as by the following synthesis. 2-t-butyl-4-(α-carbethoxy hexyloxy)phenol is prepared by the method used to make Intermediate 1 for Compound 1, but by substituting an equimolar amount of ethyl α-bromohexanoate for the ethyl α-bromo-tetradecanoate, etc., then converted to α - [4 - acetoxy-3-t-butylphenoxy)hexanoyl chloride by the same type reactions described to make Intermediate 4 for Compound 1. 1-phenyl-3-{4-[α-(4-acetoxy - 3 - t - butylphenoxy)heptanamido]anilino}-5-pyrazolone is made by reacting equimolar amounts of α-[4-acetoxy-3-t-butylphenoxy)hexanoyl chloride and 3-(4-aminoanilino)-1-phenyl-5-pyrazolone. To a glacial acetic acid solution of 1-phenyl-3-{4-[α-(4-acetoxy-3-t-butylphenoxy-heptanamido]anilino}-5-pyrazolone is added isopentyl nitrite with string to produce the corresponding 4-hydroxyimino derivative which is then converted to the corresponding 4-hydroxy derivative by treatment with an ethanol solution of ferric chloride hexahydrate and concentrated hydrochloric acid followed by hydrogenation in a low pressure Parr Hydrogenation Apparatus using 10% palladium on charcoal as a catalyst. To 2 moles of 1-phenyl-3-{4-[α-(4-acetoxy - 3 - t - butylphenoxy)heptanamido]anilino}-4-hydroxy-5-pyrazolone and 2 moles of anhydrous sodium methylate in dimethyl formamide (saturated with nitrogen) is added 1 mole of 1,4-difluorobenzene. The 1,4-bis{{1-phenyl-3-{4-[α-(4-acetoxy-3-t-butylphenoxy)heptanamido]anilino} - 4 - pyroazol - 5 - onyloxy}}benzene is then converted to Compound 22 by alkaline hydrolysis as described in preparing Compound 1 (from its Intermediate 5).

Compound 23 is prepared advantageously by reacting 1-(2-benzothiazolyl) - 3 - (3 - aminobenzamido)-5-pyrazolone with an equivalent amount of γ-(6-acetoxy-2,4-dioctyl - 2 - methyl-7-chromanyl)butyryl chloride in acetic acid using sodium acetate as the condensing agent. The product of this reaction is then converted to Compound 23 by alkaline hydrolysis (i.e., in a manner similar to that for Compound 3).

Compound 24 is advantageously prepared by reacting 1-(2-bromo-4,6- dichlorophenyl) - 3 - (4 - amino-2-chloroanilino)-5-pyrazolone with an equivalent amount of β-(6-acetoxy - 2,2 - dimethyl-7-octadecyl-4-chromanyl) propionyl chloride in acetic acid using sodium acetate as the condensing agent. The product of this reaction is converted for Compound 24 by alkaline hydrolysis (in a manner similar to that used for Compound 3).

Compound 26 is advantageously made by reacting 2 moles of 1-(2,4,6-trichlorophenyl) - 3 - {3-[α-(4-acetoxy-3 - t - butylphenoxy)tetradecanamido]benzamido}-5-pyrazolone (Intermediate used for making Compound 3) with 1 mole of sulfur dichloride followed by alkaline hydrolysis of the acetoxy group to the hydroxy group (i.e., by a method similar to that used for Compound 3).

Compound 27 is advantageously prepared by reacting 2 moles of 1-{4-[α-(4-acetoxy - 3 - t - butylphenoxy) tetradecanamido] - 2,6 - dichlorophenyl}-3-(2,4-dichloroanilino)-5-pyrazolone (Intermediate 5 for compound 1) with 1 mole of formaldehyde followed by alkaline hydrolysis of the acetoxy group to the hydroxy group (i.e., the method described in the preparation of Compound 3).

Compound 28 is prepared by reacting equimolar amounts of Intermediate 5 for Compound 1 and 4-methoxyphenyldiazonium hydrochloride, followed by alkaline

hydrolysis of the acetoxy group to a hydroxy group (i.e., in a manner similar to that used for Compound 1).

Compound 29 is prepared advantageously by reacting equimolar amounts of Intermediate 5 for Compound 1 and 2-hydroxyphenyl diazonium hydrochloride, followed by alkaline hydrolysis of the acetoxy group to the hydroxy group (i.e., in a manner similar to that used for Compound 1).

Compound 30 is advantageously prepared by reacting 1-(2,4,6-trichlorophenyl) - 3 - (3 - aminobenzamido)-5-pyrazolone with an equivalent amount of γ-(6-acetoxy-4,7-dioctyl-2-methyl - 7 - chromanyl)butyryl chloride in acetic acid using sodium acetate as the condensing agent. The product from this reaction is then converted to compound 30 by alkaline hydrolysis (i.e., in a manner similar to that used for Compound 3).

Compound 31 is advantageously prepared as follows: m-nitroaniline is reacted with γ-(6-acetoxy-2,4-dioctyl-2-methyl-7-chromanyl)-butyryl chloride to yield 3-[γ-(6-acetoxy-2,4-dioctyl - 2 - methyl - 7 - chromanyl)butyramido]nitrobenzene (Intermediate 1). This nitro compound is then reduced catalytically to yield the corresponding aniline (Intermediate 2) which is then reacted with 3,5-dinitrobenzoyl chloride. The resulting dinitro compound (Intermediate 3) is catalytically reduced and the diamine thus formed (Intermediate 4) is acylated with 2 moles of 1-methyl-3-chlorocarbonyl-5-pyrazolone. The resulting bis-pyrazolone (Intermediate 5) is then converted to Compound 31 by alkaline hydrolysis of the acetoxy group (i.e., using the method similar to that used for Compound 1).

Coupler 33 is advantageously prepared by reacting 1-phenyl-3-pentadecyl-5-pyrazolone with an equimolar amount of γ-(2-acetoxy-3-t-butyl - 5 - methylphenyl)propionaldehyde in ethyl alcohol under reflux for one hour and using acetic acid as catalyst. The precipitated reaction product is collected and is hydrogenated in glacial acetic acid using palladium on charcoal as the catalyst. The product 1-phenyl - 3 - pentadecyl-4-[γ-(3-t-butyl-2-acetoxy-5-methylphenyl)propyl]-5-pyrazolone is then given alkaline hydrolysis as described previously for coupler 1 to give coupler 33.

The novel pyrazolone couplers of my invention are synthesized from prior art pyrazolone couplers by attaching at least one stabilizer radical to the said coupler molecule in a non-coupling position. The image dyes formed from my novel couplers exhibit substantially improved stability to light. My couplers are advantageously used in emulsion layers of photographic elements either alone or with other couplers, either 4- or 2-equivalent couplers, competing couplers, DIR couplers and the like.

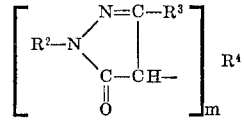
The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A light-sensitive silver halide emulsion containing a stabilizer pyrazolone coupler compound having from 1 to 2 5-pyrazolone coupler moieties and having substituted on at least one of the 1- and 3-ring positions of each of said 5-pyrazolone coupler moieties, a radical containing an essentially non-coupling phenolic stabilizer moiety selected from the class consisting of a hydroxychroman and a 4-substituted phenol such that said 5-pyrazolone coupler moiety is connected to said hydroxychroman by a photographically inert organic linkage containing a member selected from the class consisting of a carbamyalkyl group, a carbamylphenylcarbamylalkyl group, an aminophenylcarbamyalkyl group, and an amidobenzamidophenylcarbamyalkyl group with the alkyl group end of said linkage attached directly to a carbon atom in a ring of said hydroxychroman, and such that said 5-pyrazolone coupler moiety is connected to said 4-substituted phenol by a photographically inert organic linkage containing a member selected from the class consisting of a carbamylalkoxy group, a phenylcarbamylalkoxy group, a carbamylphenylcarbamylalkoxy group, an aminophenylcarbamylalkoxy group, and an amidobenzamidophenylcarbamylalkoxy group with the oxygen atom of the alkoxy end of said linkage attached directly to a carbon atom in said 4-substituted phenol ring.

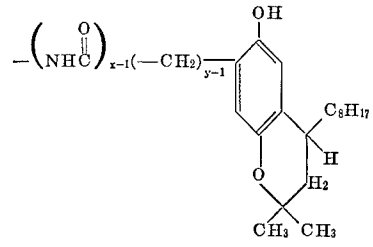
2. A light-sensitive hydrophilic colloid silver halide emulsion containing a stabilizer pyrazolone coupler compound having the formula:

I.

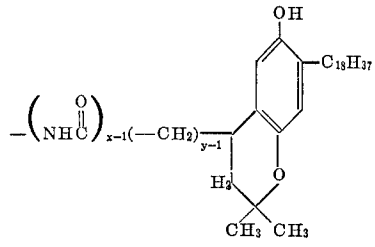


wherein R^2 represents a member selected from the class consisting of an alkyl group, an aryl group, a heterocyclic group, a carbamyl group and a thiocarbamyl group, such that said aryl group includes a stabilizer radical substituent selected from the class consisting of those having the formulas:

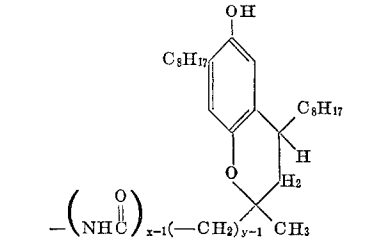
II.



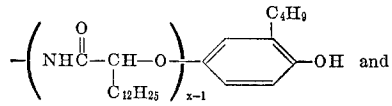
III.



IV.

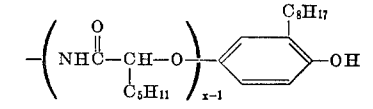


V.



and

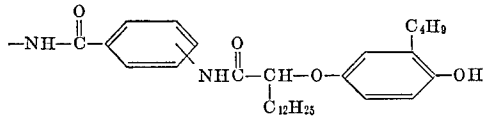
VI.



wherein x represents the integer 2; and y represents an integer of from 2 to 4; R^3 represents a member selected from the class consisting of hydrogen, an alkyl group, an aryl group, a heterocyclic group, a carboxy ester group, an alkoxy group, a phenoxy group, a lower alkthio group, a phenylthio group, an amino group, an amido group, a carbamyl group, a sulfonyl group, a ureido group, a thioureido group, and a guanidino group, such that when R^3 represents a group selected from the class consisting of an amino group, an amido group and a carbamyl group, said amino group, said amido group and said carbamyl group can include Formulas II, III, IV, V, VI in which x

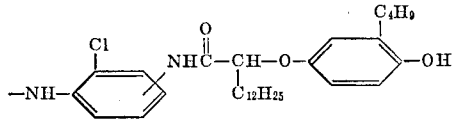
represents the integer 2 and *y* represents an integer of from 2 to 4,

VII.



and

VIII.



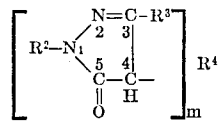
m represents an integer of from 1 to 2; R^4 represents a member selected from the class consisting of hydrogen, an alkyl group having from 1 to 22 carbon atoms, an aryloxy group, a heterocycloxy group, an arylazo group, an arylthio group, a 2-benzothiazolylthio group, an oxadiazolyl-2-thio group, an acyloxy group, an alkylidene group, an arylidene group, an arylene group, an arylenedioxy group, an arylenedithio group, a heterocyclene group, a diphenylsulfon group, and an ω,ω-phenylenealkyl group, such that R^4 represents a monovalent group when *m* represents the integer 1, and R^4 represents a divalent group when *m* represents the integer 2; and such that at least one of R^2 and R^3 contains a stabilizer radical selected from those having the Formulas II, III, IV, V, VI, VII, and VIII.

3. A light-sensitive hydrophilic colloid silver halide emulsion containing a stabilizer pyrazolone coupler compound having the formula:

(I) $$[R]_n[—R']_m$$

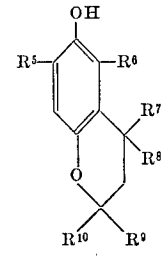
wherein *n* represents an integer of from 1 to 4; *m* represents an integer of from 1 to 2; $[—R']_m$ represents a radical containing a 5-pyrazolone coupler moiety selected from those having the formula:

(II)

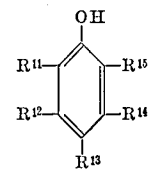


wherein *m* is as defined previously; R^2 represents a group selected from the class consisting of an alkyl group, an aryl group, a heterocyclic group, a carbamyl group, a thiocarbamyl group and R; R^3 represents a group selected from the class consisting of a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, a carboxy ester group, an oxy group, a thio group, an amino group, an amido group, a carbamyl group, a sulfonyl group, a ureido group, a thioureido group, a guanidino group and R such that at least one of R^2 and R^3 represents a group containing R; R^4 represents a member selected from the class consisting of a hydrogen atom, an alkyl group, an aryloxy group, a heterocycloxy group, an aralazo group, an arylthio group, a 2-benzothiazolylthio group, an oxadiazolyl-2-thio group, an acyloxy group, an alkylidene group, an arylidene group, an arylenedioxy group, an arylenedithio group, a heterocyclene group, a diphenylsulfon group and an ω,ω-phenylenealkyl group; such that R^4 represents a monovalent group when *m* represents the integer 1, and R^4 represents a divalent group when *m* is the integer 2; R represents a radical containing an essentially non-coupling phenolic stabilizer moiety selected from those having the formulas:

III.

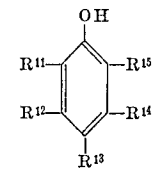


IV.



wherein R^5, R^8 and R^9 each represent a member selected from the class consisting of hydrogen, an alkyl group and a radical containing R' connected to said stabilizer moiety of Formula III by a divalent photographically inert organic linkage containing a group selected from the class consisting of a carbamylphenylcarbamylalkyl group, an aminophenylcarbamylalkyl group and an amidobenzamidophenylcarbamylalkyl group, such that the end of said linkage attached directly to a carbon atom in a ring of said stabilizer moiety of Formula III is an alkyl group, and such that from 1 to 2 of R^5, R^8 and R^9 represent said radical containing said 5-pyrazolone moiety; and R^6, R^7 and R^{10} each represent a member selected from the class consisting of hydrogen and an alkyl group; R^{11}, R^{12}, R^{14} and R^{15} each represent a member selected from the class consisting of hydrogen, an alkyl group, an alkoxy group, an aryl group, an aryloxy group, and a radical containing said 5-pyrazolone coupler moiety connected to said stabilizer of Formula IV by a divalent photographically inert organic linkage containing a group selected from the class consisting of a phenylcarbamylalkoxy group, a carbamylphenylcarbamylalkoxy group, a carbamylalkoxy group, an aminophenylcarbamylalkoxy group and an amidobenzamidophenylcarbamylalkoxy group, such that the end of said linkage attached directly to a carbon atom in the ring of said stabilizer moiety of Formula IV is an alkoxy group with the oxygen atom of said alkoxy group attached directly to a carbon atom in said ring of stabilizer moiety and R^{13} represents a member selected from the class consisting of an alkyl group, an alkoxy group, an aryl group, an aryloxy group, and said radical containing said 5-pyrazolone coupler moiety defined previously for R^{11}*m* R^{12}, R^{14} and R^{15}, providing that not more than one of R^{11}, R^{12}, R^{14} and R^{15} represents said radical containing said 5-pyrazolone coupler moiety when R^{13} represents said radical containing said 5-pyrazolone coupler moiety.

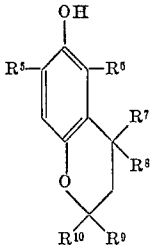
4. An image-forming layer containing light-sensitive silver halide and a stabilizer pyrazolone coupler compound having from 1 to 2 5-pyrazolone coupler moieties having substituted on at least one of the 1- and 3-ring positions of each of said 5-pyrazolone coupler moieties, a radical containing an essentially non-coupling phenolic stabilizer moiety having the formula:



wherein R^{11}, R^{12}, R^{14} and R^{15} each represent a member selected from the class consisting of hydrogen, an alkyl group, an alkoxy group, an aryl group, an aryloxy group,

and a radical containing said 5-pyrazolone coupler moiety connected to said stabilizer moiety by a divalent photographically inert organic linkage containing a group selected from the class consisting of a phenylcarbamylalkoxy group, a carbamylphenylcarbamylalkoxy group, a carbamylalkoxy group, an aminophenylcarbamylalkoxy group and an amidobenzamidophenylcarbamylalkoxy group, such that the end of said linkage attached directly to a carbon atom in the ring of said stabilizer moiety is an alkoxy group with the oxygen atom of said alkoxy attached directly to a carbon atom in said ring of stabilizer moiety and R^{13} represents a member selected from the class consisting of an alkyl group, an alkoxy group, an aryl group, an aryloxy group, and said radical containing said 5-pyrazolone coupler moiety defined previously for $R^{11}m$, R^{12}, R^{14} and R^{15}, providing that not more than one of R^{11}, R^{12}, R^{14} and R^{15} represents said radical containing said 5-pyrazolone coupler moiety when R^{13} represents said radical containing said 5-pyrazolone coupler moiety.

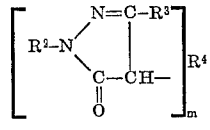
5. An image-forming layer containing light-sensitive silver halide and a stabilizer pyrazolone coupler compound having from 1 to 2 5-pyrazolone coupler moieties having substituted on at least one of the 1- and 3-ring positions of each of said 5-pyrazolone coupler moieties a radical containing an essentially non-coupling phenolic stabilizer moiety having the formula:



wherein R^5, R^8 and R^9 each represent a member selected from the class consisting of hydrogen, an alkyl group, and a radical containing said 5-pyrazolone coupler moiety connected to said stabilizer moiety by a divalent photographically inert organic linkage containing a group selected from the class consisting of a carbamylphenylcarbamylalkyl group, an aminophenylcarbamylalkyl group and an amidobenzamidophenylcarbamylalkyl group, such that the end of said linkage attached directly to a carbon atom in a ring of said stabilizer moiety is alkyl, and such that from 1 to 2 of R^5, R^8 and R^9 represents said radical containing said 5-pyrazolone moiety; and R^6, R^7 and R^{10} each represent a member selected from the class consisting of hydrogen, and an alkyl group.

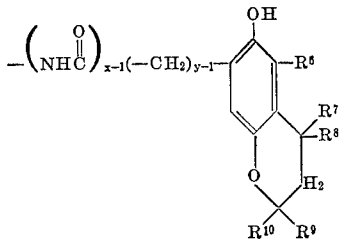
6. A light-sensitive hydrophilic colloid silver halide emulsion containing a stabilizer pyrazolone coupler compound having the formula:

I.

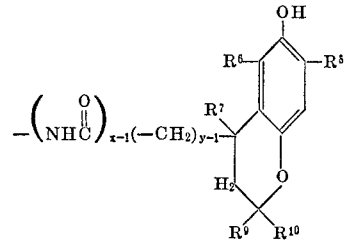


wherein R^2 represents a member selected from the class consisting of an alkyl group, an aryl group, a heterocyclic group, a carbamyl group and a thiocarbamyl group, such that said aryl group can include a stabilizer radical substituent selected from the class consisting of those having the formulas:

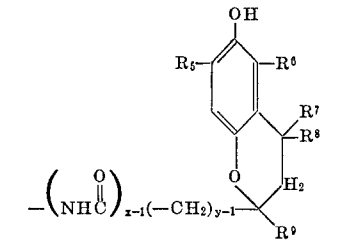
II.



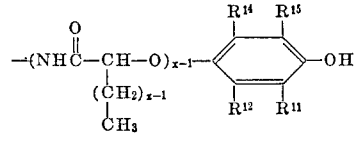
III.



IV.

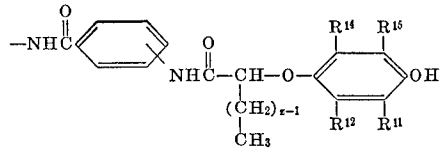


V.

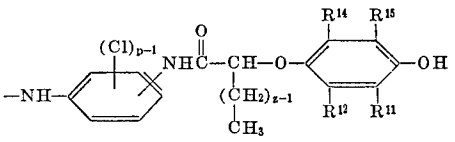


wherein x represents the interger 2; y represents an integer of from 2 to 4; z represents an integer of from 1 to 18; R^5, R^6, R^7, R^8, R^9 and R^{10} each represent a member selected from the class consisting of hydrogen and an alkyl group; R^{11}, R^{12}, R^{14} and R^{15} each represent a member selected from the class consisting of hydrogen, an alkyl group, an alkoxy group, an aryl group and an aryloxy group; R^{13} represents a member selected from the class consisting of an alkyl group, an alkoxy group, an aryl group and an aryloxy group; R^3 represents a member selected from the class consisting of hydrogen, an alkyl group, an aryl group, a heterocyclic group, a carboxy ester group, an alkoxy group, a phenoxy group, a lower alkthio group, a phenylthio group, an amino group, an amido group, a carbamyl group, a sulfonyl group, a ureido group, a thioureido group and a guanidino group, such that when R^3 represents a group selected from the class consisting of an amino group, an amido group and a carbamyl group, said amino, amido and carbamyl groups can include a group of Formulas II, III, IV, V, each described previously in which x represents the integer 2.

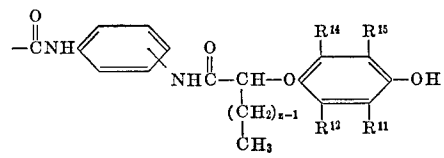
VI.



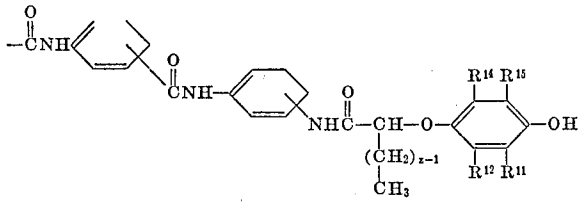
VII.



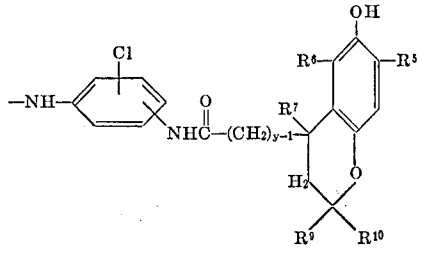
VIII.



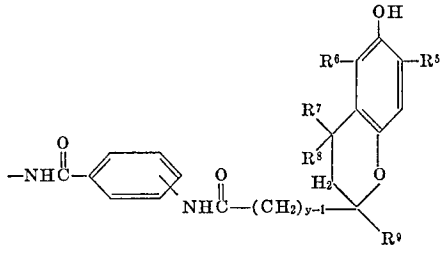
IX.



X.

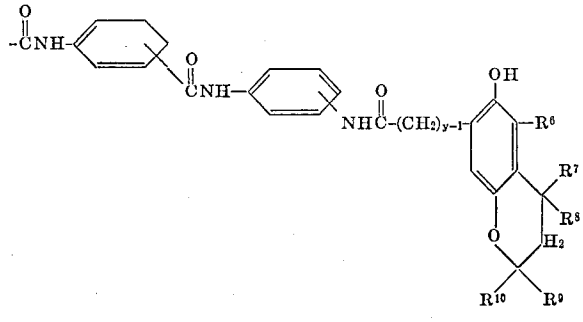


XI.



and

XII.



wherein R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{14}, R^{15} y and z are defined previously; m represents an integer of from 1 to 2; p represents an integer of from 1 to 2; R^4 represents a member selected from the class consisting of hydrogen, an alkyl group having from 1 to 22 carbon atoms, an aryloxy group, a heterocycloxy group, an arylazo group, an arylthio group, a 2-benzothiazolylthio group, an oxadiazolyl-2-thio group, an acyloxy group, an alkylidene group, an arylidene group, an arylene group, an arylenedioxy group, an arylenedithio group, a heterocyclene group, a diphenylsulfon group, and an ω,ω-phenylenealkyl group, such that R^4 represents a monovalent group when m represents the integer 1, and R^4 represents a divalent group when m represents the integer 2; and such that said stabilizer pyrazolone coupler compound has at least one of said stabilizer radicals.

7. A light-sensitive hydrophilic colloid silver halide emulsion containing a stabilizer pyrazolone coupler selected from the class consisting of 1-{4-[α-(3-t-butyl-4 - hydroxyphenoxy)tetradecanamido]-2,6-dichlorophenyl}-3-(2,4-dichloroanilino)-5-pyrazolone, 1-(2-chloro-4,6-dimethylphenyl) - 3-{3-[α- (3-t-butyl-4-hydroxyhenoxy) tetradecanamido]benzamido}-5-pyrazolone, 1 - (2,4,6-trichlorophenyl) - 3 - {3-[α- (3-t-butyl-4-hydroxyphenoxy) tetradecanamido]benzamido}-5-pyrazolone, 1 - (2,4,6,trichloropheny) - 3 - {5- [α-(3-t-butyl-4-hydroxyphenoxy) tetradecanamido] - 2 - chloroanilino} - 5 - pyrazolone, 1-{4 - [α - (3-t-butyl-4-hydroxyphenoxy)tetradecanamido]-2,6-dichlorophenyl}-3-(2,4-difluoroanilino)-5-pyrazolone, 1 - {4-[α(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]-2,6-dichlorophenyl}-3-(2-bromo-4-cyanoanilino)-5-pyrazolone, 1-(2-bromo-4,6-dichlorophenyl) -3-{2-chloro-4-[β-(2,2 - dimethyl-6-hydroxy-7-octadecyl-4-chromanyl) propionamido]anilino}-5-pyrazolone, and 1-(2,4,6,-trichlorophenyl) - 3 - {3 - [γ - (4,7-dioctyl-6-hydroxy-2-methyl-2-chromanyl)butyramido]benzamido}-5-pyrazolone.

8. A light-sensitive hydrophilic colloid silver halide emulsion containing the coupler 1 - {4 - [α-(3-t-butyl-4-hydroxyphenoxy) tetradecanamido] -2,6-dichlorophenyl}-3-(2,4-dichloroanilino)-5-pyrazolone.

9. A light-senstive hydrophilic colloid silver halide emulsion containing the coupler 1-(2-chloro-4,6-dimethylphenyl) - {3-[α-(3-t-butyl-4-hydroxyphenoxy) tetradecanamido]benzamido}-5-pyrazolone.

10. A light-sensitive hydrophilic colloid silver halide emulsion containing the coupler 1-(2-chloro-4,6-dimethylphenyl)-3-{3-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanamido]-5-pyrazolone.

11. A light-sensitive hydrophilic colloid silver halide emulsion containing the coupler 1-{4-[α-(3-t-butyl-4-hydroxyphenoxy) tetradecanamido]-2,6 - dichlorophenyl}-3-(4-cyanoanilino)-5-pyrazolone.

12. A light-sensitive hydrophilic colloid silver halide emulsion containing the coupler 1-(2,4,6-trichlorophenyl) - 3 - {5-[α- (3-t-butyl-4-hydroxyphenoxy) tetradecanamido]-2-chloroanilino}-5-pyrazolone.

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J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

96—56, 74

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,519,429 Dated July 7, 1970

Inventor(s) Gregory J. Lestina

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

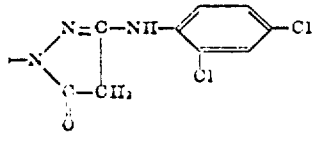
Column 1, line 15, replace "aid" with --- said ---;

Column 2, line 42, replace "intened" with --- intended ---;

Column 3, line 17, replace "in" with --- an ---; and line 32, after "spectral" delete the comma "(,)"; and line 69, replace "sulfoamido" with --- sulfonamido ---; and line 70, replace "sulfonyl" with --- sulfamyl ---;

Column 5, line 10, replace "quinalyene" with --- quinolyene---;

Column 6, line 46, replace the line with --- (1) 1-{4-[α-(3-t-butyl-4-hydroxyphenoxy)tetradecanami- ---; and line 49, correct the bonding of the formula to read (in the pyrazolone ring):



and line 59, correct the line to read as follows --- (2) 1-(2-chloro-4,6-dimethylphenyl)-3-{3-[α-(3-t-butyl- --- ;

Column 7, line 27-28, replace"[β-(3-t-butyl-4" with --- [β-(3-t-butyl,4 ---; and line 59, after "4-carboxy-phenoxy" insert a parenthesis --- ( )) ---;

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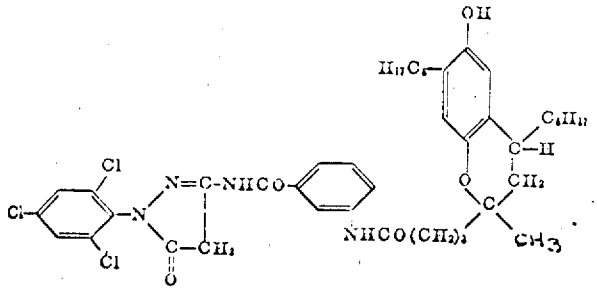
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,519,429 Dated July 7, 1970

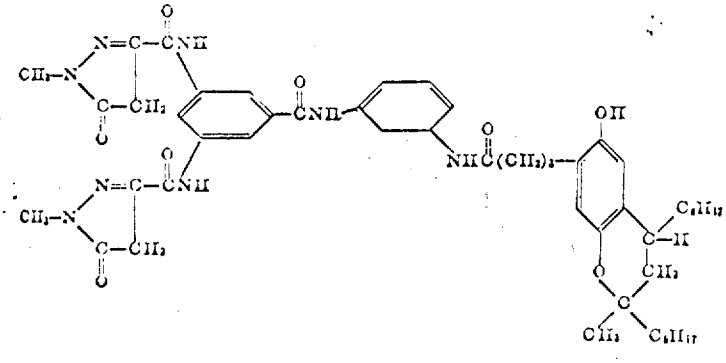
Inventor(s) Gregory J. Lestina PAGE - 2

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

Column 9, lines 31-61, Correct the bonding of the formulae, the methyl substituent group, and the description and positioning of Compound (31) to read as follows: ---



(31) 7 - {{γ - {3 - [3,5 - bis - (1 - methyl-3-pyrazol-5-onyl-carbonamido)benzamido]phenylcarbamyl}propyl}}-2,4-dioctyl-2-methyl-6-hydroxychroman



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CERTIFICATE OF CORRECTION

Patent No. 3,519,429 Dated July 7, 1970

Inventor(s) Gregory J. Lestina

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

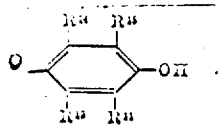
Column 11, line 25, replace "disposed" with --- dispersed ---; and line 49, replace "tests" with --- test ---.

Column 16, line 25, after "butylphenoxy" insert a parenthesis --- ( )) ---; and line 27, replace "string" with --- stirring ---.

Column 20, line 53, replace "R_m" with --- R^{11} ---; and line 5, after the formula insert --- and ---;

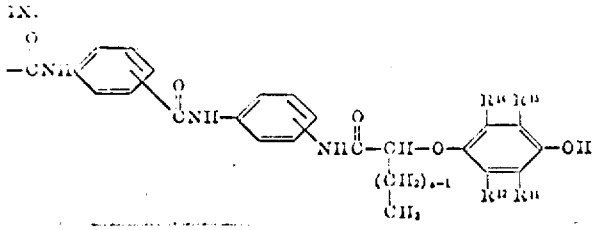
Column 21, line 16, replace "R_m" with --- R^{11} ---;

Column 22, line 52, replace the period "(.)" with a comma --- (,) ---; and line 70, correct formula VIII by inserting a bond between the oxygen atom and the right hand substituted phenyl moiety as follows: ---



--- ;

Column 23, line 5, correct formula IX to read as follows ---



--- ;

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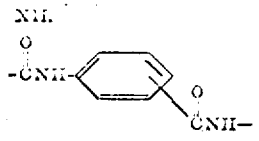
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,519,429 Dated July 7, 1970

Inventor(s) Gregory J. Lestina PAGE - 4

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

and line 35, correct the bonding of the left hand phenyl ring to read ---



---;

and line 49, after "R^{15}" insert a comma --- (,) ---;

Column 24, line 13, replace "chloropheny)" with --- chlorophenyl) ---; and line 30, after "phenyl)" insert --- -3 ---; and line 34, replace line to read --- phenyl)-3-[3-(3-t-butyl-4-hydroxyphenoxy)tetradecan- ---.

SIGNED AND
SEALED
JAN 19 1971

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents