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COLOR PHOTOGRAPHY

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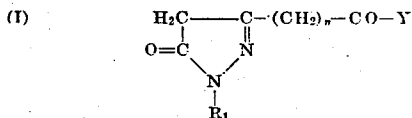
This invention relates to the production of colored photographic images by color development.

It is known that a colored image may be formed simultaneously with the silver image obtained by developing a silver halide emulsion with an aromatic amino developing agent, if a substance known as a color former is present, for example, in the developing solution or in the silver halide emulsion. The colored image may be revealed by bleaching out the silver image with Farmer's reducer or other photographic bleaching agent.

The present invention has for an object the production of new color formers which are useful in color photography. A further object is the preparation of photographic emulsions which contain new and improved color formers which are substantially water insoluble and which yield dyes by coupling with the oxidation products of aromatic amino developing agents. A further object is the provision of new photographic developing processes. A still further object is the preparation of photographic elements bearing an emulsion which contains one or more of the new color formers, which do not migrate; another object is the preparation of multi-layer photographic films containing color formers which do not migrate from layer to layer or into the processing baths. Yet another object is the preparation of finished photographs which contain stable dyed images which are formed of water-insoluble dyes. Other objects include the preparation of color photographs and color forming emulsions upon opaque or transparent supports. Still other objects will appear hereinafter.

The present invention is concerned with new color formers which are chemical compounds containing pyrazolone nuclei. The most common color-former of this type is 1-phenyl-3-methyl-5-pyrazolone which yields a magenta image on development. However, this compound is not very satisfactory in regard to the shade of the magenta image and it is a further and most important object of this invention to provide a new range of pyrazolone color formers which yield magenta images of more satisfactory shade and which are accordingly of especial value in subtractive processes of three-color photography.

The above and other objects are accomplished by the preparation and use in photographic processes and emulsions of color formers which are esters, amides and substituted amides of the general formula:



where R_1 is a hydrogen atom, a hydrocarbon

group or a heterocyclic group, Y is a $-\text{OR}_2$ group or an



group, where R_2 is a hydrocarbon group and R_3 and R_4 are the same or different and are hydrogen atoms or hydrocarbon groups, and n is a small positive integer, e. g. 1, 2 or 3, but is preferably 1.

As indicated above, the groups R_1 , R_2 , R_3 and R_4 in the general Formula I may be the same or different hydrocarbon groups. Thus they may be alkyl groups (e. g. methyl, ethyl, propyl, butyl or higher alkyl groups), aryl groups (e. g. phenyl or naphthyl groups), or aralkyl groups (e. g. benzyl groups). Such groups may themselves be substituted for example, aryl groups may be substituted with hydroxy, alkoxy, oxyalkyl, amino or nitro groups or with halogen atoms. The groups R_3 and R_4 may together constitute the residue of a cyclic nucleus, e. g. a carbocyclic nucleus such as a cycloaliphatic or aromatic nucleus or a heterocyclic nucleus. Also, as indicated above, R_1 may be a heterocyclic group. Suitable heterocyclic nuclei for R_1 , R_3 and R_4 are, for example, pyridine, quinoline, thiazole, benzthiazole, naphthathiazole, oxazole, benzoxazole, selenazole, pyrimidine, quinazoline, thiophene, coumarane and other heterocyclic nuclei. Suitable cycloaliphatic nuclei include cyclohexyl and methylcyclohexyl nuclei. Color formers of the amide type wherein one of R_3 and R_4 is a polynuclear residue, e. g. a diphenyl residue or naphthalene residue, have the advantage that the presence of such groups improves the substantivity of the color formers and makes them less liable to diffuse out of emulsion layers. Moreover, the presence of such polynuclear groups tends to change the shade of the final dye image, generally making it more blue.

The color formers of the type wherein Y in the above general Formula I is an $-\text{OR}_2$ group, may be prepared by condensing an ester of the general Formula II



(where R_2 and n have the significance given them above and R_5 is a hydrocarbon group, which may be of the same type or of a different type from R_2) with hydrazine or a mono-substituted hydrazine. Examples of suitable esters of the above Formula II are the di-esters of acetone dicarboxylic acid, β -keto adipic acid, β -ketopimelic acid and homologous compounds containing higher numbers of carbon atoms. In the preferred embodiment of the invention, n is 1 and the esters of acetone dicarboxylic acid are the preferred reactants. Examples of suitable sub-

stituted hydrazines are methyl hydrazine, ethyl hydrazine, phenyl hydrazine, substituted phenyl hydrazines, naphthyl hydrazines, substituted naphthyl hydrazines and heterocyclic hydrazines, e. g. quinolyl and benzthiazolyl hydrazines.

Color formers of the type in which Y is an



group may be prepared by reacting a compound of the above general Formula I where Y is $-OR_2$ with ammonia or an amine of the formula



Examples are mono- or di-alkylamines, e. g. ethylamine, diethylamine and higher homologues, mono- and di-arylamines, e. g. aniline, diphenylamine and naphthylamines, mono and di-arylamines, e. g. benzylamine, alkyl arylamines, e. g. N-ethylaniline, alkyl aralkyl amines, e. g. N-ethyl benzylamine, aralkyl arylamines, e. g. benzyl aniline, heterocyclic amines, e. g. pyridine, piperidine, quinoline, thiazoles, oxazoles, pyrimidines, quinazolines and the like and diamines, e. g. o- and p-phenylene-diamine, benzidine, dianisidine, diamino stilbenes and dinaphthylamines. Aryl nuclei present in the amines may themselves be substituted, e. g. by alkyl, nitro, halogen, alkoxy, or oxyalkyl groups. Where the amine employed is a diamine, reaction may take place at both amino groups so that the final product contains two pyrazolone nuclei. Also, where the diamine is unsymmetrically substituted, unsymmetrical products may be obtained.

The new color formers may be incorporated in amino developing solutions or in photographic silver halide emulsions. The aromatic amino developing agents are the most readily available color developing agents and of these the diamino aryl compounds such as p-phenylene diamine and its substitution products are preferred.

These developers may be substituted in the amino groups as well as in the ring, preferably the former, to constitute compounds such as the mono- and di-alkyl arylene-diamines including the mono- and di-alkyl naphthylene diamines, alkyl phenylene diamines and alkyl toluylene diamines. The developing compounds must, of course, have one free or unsubstituted amino group which enables the oxidation product of the developer to couple with the color formers.

As examples of developers which may be employed there may be mentioned the following: p-phenylene diamine, mono ethyl-p-phenylene diamine, di ethyl-ortho-phenylene diamine, chloro-p-phenylene diamine, amino-p-phenylene diamine, 1,2,5-toluene diamine, 2-amino-5-diethylamine toluene, p-amino phenylene piperidine, methyl-oxyethyl-p-phenylene diamine, ethyl-oxyethyl-p-phenylene diamine, butyl-oxyethyl-p-phenylene diamine, 2-amino-5-oxyethyl-1-butylaminotoluene and its dihydrochloride, β - γ -di-oxypropyl-p-phenylene diamine, 4:4'-diaminodiphenylamine and α -amino-aceto-acetic acid ethyl ester. These compounds are preferably used in the form of their salts either of organic or inorganic type, since the salts are more soluble and stable than the free bases. The hydrochlorides, sulphates and acetates are examples of suitable salts.

By way of example a suitable developing solution (referred to for convenience in the subse-

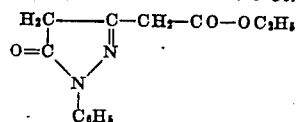
quent examples as "Developing solution A") containing a color-former in accordance with the present invention may be made up as follows:

5	p-Diethylamino aniline hydrochloride-----	
	-----grams-----	1.0
	Sodium carbonate crystals, $Na_2CO_3 \cdot 10H_2O$ -----	
	-----grams-----	80
	Sodium sulphite crystals, $Na_2SO_3 \cdot 7H_2O$ -----	
	-----grams-----	12.5
10	Color-former solution (i. e. a 1% solution or a saturated solution at room temperature, in alcohol or other solvent, e. g. ethylene glycol mono methyl ether, whichever is the weaker solution)-----	ccs. 100
15	Distilled water to make-----	ccs. 1000

The sodium sulphite may be omitted if desired. The following examples illustrate the method of production of the color-formers of the invention:

