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3,282,913

3-CARBAMYLPYRAZOLONE AZO COMPOUNDS

Milton Green, Newton Centre, Mass., assignor to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

No Drawing. Filed Aug. 9, 1963, Ser. No. 301,197
11 Claims. (Cl. 260—163)

This invention relates to photography and more particularly to novel chemical compounds for use in products, compositions and processes for the development of photosensitive silver halide elements.

This application is in part a continuation of my copending application Serial No. 130,468, filed August 10, 1961, now abandoned. The photographic utilization of the novel compounds of the present invention is claimed in my copending application Serial No. 301,181, filed concurrently herewith, now U.S. Patent 3,141,772, issued July 21, 1964.

A principal object of this invention is to provide novel chemical compounds.

Another object of this invention is to provide novel syntheses for preparing the novel compounds of the present invention.

Another object of the present invention is to provide novel processes and compositions for the development of silver halide emulsions, in which colored developing agents are used to develop a latent image.

Another object is to provide novel processes and compositions for the development of silver halide emulsions, in which the novel developing agent is capable of developing a latent image and imparting a reversed or positive colored image of said latent image to a superposed image-receiving material.

A further object is to provide novel products, processes and compositions suitable for use in preparing monochromatic and multichromatic photographic images.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the processes involving the several steps and the relation and order of one or more of such steps with respect to each of the others, and the products and compositions possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

The novel photographic developing agents employed in this invention possess the properties of both a dye and a developing agent; thus they may be referred to as dye developers. The nature of these dye developers will be described hereinafter.

The photographic processes and compositions disclosed herein are particularly useful in the treatment of an exposed silver halide emulsion, whereby a positive dye image may be imparted to another element, herein referred to as an image-carrying or image-receiving element.

U.S. Patent No. 2,983,606, issued May 9, 1961, to Howard G. Rogers, discloses diffusion transfer processes wherein a photographic negative material, such as a photographic element comprising an exposed silver halide emulsion is developed in the presence of a dye developer to impart to an image-receiving layer a reversed or positive dye image of the developed image by permeating into said emulsion layer a suitable liquid processing composition and bringing said emulsion layer into superposed relationship with an appropriate image-receiving layer.

It is an object of this invention to provide additional dye developers suitable for use in such processes.

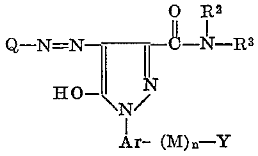
In carrying out the process of this invention, a photosensitive element containing a silver halide emulsion is exposed and wetted with a liquid processing composition, for example, by immersing, coating, spraying, flowing, etc., in the dark, and the photosensitive element superposed, prior to, during or after wetting, on an image-receiving element. In a preferred embodiment, the photosensitive element contains a layer of dye developer, and the liquid processing composition is applied to the photosensitive element in a uniform layer as the photosensitive element is brought into superposed position with an image-receiving element. The liquid processing composition permeates the emulsion to provide a solution of dye developer substantially uniformly distributed therein. As the exposed silver halide emulsion is developed, the oxidation product of the dye developer is immobilized or precipitated in situ with the developed silver, thereby providing an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition. This immobilization is apparently, at least in part, due to a change in the solubility characteristics of the dye developer upon oxidation, and especially as regards its solubility in alkaline solutions. It also may be due, in part, to a tanning effect on the emulsion by the oxidized developing agent. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer. Under certain circumstances, the layer of the liquid processing composition may be utilized as the image-receiving layer. The image-receiving layer receives a depthwise diffusion, from the emulsion, of unoxidized dye developer, without appreciably disturbing the imagewise distribution thereof, to provide a reversed or positive, colored image of the developed image. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer. If the color of the diffused dye developer is affected by changes in the pH of the image-receiving element, this pH may be adjusted in accordance with well-known techniques to provide a pH affording the desired color. Imbibition periods of approximately one minute have been found to give good results, but this contact period may be adjusted where necessary to compensate for variations in temperature or other conditions. The desired positive image is revealed by stripping the image-receiving element from the photosensitive element at the end of the imbibition period.

The dye developers of this invention may be utilized in the photosensitive element, for example in, on or behind the silver halide emulsion, or they may be utilized in the image-receiving element or in the liquid processing composition. In a preferred embodiment, a coating or layer of the dye developer is placed behind the silver halide emulsion, i.e., on the side of the emulsion adapted to be located most distant from the photographed subject when the emulsion is exposed and preferably also adapted to be most distant from the image-receiving element when in superposed relationship therewith. Placing the dye developer behind the emulsion layer, as in the preferred embodiment, has the advantage of providing increased contrast in the positive image, and also minimizes any light-filtering action by the colored dye developer. In this preferred embodiment, the layer of dye developer may be applied by using a coating solution containing about 0.5 to 8%, by weight, of the dye developer. Similar concentrations may be used if the dye developer is utilized as a component of the liquid processing composition. In an especially useful mode of dispersing the dye developers in the photosensitive elements, the dye developer is dissolved in a water-immiscible solvent and then dispersed in a gelatin coating solution.

The liquid precessing composition above referred to comprises at least an aqueous solution of an alkaline compound, for example, diethylamine, sodium hydroxide or sodium carbonate, and may contain the dye developer. In some instances, it may contain a minor amount of a conventional developing agent. If the liquid processing composition is to be applied to the emulsion by being spread thereon, preferably in a relatively thin, uniform layer, it may also include a viscosity-increasing compound constituting the film-forming material of the type which, when said composition is spread and dried, will form a relatively firm and relatively stable film. A preferred film-forming material is a high molecular weight polymer such as a polymeric, water-soluble ether inert to an alkali solution, as for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Other film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected when left in solution for a long period of time may also be used.

The novel chemical compounds of the present invention may be represented by the formula:

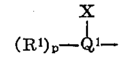
(A)



wherein Q is the radical of a diazotizable amine, Ar is a phenylene radical, M is a lower alkylene radical, *n* is an integer from 0 to 1, inclusive, Y is an ortho- or para-dihydroxyphenyl radical and alkyl and halogen derivatives thereof, R^2 and R^3 each may be hydrogen or an alkyl radical, and R^2 and R^3 together may be a divalent aliphatic radical, e.g., a pentamethylene radical completing, with the nitrogen atom, a piperidine ring. Preferably R^2 and R^3 contain no more than 10 to 12 carbons. It should also be understood that the term "alkyl," as represented by R^2 and R^3, is intended to include substituted alkyl radicals, e.g., hydroxyalkyl radicals.

Q, the diazotizable amine, is preferably a primary amine of the benzene or naphthalene series. The radical, Q, thus may be represented by the formula:

(B)

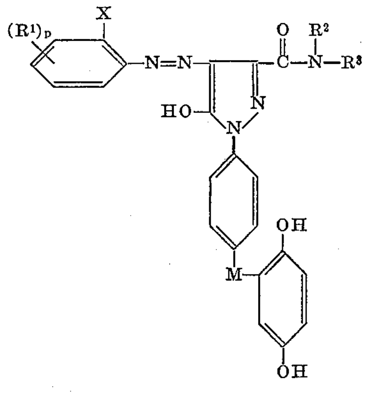


$$(R^1)_p-\overset{X}{\overset{|}{Q^1}}-$$

wherein Q^1 is a phenyl or naphthyl group, X is a hydrogen, halogen, lower alkyl, lower alkoxy, sulfonamido or trifluoromethyl radical, and X being located ortho to said —N=N— group, R^1 is a lower alkoxy, halogen, lower alkyl, trifluoromethyl or sulfonamido radical, and *p* is an integer from 0 to 4, inclusive.