EXAMPLE 1

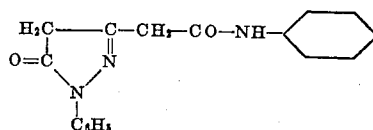
1-phenyl-5-pyrazolone-3-acetic ethyl ester



50.5 gms. of acetone dicarboxylic acid diethyl ester were mixed with 27.0 gms. of phenyl hydrazine in a 500 cc. flask fitted with a condenser, the mixture being kept cool during the operation. The mixture was then allowed to stand overnight, when the clear solution became opaque and water separated out. The solution was then warmed on a water bath until it turned red and again became clear. The solution was then steam-distilled to remove unchanged phenyl hydrazine. The residue was transferred to a beaker, cooled in a freezing mixture and stirred with 200 ccs. of 50% aqueous ethyl alcohol. A brown crystalline solid separated which, on recrystallisation from petroleum ether, had a melting point of 78-82° C.

EXAMPLE 2

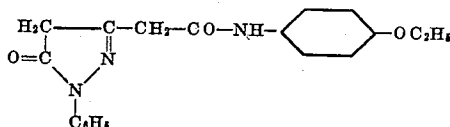
1-phenyl-3-acetanilido-5-pyrazolone



2.46 gms. of 1-phenyl-5-pyrazolone-3-acetic ethyl ester prepared as in Example 1 were mixed with 1.8 gms. of aniline and the mixture boiled for one hour. On cooling the mixture set solid. It was dissolved in 10 ccs. of ethyl alcohol and cooled in a freezing mixture. A white solid separated which on recrystallisation from 30 ccs. of ethyl alcohol had a melting point of 186° C.

EXAMPLE 3

1-phenyl-3-p-ethoxy-acetanilido-5-pyrazolone

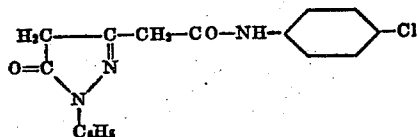


1.23 gms. of 1-phenyl-5-pyrazolone-3-acetic-ethyl ester and 1.37 gms. of p-phenetidine were heated in an oil bath at 200° C. for one hour. The mixture was then cooled and a small volume of ethyl alcohol added, whereupon the product separated as a crystalline white compound having a melting

point of 215–220° C. after recrystallisation from ethyl alcohol.

EXAMPLE 4

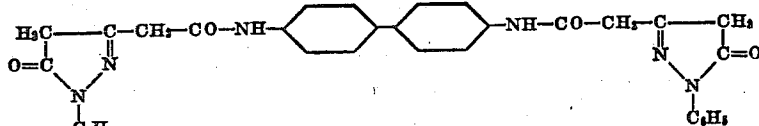
1-phenyl-3-p-chlor-acetanilido-5-pyrazolone



This compound was prepared by a method similar to Example 3 using 1.28 gms. of p-chloraniline instead of the p-phenetidine. The recrystallised product had a melting point of 242° C.

EXAMPLE 5

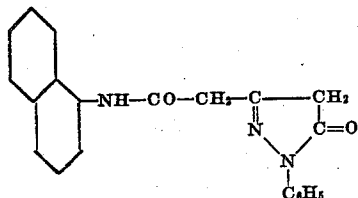
Di(1-phenyl-5-pyrazolone-3-acet-benzidide)



This compound was prepared by fusing together 2.46 gms. of 1-phenyl-5-pyrazolone-3-acetic ethyl ester and 1.84 gms. of benzidine on an oil bath for two hours at 200° C. The product was boiled out with 20 ccs. of ethyl alcohol and filtered and the product thus separated. It had a melting point of 201° C.

EXAMPLE 6

1-phenyl-3-acet-α-naphthylamido-5-pyrazolone



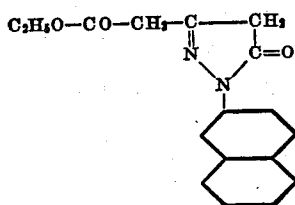
This compound was prepared by fusing 2.46 gms. of 1-phenyl-5-pyrazolone-3-acetic ethyl ester and 1.43 gms. of α-naphthylamine on an oil bath for two hours at 200° C. The mixture was dissolved in 10 ccs. of hot ethyl alcohol and allowed to cool. The product separated out and had a melting point of 188° C.

Other specific compounds which may be em-

ployed as color formers in accordance with this invention are as follows:

EXAMPLE 7

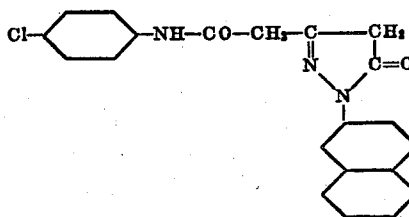
1-β-naphthyl-3-acetic-ethyl-ester-5-pyrazolone



prepared from acetonedicarboxylic acid-di-ethyl-ester and β-naphthylhydrazine. Melting point 114–115° C.

EXAMPLE 8

5 1-β-naphthyl-3-p-chloracetanilido-5-pyrazolone

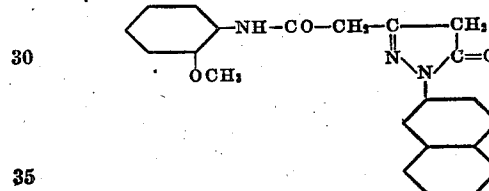


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prepared from the compound of Example 7 and p-chloraniline. Melting point 180–190° C.

EXAMPLE 9

1-β-naphthyl-3-acet-o-anisidido-5-pyrazolone



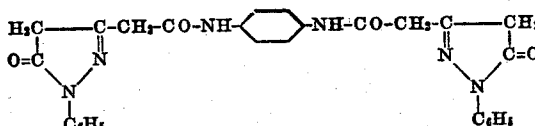
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prepared from the compound of Example 7 and o-anisidine. Melting point 120° C.

EXAMPLE 10

40 p,p'-Di-(1-phenyl-5-pyrazolone-3-acetamino)-benzene

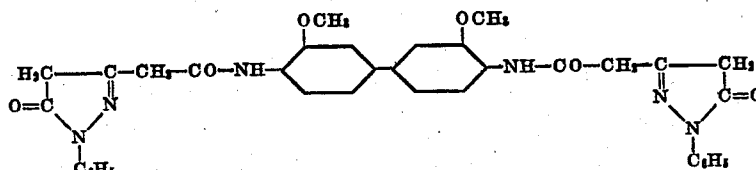


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prepared from 1-phenyl-5-pyrazolone-3-acetic ethyl ester and p-phenylene diamine. Melting point 278° C.

EXAMPLE 11

p,p'-Di-(1-phenyl-5-pyrazolone-3-acetamino)-m,m'-di-methoxy-di-phenyl

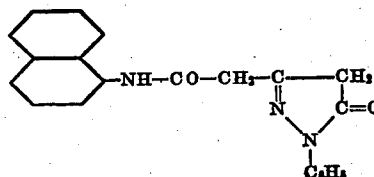


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EXAMPLE 12

1-phenyl-3-acet-α-naphthylamido-5-pyrazolone

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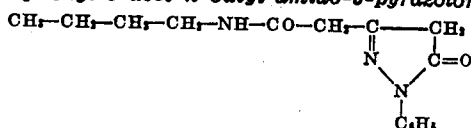


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prepared from 1-phenyl-5-pyrazolone-3-acetic ethyl ester and α -naphthylamine. Melting point 188° C.

EXAMPLE 13

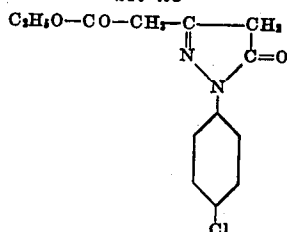
1-phenyl-3-acet-n-butyl amido-5-pyrazolone



prepared from 1-phenyl-5-pyrazolone-3-acetic ethyl ester and n-butylamine. Melting point 104° C.

EXAMPLE 14

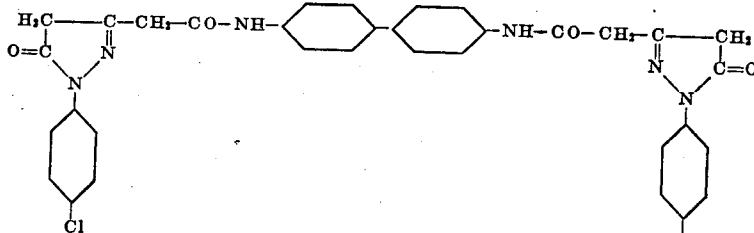
1-p-chlor-phenyl-3-acetic ethyl ester-5-pyrazolone



prepared from p-chlor-phenyl-hydrazine and acetonedicarboxylic acid diethylester. Melting point 117° C.

EXAMPLE 15

p,p'-Di-(1-p-chlor-phenyl-5-pyrazolone-3-acet-amino)-di-phenyl

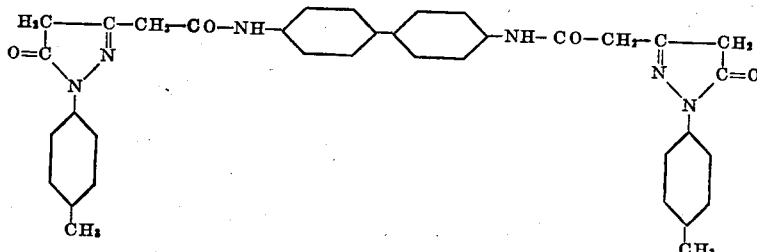


prepared from the compound of Example 14 and benzidine. Melting point 288° C.

prepared from the compound of Example 17 and 2,4-dimethylaniline. Melting point 200° C.

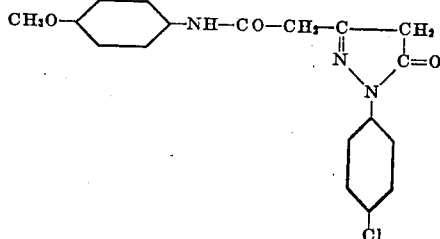
EXAMPLE 19

p,p'-Di-(1-p-tolyl-5-pyrazolone-3-acetamino)-di-phenyl



EXAMPLE 16

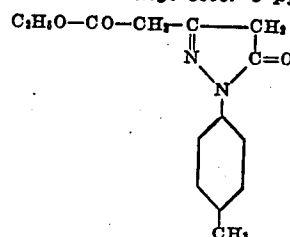
1-p-chlorphenyl-3-acet-p-anisidido-5-pyrazolone



prepared from the compound of Example 14 and p-anisidine. Melting point 244° C.

EXAMPLE 17

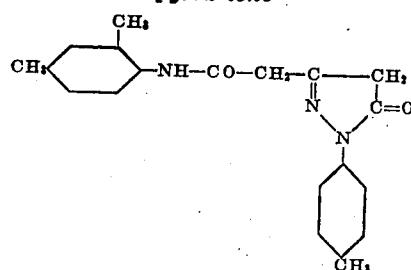
1-p-tolyl-3-acetic-ethyl-ester-5-pyrazolone



prepared from acetone-di-carboxylic acid-di-ethyl-ester and p-tolyhydrazine. Melting point 105° C.

EXAMPLE 18

1-p-tolyl-3-(acet-2',4'-dimethylanilido)-5-pyrazolone



prepared from the compound of Example 17 and benzidine. Melting point 305° C.

In the above examples the pyrazolone nuclei are N-substituted by aryl and substituted aryl groups. It is to be clearly understood, however, that the N-substituent can be any of the other types of group listed above as possible values for the group R₁.

The products of the above examples, when included in "Developing solution A" and used for the development of an exposed silver halide emulsion each yielded an excellent magenta image in addition to the silver image.

EXAMPLE 20

This example illustrates the incorporation of the color-formers of this invention in emulsion layers. 20 ccs. of a 1% solution in ethylene glycol monomethyl ether of one of the products of Examples 1 to 19 were added to 25 ccs. of a 10% aqueous solution of gelatin and the mixture added to 50 ccs. of a melted photographic "Gaslight" emulsion containing approximately 20 gms. of silver halide, chiefly silver chloride, per pound weight of emulsion. The emulsion thus prepared was coated on a paper support and dried. The paper coated with emulsion was exposed under a negative and was then developed with a "Developing solution A" excluding the color-former but including an equivalent quantity of the water-miscible liquid such as ethylene glycol monomethylether. Magenta images of various shades were produced together with the silver image in each case.

The process of development employing the color-formers in accordance with the present invention may be applied to a latent image in an emulsion of silver halide (including simple and mixed emulsions, e. g. silver chloride, bromide, chlorobromide and iodobromide emulsions) which has been exposed to the action of light, for example, in a camera or behind a photographic negative image. The process may also be applied to a silver salt image which has been obtained by dissolving away an initial reduced silver image and exposing to light the residual unaltered silver salt, for example in the reversal process of development. The process may also be applied to a developable silver salt image obtained by removing the unaltered silver halide by means of solvents from a developed photographic image in metallic silver and then converting the metallic silver to a developable silver salt by means of known photographic bleaching agents. The process may also be applied to the development of silver halide photographic emulsions which have been rendered developable by means other than exposure to light, for example, by chemical means.

As a modification, the production of colored images by means of the color-formers of this invention may be applied to colloid layers sensitised by bi-chromate. Thus the color-formers may be incorporated in bichromate-sensitised colloid layers (e. g. gelatin, gum arabic or albumin), the layers exposed, the unexposed colloid removed, for example by treatment with hot water, and the color developed in the exposed portions by treatment with p-nitroso-dialkyl-aniline or its derivatives.

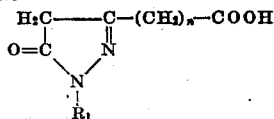
The color formers and elements containing them according to this invention are not restricted in their use to the processes of color development referred to above. Thus they may be treated with diazo compounds to form azo dyes which may then be differentially bleached to form dyed images.

The new color formers of this invention possess many advantages. As indicated above they do not migrate from one emulsion layer to another and they do not tend to diffuse from the emulsion layers during processing treatments. Moreover, the new color formers are strongly resistant to the bleaching action of the sulphite commonly contained in photographic developing solutions; that is, they yield dye images of satisfactory depth even though sulphite is present in the developer employed. Moreover, the dye images produced are very stable and many of

the dyestuffs yield dye images which are substantially pure magentas and therefore of especial value in three color subtractive processes of color photography.

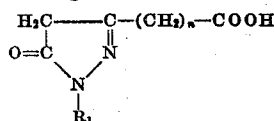
We claim:

1. A light-sensitive photographic emulsion containing as a color former a compound selected from the class consisting of the esters, amides and substituted amides of compounds of the general formula:



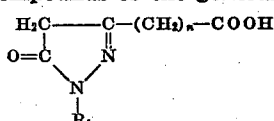
where R_1 is selected from the group consisting of hydrogen atoms, hydrocarbon groups and heterocyclic groups and n is a small positive integer.

2. A photographic element containing a light-sensitive silver salt and, as a color former, a compound selected from the class consisting of the esters, amides and substituted amides of compounds of the general formula:



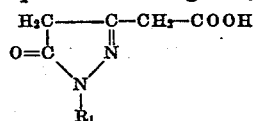
where R_1 is selected from the group consisting of hydrogen atoms, hydrocarbon groups and heterocyclic groups and n is a small positive integer.

3. A photographic element comprising a light-sensitive silver halide emulsion containing as a color former a compound selected from the class consisting of the esters, amides and substituted amides of compounds of the general formula:



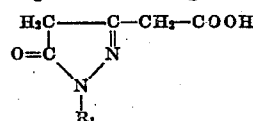
where R_1 is selected from the group consisting of hydrogen atoms, hydrocarbon groups and heterocyclic groups and n is a small positive integer.

4. A photographic element comprising a light-sensitive silver halide emulsion containing as a color former a compound selected from the class consisting of the esters, amides and substituted amides of compounds of the general formula:



where R₁ is selected from the group consisting of hydrogen atoms, hydrocarbon groups and heterocyclic groups.

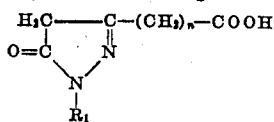
5. A photographic element comprising a light-sensitive silver halide emulsion containing as a color former a mono-N-hydrocarbon substituted amide of a compound of the general formula:



where R₁ is selected from the group consisting of hydrogen atoms, hydrocarbon groups and heterocyclic groups.

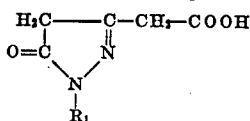
6. A photographic color forming developer which comprises an aromatic amino developing agent having an unsubstituted amino group and

a color former which is selected from the class consisting of the esters, amides and substituted amides of compounds of the general formula:



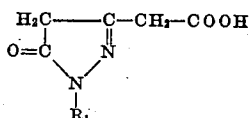
where R_1 is selected from the group consisting of hydrogen atoms, hydrocarbon groups and heterocyclic groups and n is a small positive integer.

7. A photographic color forming developer which comprises an aromatic amino developing agent having an unsubstituted amino group and a color former which is selected from the class consisting of the esters, amides and substituted amides of compounds of the general formula:



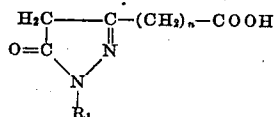
where R_1 is selected from the group consisting of hydrogen atoms, hydrocarbon groups and heterocyclic groups.

8. A photographic color forming developer which comprises an aromatic amino developing agent having an unsubstituted amino group and a color former which is a mono-N-hydrocarbon substituted amide of a compound of the general formula:



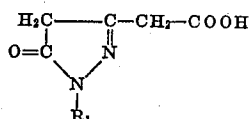
where R_1 is selected from the group consisting of hydrogen atoms, hydrocarbon groups and heterocyclic groups.

9. A method of producing a colored image in a silver halide emulsion which has a latent image formed in it which comprises developing the emulsion with an aromatic amino developing agent having an unsubstituted amino group in the presence of a compound selected from the class consisting of the esters, amides and substituted amides of compounds of the general formula:



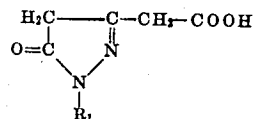
where R_1 is selected from the group consisting of hydrogen atoms, hydrocarbon groups and heterocyclic groups and n is a small positive integer.

10. A method of producing a colored image in a silver halide emulsion which has a latent image formed in it which comprises developing the emulsion with an aromatic amino developing agent having an unsubstituted amino group in the presence of a compound selected from the class consisting of the esters, amides and substituted amides of compounds of the general formula:



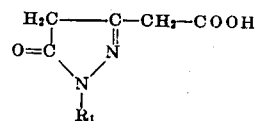
where R_1 is selected from the group consisting of hydrogen atoms, hydrocarbon groups and heterocyclic groups.

11. A method of producing a colored image in a silver halide emulsion which has a latent image formed in it which comprises developing the emulsion with an aromatic amino developing agent having an unsubstituted amino group in the presence of a mono-N-hydrocarbon substituted amide of a compound of the general formula:



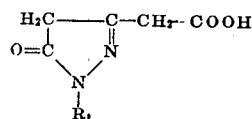
where R_1 is selected from the group consisting of hydrogen atoms, hydrocarbon groups and heterocyclic groups.

12. A photographic color forming developer which contains an arylene diamine developing agent having at least one unsubstituted amino group and a color former selected from the class consisting of the esters, amides and substituted amides of compounds of the general formula:



where R_1 is selected from the group consisting of hydrogen atoms, hydrocarbon groups and heterocyclic groups.

13. A method of producing a colored image in a silver halide emulsion containing a latent image which comprises developing the emulsion with an arylene diamine developing agent having at least one unsubstituted amino group in the presence of a compound selected from the class consisting of the esters, amides and substituted amides of compounds of the general formula:



where R_1 is selected from the group consisting of hydrogen atoms, hydrocarbon groups and heterocyclic groups.

14. A method of producing a colored image which comprises developing a photographic element having a reducible silver salt image with an aromatic amino developing agent having an unsubstituted amino group in the presence of di(1-phenyl-5-pyrazolone)-3-acet-benzidide.

15. A method of producing a colored image which comprises developing a photographic element having a reducible silver salt image with an aromatic amino developing agent having an unsubstituted amino group in the presence of 1-beta-naphthyl-3-acet-ortho-anisidido-5-pyrazolone.

16. A method of producing a colored image which comprises developing a photographic element having a reducible silver salt image with an aromatic amino developing agent having an unsubstituted amino group in the presence of 1-para-chlor-phenyl-3-acetic ethyl ester-5-pyrazolone.

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