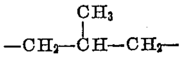
In a preferred embodiment, Q^1 is a substituted phenyl group, *n* is 1, and Y is a para-dihydroxphenyl radical. Such compounds may be represented by the formula:

(C)



wherein R^1, *p*, X, R^2, R^3 and M have tthe same meaning as above.

As examples of alkylene radicals comprehended by the radical M, mention may be made of radicals such as —CH_2—CH_2—,



$$-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-$$

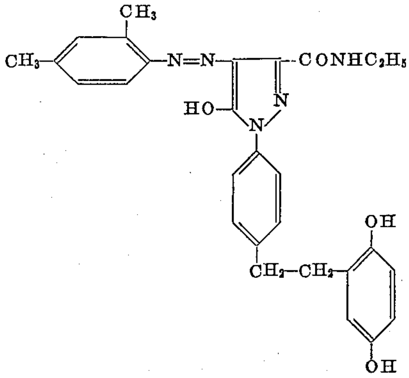
and —CH_2—CH_2—CH_2—. The preferred embodiment is a lower alkylene group, e.g., less than 6 carbons, and more preferably an ethylene group. It should be understood that M may be an alkylene group comprising 6 or more carbon atoms provided that the resulting dye developer is capable of being dissolved in the liquid processing composition, and its oxidation product rendered immobile.

As noted above, Q may be derived from any amine which is capable of diazotization. When Q is a phenyl radical, in addition to the ortho substituent X, the phenyl radical may also contain other substituents, above designated R^1 in the 3, 4, 5 or 6 position or any combination thereof. The particular substituent selected and its specific position may be determined by one skilled in the art guided by the teachings of the present invention and with due regard to the substituent's effect on the color, solubility and light stability of the compound.

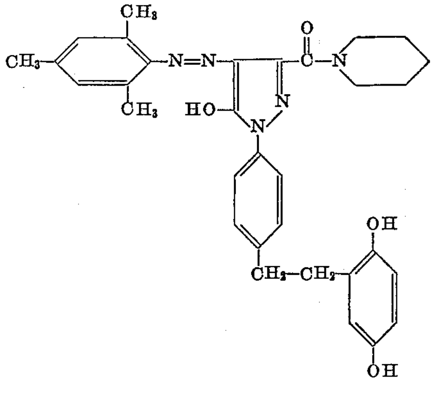
As examples of substituents represented as R^1, mention may be made of methyl, ethyl, chloro, methoxy, and ethylsulfonamido. It should be understood that R^1 may be further substituted, if desired.

The copending application of Milton Green, Serial No. 268,451, filed January 14, 1963, discloses and claims compounds within Formula B wherein X and R^1 are sulfonamido radicals.

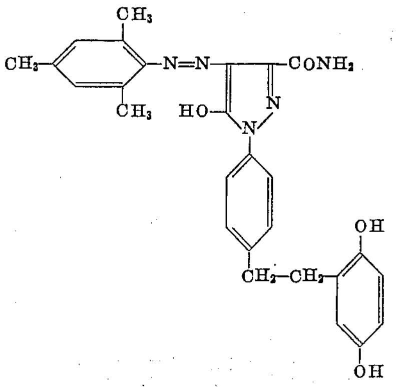
As examles of novel chemicals within the scope of the present invention, mention may be made of the following:



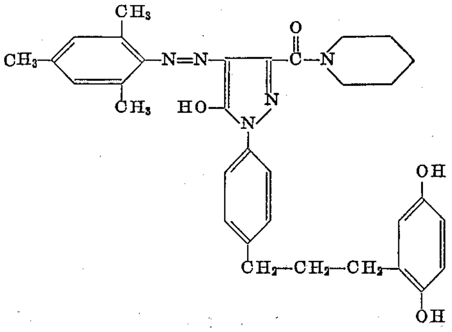
(1) 1-(4''-hydroquinonylethylphenyl)-3-N-ethylcarbamyl-4-(2'-4'-dimethylphenylazo)-5-pyrazolone



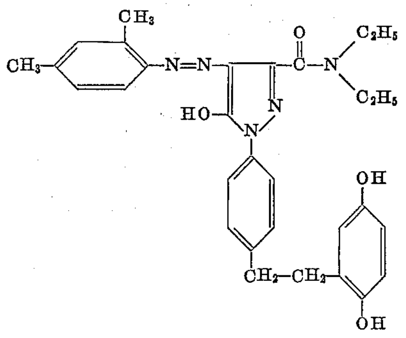
(2) 1-(4''-hydroquinonylethylphenyl)-3-(N-pentamethylene)-carbamyl-4-(2',4',6'-trimethylphenylazo)-5-pyrazolone



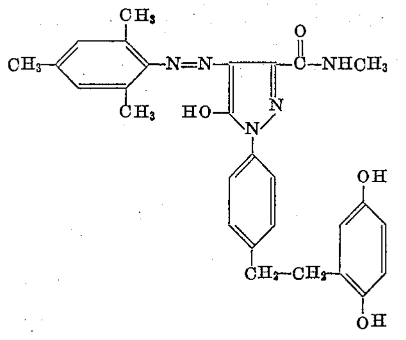
(3) 1-(4″-hydroquinonylethylphenyl)-3-carbamyl-4-(2′,4′,6′-trimethylphenylazo)-5-pyrazolone



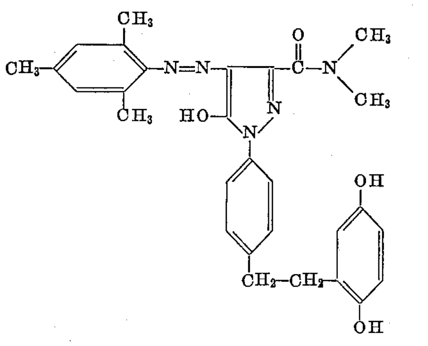
(4) 1-(4″-hydroquinonylethylphenyl)-3-(N-pentamethylene)-carbamyl-4-(2′,4′,6′-trimethylphenylazo)-5-pyrazolone



(5) 1-(4″-hydroquinonylethylphenyl)-3-N,N-diethylcarbamyl-4-(2′,4′-dimethylphenylazo)-5-pyrazolone

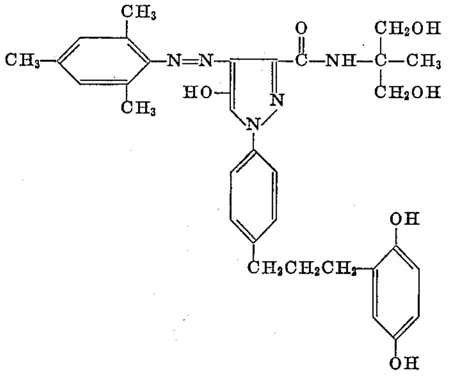


(6) 1-(4″-hydroquinonylethylphenyl)-3-N-methylcarbamyl-4-(2′,4′,6′-trimethylphenylazo)-5-pyrazolone

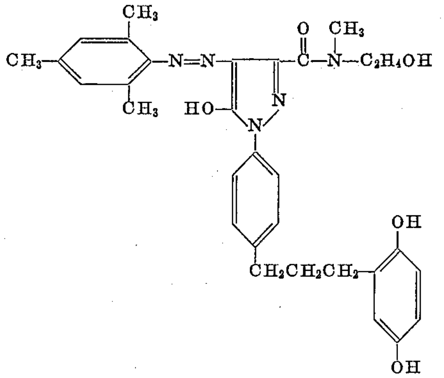


(7) 1-(4″-hydroquinonylethylphenyl)-3-N,N-dimethylcarbamyl-4-(2′,4′,6′-trimethylphenylazo)-5-pyrazolone

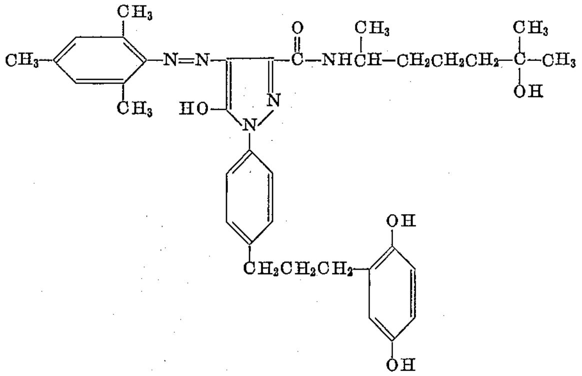
(8) 1-(4″-hydroquinonylpropylphenyl)-3-carbamyl-4-(2′,4′,6′-trimethylphenylazo)-5-pyrazolone



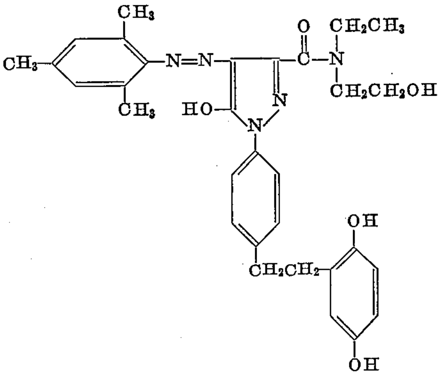
(9) 1-(4″-hydroquinonylpropylphenyl)-3-(N-*a*,*a*′-bishydroxymethyl)-ethyl-carbamyl-4-(2′,4′,6′-trimethylphenylazo)-5-pyrazolone



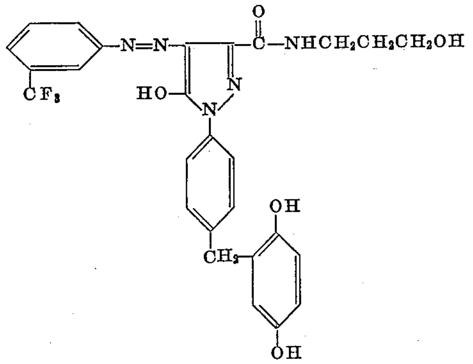
(10) 1-(4″-hydroquinonylpropylphenyl)-3-(N-ethyl-N′-hydroxyethylcarbamyl)-4-(2′,4′,6′-trimethylphenylazo)-5-pyrazolone



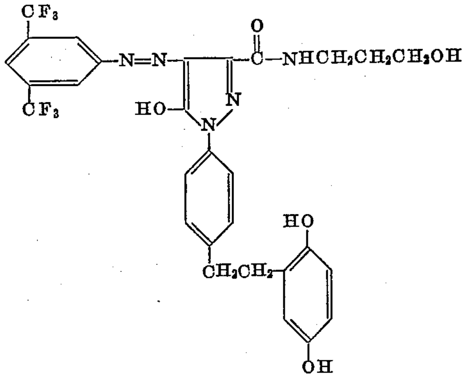
(11) 1-(4″-hydroquinonylpropylphenyl)-3-(N-[1′,5′-dimethyl-5′-hydroxyhexyl])-carbamyl-4-(2′,4′,6′-trimethylphenylazo)-5-pyrazolone



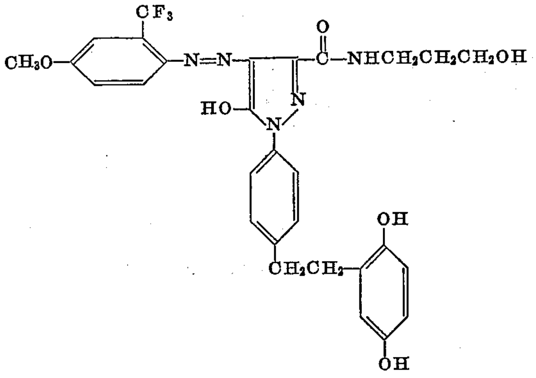
(12) 1-(4″-hydroxyquinonylethylphenyl)-3-[N-ethyl, N-(β-hydroxy) - ethyl]-carbamyl-4-(2′,4′,6′-trimethylphenylazo)-5-pyrazolone



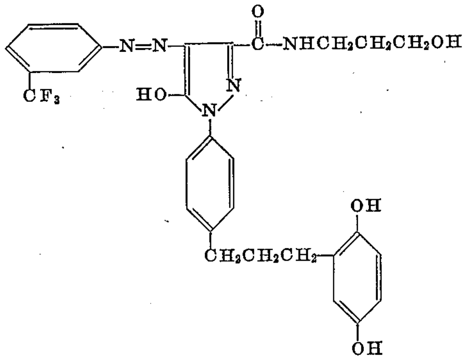
(13) 1-(4″-hydroquinonylmethylphenyl) - 3 - (N-hydroxypropyl)-carbamyl - 4 - (3′ - trifluoromethylphenylphenylazo)-5-pyrazolone



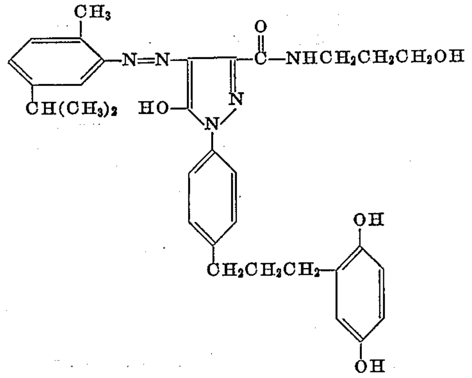
(14) 1-(4″-hydroquinonylethylphenyl)-3-(N-hydroxypropyl)-carbamyl-4-(3′,5′-ditrifluoromethylphenylazo)-5-pyrazolone



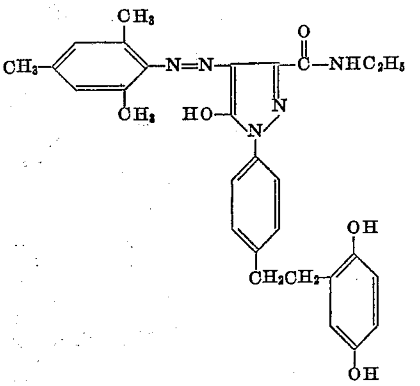
(15) 1-(4″-hydroquinonylethylphenyl)-3-(N-hydroxypropyl)-carbamyl-4-(2′-trifluoromethyl - 4′ - methoxyphenylazo)-5-pyrazolone



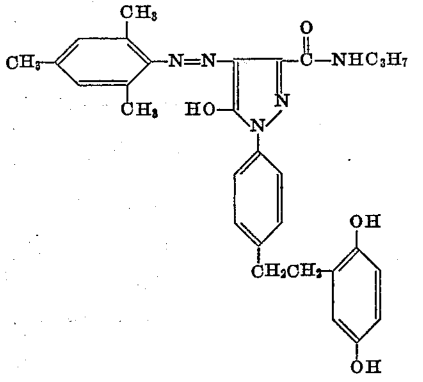
(16) 1-(4″-hydroquinonylpropylphenyl)-3-N-(3′-hydroxypropyl)-carbamyl-4-(3′-trifluoromethylphenylazo)-5-pyrazolone



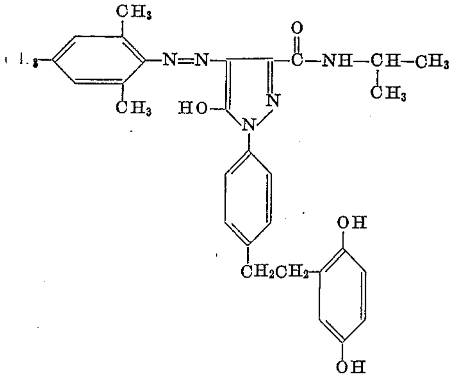
(17) 1-(4″-hydroquinonylpropylphenyl)-3-N-(3′-hydroxypropyl)-carbamyl - 4 - (2′-methyl-5′-isopropylphenylazo)-5-pyrazolone



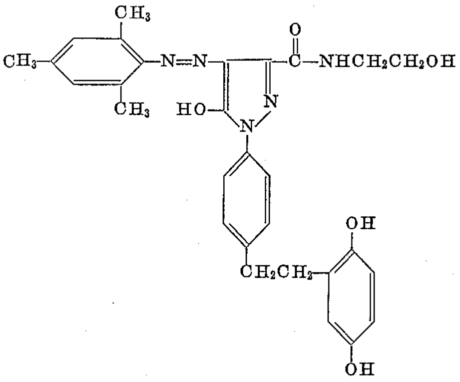
(18) 1-(4″-hydroquinonylethylphenyl)-3-N-propylcarbamyl-4-(2′,4′,6′-trimethylphenylazo)-5-pyrazolone



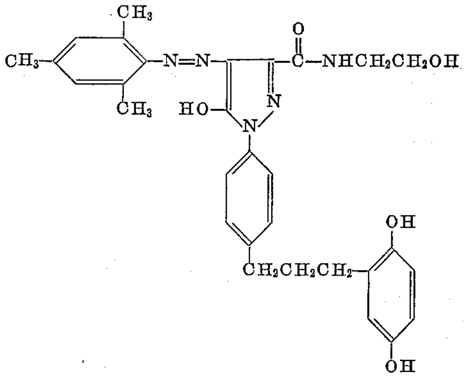
(19) 1-(4″-hydroquinonylethylphenyl)-3-N-n-propylcarbamyl-4-(2′,4′,6′-trimethylphenylazo)-5-pyrazolone



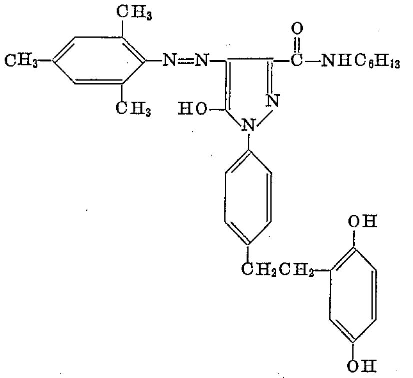
(20) 1-(4''-hydroquinonylethylphenyl)-3-N-isopropylcarbamyl-4-(2',4',6'-trimethylphenylazo)-5-pyrazolone



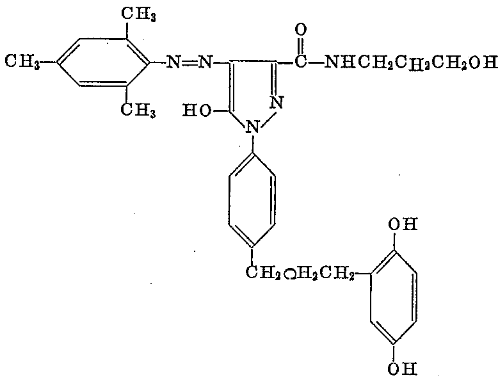
(21) 1-(4''-hydroquinonylethylphenyl)-3-(N-hydroxyethyl)-carbamyl-4-(2',4',6'-trimethylphenylazo)-5-pyrazolone



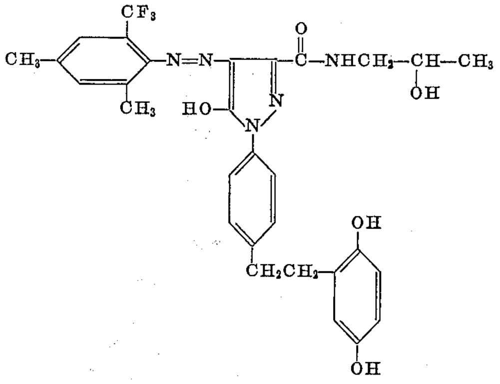
(22) 1-(4''-hydroquinonylpropylphenyl)-3-(N-hydroxyethyl)-carbamyl-4-(2',4',6'-trimethylphenylazo)-5-pyrazolone



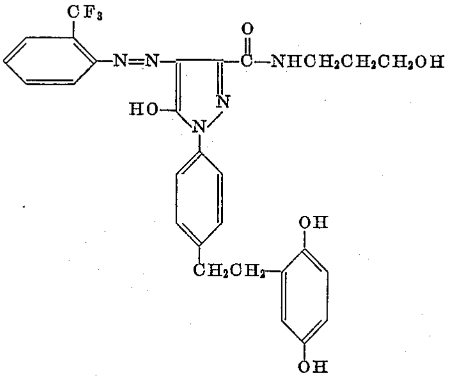
(23) 1-(4''-hydroquinonylethylphenyl)-3-hexylcarbamyl-4-(2',4',6'-trimethylphenylazo)-5-pyrazolone



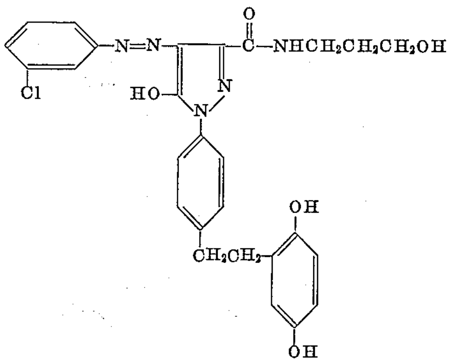
(24) 1-(4''-hydroquinonylpropylphenyl) - 3 - (N-hydroxypropyl)-carbamyl-4-(2',4',6'-trimethylphenylazo)-5-pyrazolone



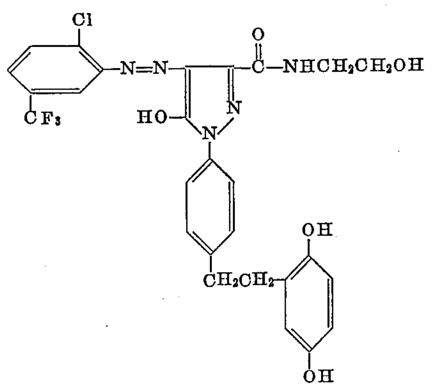
(25) 1-(4''-hydroquinonylethylphenyl)-3-(2'-hydroxypropyl)-carbamyl-4-(2',4',6'-trimethylphenylazo)-5-pyrazolone



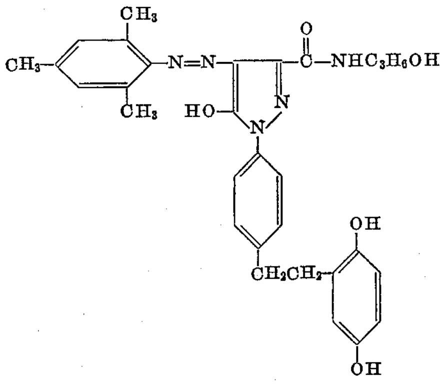
(26) 1-(4''-hydroquinonylethylphenyl)-3-(N-hydroxypropyl)-carbamyl-4-(2'-trifluoromethylphenylazo)-5-pyrazolone



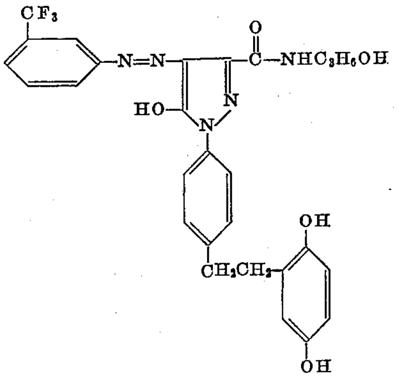
(27) 1-(4''-hydroquinonylethylphenyl)-3-(N-hydroxypropyl)-carbamyl-4-(3'-chlorophenylazo)-5-pyrazolone



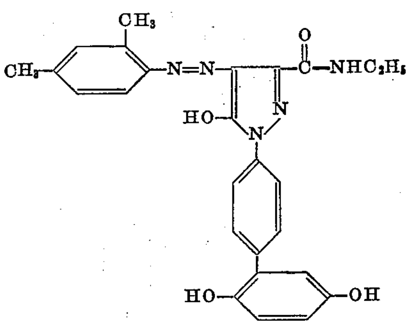
(28) 1-(4''-hydroquinonylethylphenyl)-3-(N-hydroxypropyl)-carbamyl-4-(2'-chloro - 5' - trifluoromethylphenylazo)-5-pyrazolone



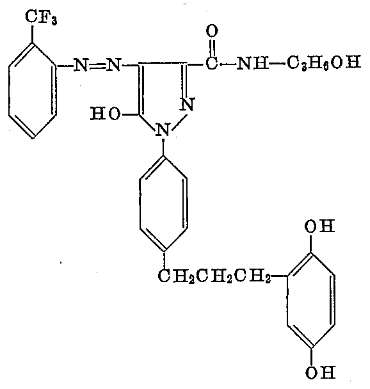
(29) 1-(4''-hydroquinonylethylphenyl)-3-N-(hydroxypropyl)-carbamyl-4-(2',4',6'-trimethylphenylazo)-5-pyrazolone



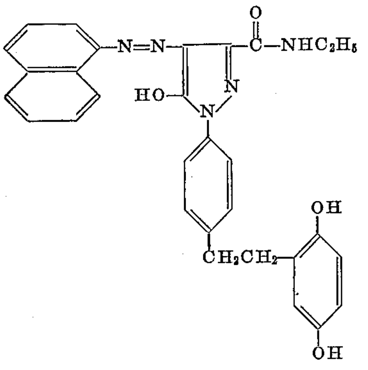
(30) 1-(4''-hydroquinonylethylphenyl)-3-N-(hydroxypropyl)-carbamyl-4-(3'-trifluoromethylphenylazo)-5-pyrazolone



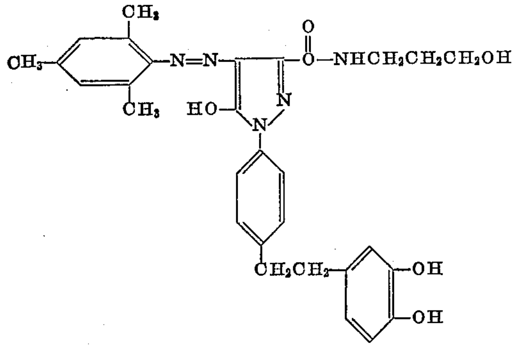
(31) 1-(4''-hydroquinonylphenyl)-3-N-ethylcarbamyl-4-(2',4'-dimethylphenylazo)-5-pyrazolone



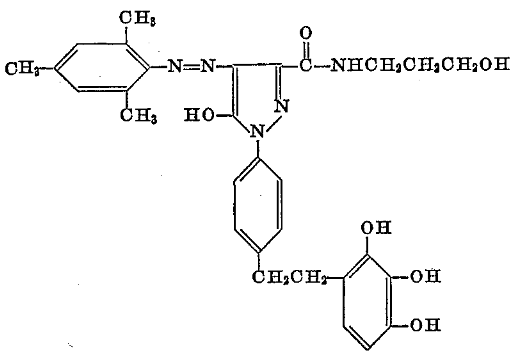
(32) 1-(4''-hydroquinonylpropylphenyl)-3-N-(3'-hydroxypropyl)-carbamyl-4-(2'-trifluoromethylphenylazo)-5-pyrazolone



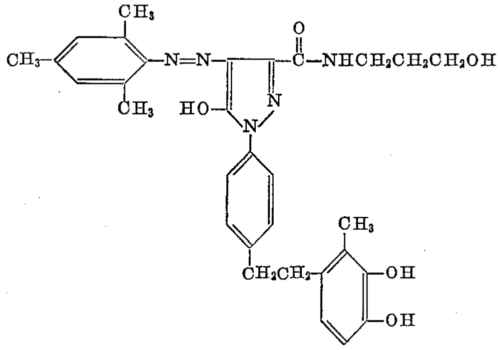
(33) 1-(4''-hydroquinonylethylphenyl)-3-N-ethylcarbamyl-4-(1'-naphthylazo)-5-pyrazolone



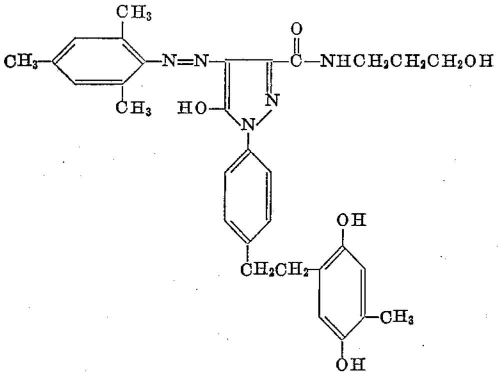
(34) 1-[4''-(β-[3''',4'''-dihydroxyphenyl]-ethyl) - phenyl]-3-carbethoxy-4-(2',4',6-trimethylphenylazo-5-pyrazolone



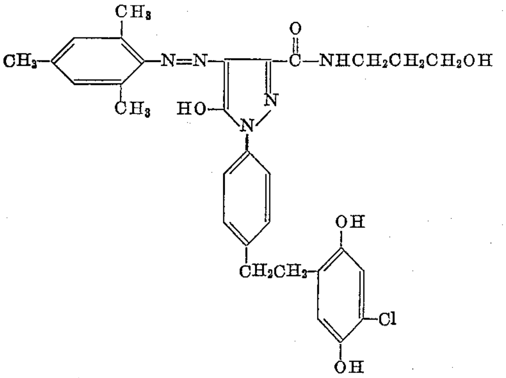
(35) 1-[4''-(β-[2'''-chloro-3''',4'''-dihydroxyphenyl]-ethyl)-phenyl] - 3 - carbethoxy-4-(2',4',6'-trimethylphenylazo)-5-pyrazolone



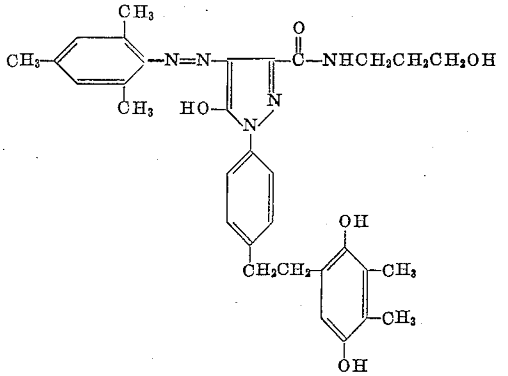
(36) 1-[4′′-(β-[2′′′-methyl-3′′′,4′′′dihydroxyphenyl]-ethyl)-phenyl] - 3 - carbethoxy-4-(2′,4′,6′-trimethylphenylazo)-5-pyrazolone



(37) 1-[4′′-(β-[4′′′-methyl-2′′′,3′′′-dihydroxyphenyl]-ethyl)-phenyl]-3-(N-hydroxypropyl)-carbamyl-4-(2′,4′,6′-trifluoromethylphenylazo)-5-pyrazolone

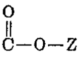


(38) 1-[4′′-(β-[4′′′-chloro-2′′′,5′′′-dihydroxyphenyl]-ethyl)-phenyl]-3-(N-hydroxypropyl) - carbamyl-4-(3-trifluoromethylphenylazo)-5-pyrazolone



(39) 1-[4′′-(β-[3′′′,4′′′-dimethyl-2′′′,5′′′-dihydroxyphenyl]-ethyl)-phenyl]-3-(N-hydroxypropyl)-carbamyl - 4 - (2′,4′,6′-trifluoromethylphenylazo)-5-pyrazolone

The dye developers disclosed and claimed in the copending application of Milton Green, Serial No. 301,198, filed concurrently herewith, when the radical in the 3-position is an ester, have been found to be susceptible to hydrolysis, during synthesis, of the



$$-\overset{\overset{\large O}{\|}}{C}-O-Z$$

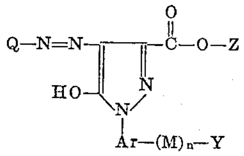
radical in the 3-position of the pyrazolone ring, wherein Z is an alkyl radical. The corresponding free acid is difficult to separate from the corresponding ester, and the presence of the free acid may detract from the usefulness of such dye developers in some (but not all) photographic applications e.g., by giving undesired transfer in diffusion transfer applications because of the greater solubility and mobility of the free acid than of the corresponding ester.

It has now been found that the compounds of the present invention wherein the carboxylate radical has been replaced by a carbamyl radical retain many of the desirable properties of said dye developers but without the susceptibility to hydrolysis.

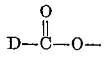
The dye developers of this invention, compared to the dye developers of this copending application of Milton Green, Serial No. 301,198, filed concurrently herewith, wherein the radical in the 3-position is an ester radical, do not exhibit hydrolysis of the 3-carbamyl group during synthesis, e.g., during hydrolysis of the acylated Y radical during synthesis, or under the conditions present during photographic utilization. By the replacement of the ester group by an amide group many advantages of the dye developers of the copending application, e.g., improved silver halide developing properties and increased light stability characteristics, have been retained while a serious disadvantage, i.e., the tendency of the ester group, particularly a 3-carbethoxy group, to undergo hydrolysis during synthesis, has been eliminated.

The novel chemical compounds of the present invention may be prepared by replacement of the 3-carboxylate group with an amide group in a compound of the formula:

(D)



wherein Z is a lower alkyl radical and Q, Ar, M, *n* and Y have the same meaning as above, by reacting said compound with an amine. The novel compounds of the present invention may also be prepared from the compound of Formula D wherein the dihydroxyphenyl group is the protected derivative, preferably the acylated derivative. The term "acyloxy" is intended to signify the grouping



$$D-\overset{\overset{\large O}{\|}}{C}-O-$$

wherein D is an aryl, alkyl, arloxy, or alkoxy group. The terms "alkyl" and "aryl" as employed herein are intended to include substituted aryl and alkyl groups.

As examples of amines suitable for use in the present invention, mention may be made of alcoholic ammonia, primary amines, such as ethylamine, secondary amines, such as diethylamine, heterocyclic amines, such as piperidine, hydrazines, hydroxylamines and guanidine.

The process for the preparation of the novel chemical compounds of the present invention is disclosed and claimed in the copending application of Milton Green, Serial No. 130,467, filed August 10, 1961, now abandoned.

The following nonlimiting examples illustrate the preparation of dye developers within the scope of this invention.

Example 1

A 100 ml. stainless steel bomb containing 5.84 gm. (0.01 M) of 1-(4″-hydroquinonylphenethyl)-3-carbethoxy-4-(4′-methylphenylazo)-5-pyrazolone was chilled in a Dry Ice bath and flushed with nitrogen. 30 ml. of ethylamine were then added and the bomb was sealed and heated on the steam bath overnight. The bomb was then cooled to below room temperature and opened. The excess ethylamine was removed by passing a stream of nitrogen through the reaction mixture. The temperature of the bomb was maintained at room temperature and deaerated dilute hydrochloric acid was added. The resulting solid was filtered, washed with more dilute hydrochloric acid and dried with suction. The product, 1-(4″-hydroquinonylethylphenyl) - 3 - N - ethyl - carbambly-4-(2′,4′-dimethylphenylazo)-5-pyrazolone, melted at 245° C. with decomposition and showed the following analysis calculated for $C_{23}H_{29}N_5O_4$:

Calculated: C, 67.4; H, 5.7; N, 14.0. Found: C, 67.2; H, 5.9; N, 13.6.

Eyample II

100 ml. of 40% methylamine were placed in a 250 ml. round bottom flask, flushed with nitrogen for 5 minutes. 5.51 gm. (0.01 M) of 1-(4″-hydroquinonylethylphenyl)-3 - carbethoxy - 4 - (2′,4′,6′ - trimethylphenylazo) - 5-pyrazolone were added to the flask. The flask was fitted with a condenser, and an adapter and a balloon were fitted to the open end of the condenser. The mixture was left standing overnight. The excess methylamine was then boiled off on the steam bath. Deaerated dilute hydrochloric acid was added to the reaction mixture and the resulting solid was filtered, washed with dilute hydrochloric acid and sucked dry. The product, 1-(4″-hydroquinonylethylphenyl) - 3 - N - methyl - carbamy - 4-(2′,4′,6′ - trimethylphenylzo) - 5 - pyrazolone, melted at 206–7° C. with decomposition. The spectral absorption curve exhibited a $\lambda_{max.}$ at 438 mμ; $\epsilon=18,000$.

Example III

1 - (4″ - hydroquinonylethylphenyl) - 3 - carbethoxy-4 - (2′,4′,6′ - trimethylphenylazo) - 5 - pyrazolone was treated with an excess of dimethylamine for 16 hours at 90–100° C. The resulting product, 1-(4″-hydroquinonylethylphenyl) - 3 - N,N - dimethylcarbamyl - 4 - (2′,4′,6′-trimethylphenylazo)-5-pyrazolone melted at 210-11° C., with decomposition. The spectral absorption curve showed a $\lambda_{max.}$ at 415 mμ; $\epsilon=18,800$.

Example IV

1 - (4″ - hydroquinonylethylphenyl) - 3 - carbethoxy-4 - (2′,4′,6′ - trimethylphenylazo) - 5 - pyrazolone was heated with an excess of piperidine for 16 hours at 90–100° C. The resulting product, 1 - (4″ - hydroquinonylethylphenyl) - 3 - (N - pentamethylene) - carbamyl - 4-(2′,4′,6′-trimethylphenylazo) - 5 - pyrazolone melted at 219–21° C. The spectral absorption curve exhibited a $\lambda_{max.}$ at 412 mμ; $\epsilon=19,000$.

Example V

1 - (4″ - hydroquinonylethylphenyl) - 3 - carbethoxy-4 - (2′,4′,6′ - trimethylphenylazo) - 5 - pyrazolone was heated with alcoholic ammonia for 16 hours at 90–100° C. The resulting product, 1 - (4″ - hydroquinonylethylphenyl) - 3 - carbamyl - 4 - (2′,4′,6′ - trimethylphenylazo) - 5 - pyrazolone, melted at 201.5–202.5° C. The spectral absorption curve exhibited a $\lambda_{max.}$ at 440 mμ; $\epsilon=17,400$.

Example VI

1 - (4″ - hydroquinonylethylphenyl) - 3 - N,N - diethylcarbamyl - 4 - (2′,4′,6′ - trimethylphenylazo) - 5 - pyrazolone was prepared by treating 1 - (4″ - hydroquinonylethylphenyl) - 3 - carbethoxy - 4 - (2′,4′,6′ - trimethylphenylazo) - 5 - pyrazolone with an excess of diethylamine for 16 hours at 90–100° C.

Example VII

1 - (p - [2′,5′ - diacetoxyphenylpropyl] - phenyl) - 3-carbethoxy - 4 - (2′,4′,6′ - trimethylphenylazo) - 5-pyrazolone was treated with methylaminoethanol in a nitrogen atmosphere to provide 1 - (4″ - hydroquinonylpropylphenyl) - 3 - (N - ethyl - N′ - hydroxyethyl) - carbamyl - 4 - (2′,4′,6′ - trimethylphenylazo) - 5 - pyrazolone melting at 201–203° C. with decomposition.

Example VIII

1 - (p - [2′,5′ - diacetoxyphenylpropyl] - phenyl) - 3-carbethoxy - 4 - (2′,4′,6′ - trimethylphenylazo) - 5 - pyrazolone was treated with 3-amino-1-propanol at 90–95° C. to provide 1 - (4″ - hydroqinonylpropyl) - 3 - (n-hydroxypropyl) - carbamyl - 4 - (2′,4′,6′ - trimethylphenylazo)-5-pyrazolone, melting at 162–164° C.

Example IX

1 - (p - [2′,5′ - diacetoxyphenethyl] - phenyl) - 3-carbethoxy - 4 - (2′,4′,6′ - trimethylphenylazo) - 5 - pyrazolone was heated with an excess of n-propylamine to provide (4″ - hydroquinonylethylphenyl) - 3 - N - n-propylcarboxamido - 4 - (2′,4′,6′ - trimethylphenylazo)-5-pyrazolone, melting at 115–117° C.

Example X

1 - (p - [2′,5′ - diacetoxyphenylpropyl] - phenyl) - 3-carbethoxy - 4 - (2′,4′,6′ - trimethylphenylazo) - 5 - pyrazolone was heated in a nitrogen atmosphere with an excess of 2 - amino - 2 - methyl - 1,3 - propanediol to provide 1 - (4′ - hydroquinonylpropylphenyl) - 3 - (N-β,β′-bishydroxymethyl) - ethyl - carbamyl - 4 - (2′,4′,6′ - trimethylphenylazo) - 5 - pyraxolone which melted at 135–140° C.

Example XI

1 - (p - [2′,5′ - diacetoxyphenethyl] - phenyl) - carbethoxy - 4 - (2′,4′,6′ - trimethylphenylazo) - 5 - pyrazolone was treated with 1-amino-2-propanol to provide 1-(4″ - hydroquinonylethylphenyl) - 3 - (2′ - hydroqinonylethylphenyl) - 3 - (2′ - hydroxypropyl) - carbamyl - 4-(2′,4′,6′ - trimethylphenylazo) - 5 - pyrazolone, melting at 206–207° C.

The dye developers of this invention are also useful in integral multilayer photosensitive elements for use in multicolor diffusion transfer process. As an example of such photosensitive elements, mention may be made of the photosensitive elements disclosed and claimed in the copending U.S. application of Edwin H. Land and Howard G. Rogers, Serial No. 565,135, filed February 13, 1956, wherein at least two selectively sensitized photosensitive strata are superposed on a single support and are processed, simultaneously and without separation, with a single common image-receiving element. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum, said emulsions having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. In one of the preferred embodiments of photosensitive elements of this type, the dye developers are disposed in separate alkali-permeable layers behind the photosensitive silver halide emulsion stratum with which they are associated.

The photosensitive elements within the scope of this invention may be used in roll film units which contain a plurality of photosensitive frames. The photosensitive elements of this invention are especially useful in composite roll film intended for use in a "Polaroid Land Camera," or a similar camera structure such, for example, as the camera forming the subject matter of U.S. Patent No. 2,435,717, issued to Edwin H. Land on February 10, 1948. In general, such composite roll films comprise a photosensitive roll, a roll of image-receiving material and a plurality of pods containing an aqueous alkaline processing solution. The rolls and pods are so associated with each other that, upon processing, the photosensitive element may be superposed on the image-receiving element and the pods may be ruptured to spread the aqueous alkaline processing solution between the superposed elements. The nature and construction of the pods used in such units are well known to the art. See, for example, U.S. Patents Nos. 2,543,181 and 2,634,886, issued to Edwin H. Land.

It will be noted that the liquid processing composition may contain one or more auxiliary or accelerating silver halide developing agents, such as p-methylaminophenol (Metol); 2,4-diaminophenol (Amidol); benzylaminophenyl; hydroquinone; a substituted hydroquinone such as toluhydroquinone, phenylhydroquinone, or 4′-methylphenylhydroquinone; or a 3-pyrazolidone such as 1-phenyl-3-pyrazolidone. These silver halide developing agents are substantially colorless, at least in their unoxidized form. It is possible that some of the dye developer oxidized in exposed areas may be oxidized by an energy transfer reaction with oxidized auxiliary developing agent.

In addition, development may be effected in the presence of an onium compound, particularly a quaternary ammonium compound, in accordance with the processes disclosed and claimed in the copending U.S. application of Milton Green and Howard G. Rogers, Serial No. 50,851, filed August 22, 1960, and now U.S. Patent No. 3,173,786.

The dye developers of this invention may be used also in conventional photographic processes, such as tray or tank development of conventional photosensitive films, plates or papers to obtain black and white, monochromatic or toned prints or negatives. By way of example, a developer composition suitable for such use may comprise an aqueous solution of approximately 1–2% of the dye developer, 1% sodium hydroxide, 2% sodium sulfite and 0.05% potassium bromide. After development is completed, any unreacted dye developer is washed out of the photosensitive element, preferably with an alkaline washing medium or other medium in which the unreacted dye developer is soluble. The expression "toned" is used to designate photographic images wherein the silver is retained with the precipitated dye, whereas "monochromatic" is intended to designate dye images free of silver.

It should be noted that the dye developers of this medium are self sufficient to provide the desired color image and do not depend upon coupling reactions to produce the desired color. They thus provide a complete departure from conventional photographic color processes in which the color is produced by a coupling reaction between a "color former" or "coupler" and the oxidized developing agent, as well as so-called auto-coupling processes in which color is obtained by a reaction of the oxidized developing agent with unoxidized develoipng agent.

It will be apparent that, by appropriate selection of the image-receiving element from among suitable known opaque and transparent materials, it is possible to obtain either a colored positive reflection print or a colored positive transparency. Likewise, the inventive concepts herein set forth are adaptable for multicolor work by the use of special photographic materials, for example, film materials of the type containing two or more photosensitized elements associated with an appropriate number of image-receiving elements and adapted to be treated with one or more liquid processing compositions, appropriate dye developers suitable to impart the desired subtractive colors being incorporated in the photosensitized elements or in the liquid processing compositions. Examples of such photographic materials are disclosed in U.S. Patent No. 2,647,049 to Edwin H. Land.

As examples of useful image-receiving materials, mention may be made of nylon, e.g., N-methoxymethyl-polyhexamethylene adipamide, polyvinyl alcohol, and gelatin, particularly polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine. The image-receiving element also may contain a development restrainer, e.g., 1-phenyl-5-mercaptotetrazole, as disclosed in the copending application of Howard G. Rogers and Harriet W. Lutes, Serial No. 50,849, filed August 22, 1960.

The inventive concepts herein set forth are also adaptable for the formation of colored images in accordance with the photographic products and processes described and claimed in U.S. Patent No. 2,968,559, issued to Edwin H. Land on January 17, 1961.

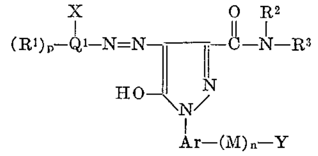
The novel compounds herein disclosed are also suitable for use as dyes for textile fibres, such as nylon.

In the preceding portions of the specification the expression "color" has been frequently used. This expression is intended to include the use of a plurality of colors to obtain black.

Since certain changes may be made in the above products, compositions and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A compound of the formula:



wherein R^1 is a radical selected from the group consisting of lower alkyl, lower alkoxy, chlorine and trifluoromethyl radicals; *p* is an integer from 0 to 4, inclusive; X is a radical selected from the group consisting of hydrogen, chlorine, lower alkyl, lower alkoxy, and trifluoromethyl radicals, said X being located ortho to said —N=N— group; Q^1 is a radical selected from the group consisting of phenyl and naphthyl radicals; Ar is a phenylene radical; M is a lower alkylene radical; *n* is an integer from 0 to 1, inclusive; Y is a radical selected from the group consisting of ortho- and para-dihydroxyphenyl radicals and lower alkyl and chlorine derivatives thereof; and R^2 and R^3 each are selected from the group consisting of hydrogen and lower alkyl radicals, and R^2 and R^3 taken together may be a pentamethylene radical.

2. 1 - (4″ - hydroquinonylethylphenyl)-3-N-ethylcarbamly-4-(2′,5′-dimethylphenylazo)-5-pyrazolone.

3. 1-(4″-hydroquinonylethylphenyl) - 3 - (N - pentamethylene)-carbamyl - 4 - (2′,4′,6′-trimethylphenylazo)-5-pyrazolone.

4. 1-(4″-hydroquinonylethylphenyl) - 3 - carboxamido-4-(2′,4′,6′-trimethylphenylazo)-5-pyrazolone.

5. 1-(4″-hydroquinonylethylphenyl) - 3 - N,N-diethylcarbamyl-4-(2′,4′,6′-trimethylphenylazo)-5-pyrazolone.

6. 1-(4″-hydroquinonylethylphenyl) - 3 - N - methylcarbamyl-4-(2′,4′,6′-trimethylphenylazo)-5-pyrazolone.

7. 1-(4″-hydroquinonylpropylphenyl) - 3 - (N - hydroxypropyl)-carbamyl - 4 - (2′ - trifluoromethylphenylazo)-5-pyrazolone.

8. 1 - (4″ - hydroquinonylethylphenyl)-3-(N-hydroxypropyl)-carbamyl - 4-(3′ - trifluoromethylphenylazo)-5-pyrazolone.

9. 1-(4″-hydroquinonylpropylphenyl) - 3 - (N - hydroxypropyl)-carbamyl - 4 - (3′ - trifluoromethylphenylazo)-5-pyrazolone.

10. 1-(4″-hydroquinonylpropylphenyl) - 3 - (N - hydroxypropyl) - carbamyl-4-(2′,4′,6′-trimethylphenylazo)-5-pyrazolone.

11. 1-(4″-hydroquinonylethylphenyl) - 3 - (N - hydroxypropyl) - carbamyl-4-(2′,4′,6′-trimethylphenylazo)-5-pyrazolone.

References Cited by the Examiner

FOREIGN PATENTS

554,935	8/1957	Belgium.

CHARLES B. PARKER, *Primary Examiner.*

F. D. HIGEL, *Assistant Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,282,913

November 1, 1966

Milton Green

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 71, for "precessing" read -- processing --; column 3, line 49, for "and" read -- said --; column 4, line 35, for "examles" read -- examples --; column 10, line 20, for "CF_3" read -- CH_3 --; column 12, line 67, for "OH" read -- Cl --; column 13, line 15, for "4‴" read -- 4‴- --; line 53, for "(3-trifluorometh-" read -- (3′-trifluorometh --; column 14, line 20, for "this" read -- said --; column 15, line 10, for "carbamly-" read -- carbamyl- --; line 16, for "Eyample" read -- Example --; line 29, for "carbamy" read -- carbamyl --; column 16, line 28, for "pyraxolone" read -- pyrazolone --; line 41, for "process" read -- processes --; column 18, lines 41 and 42, for "carbamly" read -- carbamyl --.

Signed and sealed this 5th day of September 1967.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents