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UNITED STATES PATENT OFFICE

2,213,986

PRODUCTION OF COLORED PHOTOGRAPHIC IMAGES

John David Kendall and Ronald Bernard Collins, Ilford, England, assignors to Ilford Limited, Ilford, Essex, England, a British company

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16 Claims. (Cl. 95—6)

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

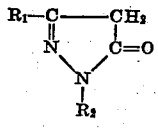
It is known that a colored image may be formed simultaneously with the silver image obtained by developing an exposed silver halide emulsion in the presence of a substance known as a "color former", for example, if the color former is mixed with the developer or the emulsion. The colored image thus produced may be revealed by dissolving out the silver image with the aid of Farmer's Reducer or other known suitable silver solvents.

It is an object of this invention to provide a new range of color formers. A further object of the invention is to provide a method of producing colored photographic images with the aid of such color formers and a still further object is to provide light sensitive silver halide photographic materials containing the new color formers.

Other objects of the invention will appear hereinafter.

According to the present invention colored photographic images are produced by developing silver halide photographic emulsions, in which a latent image has been formed, with an aromatic amino compound as the developer, in the presence of a color former which is the condensation product of one molecule of an aldehyde or ketone with one molecule of a pyrazole-5-one which has a reactive methylene group in the 4-position and in which the 1 and 3 positions may or may not be substituted.

The pyrazole-5 ones may be represented by the following general formula:



in which R_1 and R_2 may be the same or different and each represent a hydrogen atom, a hydrocarbon radical, e. g., an alkyl, aryl, aralkyl, substituted alkyl, substituted aryl or substituted aralkyl group or a heterocyclic group. Thus, for example, R_1 or R_2 may be a methyl, ethyl, propyl or higher alkyl group a carbmethoxy or higher carbalkoxy group, a phenyl or naphthyl group, a benzyl or phenyl-ethyl group, or a furyl, coumaryl, thienyl or benzthiazolyl group and such groups may be substituted by other atoms or groups e. g., chlorine or bromine atoms, nitro groups, hydroxy, methoxy and other alkoxy groups, carbethoxy and other carbalkoxy groups and carbalkoxyalkyl groups. Thus, for instance, R_1 or R_2 may be, instead of a phenyl group, a p-nitrophenyl group, a 2:4-dinitrophenyl group, a hydroxyphenyl group, a chlorphenyl group or a dichlorphenyl group.

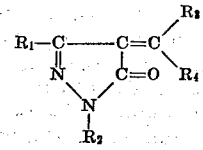
The aldehyde or ketone employed may be represented by the following general formula:



in which R_3 and R_4 may be the same or different and each represent a hydrogen atom or a hydrocarbon radical, e. g., alkyl, cycloalkyl, aryl, aralkyl, substituted alkyl, substituted aryl, substituted aralkyl or R_3 and R_4 may together form part of a carbocyclic or heterocyclic group.

Examples of suitable aldehydes are formaldehyde, benzaldehyde, phenylacetaldehyde, salicylaldehyde, m-hydroxybenzaldehyde, p-hydroxybenzaldehyde, furfuraldehyde, N-dimethylaminobenzaldehyde and cinnamic aldehyde, and examples of suitable ketones are acetone, acetophenone, benzophenone, cyclopentanone, acetoacetic ester and methyl-β-naphthyl ketone.

The nature of the condensation product varies with the conditions of the reaction, and the relative proportions of the reactants. One molecule of the pyrazole 5-one reacts with one molecule of the aldehyde or ketone to give products represented by the following general formula:

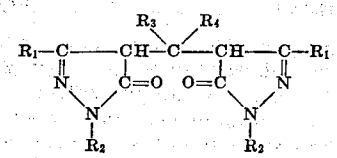


(I)

in which R_1, R_2, R_3, and R_4 have the meanings assigned to them above.

The condensation may be carried out at ordinary temperatures in the presence of a condensing agent such as piperidine or hydrochloric acid, but is preferably carried out at higher temperatures, e. g., 40° to 200° C. and preferably 140° to 180° C.

The reaction product chiefly consists of a compound represented by Formula I but there is a probability of small amounts of a compound represented by the following formula being formed in admixture therewith:



(II)

wherein R_1, R_2, R_3 and R_4 have the same significance as in Formula I.

The presence of minor amounts of a symmetrical compound of Formula II is immaterial, since it has been found that both types of compound, or mixtures of them, function satisfactorily as color formers. The unsymmetrical compounds may be purified so that they are free from symmetrical compounds.

Simple pyrazolones have been previously employed as color formers, but suffer from the disadvantages of their appreciable solubility in developing solutions and their tendency to diffuse from one emulsion layer to another, when incorporated in emulsion layers of photographic multi-layered material. The compounds of the present invention are much less soluble and are much more substantive towards gelatine, so that they possess a greatly reduced tendency to diffuse out of an emulsion layer.

The color formers may be employed in two different ways. Thus they may be incorporated in the silver halide emulsion which is to be developed or they may be added to the developer solution. In either case, the result on development is to yield images in shades ranging from magenta to mauve.

Suitable aromatic amino compounds which may be employed as the developers in conjunction with the color-formers of this invention are derivatives of p-phenylene diamine and particularly of the asymmetric dialkyl p-phenylenediamines, e. g., p-aminodimethylaniline, p-aminodiethylaniline and p-aminodibutylaniline. Other developing agents which may be used include p-phenylenediamine itself, p-methylaminoaniline, p-ethylaminoaniline and p-aminophenol, N.N-diethyl-o-phenylenediamine, chloro-p-phenylenediamine, 1.2.5.-toluylenediamine, 2-amino-5-diethylaminotoluene, N-p-aminophenylpiperidine, N-methyl-N-hydroxyethyl-p-phenylenediamine, N-butyl-N-hydroxyethyl-p-phenylenediamine, 2-amino-5-hydroxyethyl-butyl aminotoluene and its dihydrochloride and α-γ-dihydroxypropyl-p-phenylene diamine. These aromatic amino-developing agents may be used in the form of their salts, which may be either inorganic or organic. The salts are in general more stable than the free bases. As examples of suitable salts mention is made of the hydrochlorides, sulfates and acetates.

In the succeeding examples, the following solution is given by way of example as illustrating the nature of developing solutions which may be employed embodying a color former in accordance with the invention.

"Developing Solution A"

Diethyl-p-phenylenediaminehydrochloride ____gm__	1
Sodium carbonate (crystals) $Na_2Co_310H_2O$ ____gms__	80
Sodium sulphite (crystals) $Na_2SO_37H_2O$ ____gms__	12.5
Color former solution (1% or saturated solution, whichever is weaker) ____ccs__	100
Water to make____litre__	1

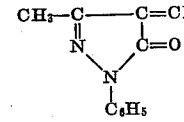
The color former is dissolved in a suitable water-miscible solvent such as ethyl alcohol or ethylene glycol mono-methyl ether.

A suitable development time, using this solution, is two minutes, at a temperature of 65° F.

The following specific examples illustrate the method of production of the new color formers, and their use:—

Example 1

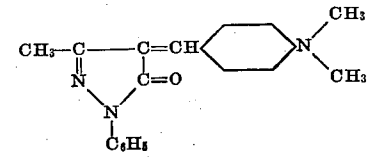
1-phenyl-3-methyl-4-benzal-5-pyrazolone



1.74 gms. of 1-phenyl-3-methyl-5-pyrazolone and 1.06 gms. of benzaldehyde were heated together on an oil-bath at 140° C. for about one hour. A red oil was produced which was cooled and dissolved in 10 ccs. of warm alcohol, from which 1.93 gms. of a red crystalline solid deposited on cooling. This solid was crystallised from a further 15 ccs. of alcohol yielding 1.3 gms. of red crystals melting at 106—107° C. Developing Solution A, when including this compound and used for the development of photographic silver halide images, produced a magenta image together with the silver image.

Example 2

1-phenyl-3-methyl-4-paradimethylaminobenzal-5-pyrazolone

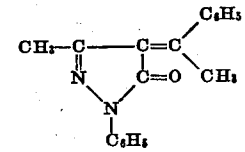


4.35 gms. of 1-phenyl-3-methyl-5-pyrazolone, 3.74 gms. of p-dimethylaminobenzaldehyde, 30 ccs. of glacial acetic acid and 10 ccs. of dry alcohol were mixed together and the mixture boiled gently under a reflux condenser on a water bath for about one and a quarter hours. The solution first became red and later crystals were deposited. The mixture was cooled, filtered and the solid residue was washed with acetic acid, alcohol and water and then dried. The solid was then purified by boiling successively with three 250 ccs. lots of methyl alcohol and filtering off, leaving 4.06 gms. of shining red crystals melting at 197° C.

Developing Solution A when including this compound and used for the development of silver halide photographic emulsions produced a weak magenta image together with the silver image, the weakness of the image being due to the insolubility of the compound in ethyl alcohol and the developer solution.

Example 3

1-phenyl-3-methyl-4-phenyl methyl methylene-5-pyrazolone

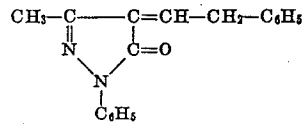


1.74 gms. of 1-phenyl-3-methyl-5-pyrazolone, 1.20 gms. of acetophenone, 10 ccs. of glacial acetic acid and 3.5 ccs. of dry alcohol were heated on a water bath for two hours and then boiled gently under a reflux condenser for a further hour. A yellow crystalline solid was formed which was filtered off and washed and recrystallised from 20 ccs. of alcohol yielding 0.23 gm. of small deep yellow crystals melting at 87° C.

Developing Solution A when including this substance and used for the development of silver halide photographic emulsions produced a deep violet image, together with the silver image.

Example 4

1-phenyl-3-methyl-4-phenylethylidene-5-pyrazolone

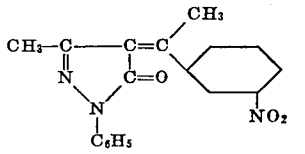


1.74 gms. 1-phenyl-3-methyl-5-pyrazolone and 1.74 gms. phenylacetaldehyde were heated in an oil bath at 160° C. for 3 hours. The residual oil was extracted with benzene and ethyl alcohol separately leaving a brown solid. This was recrystallised from benzene with addition of petroleum ether to induce crystallisation giving 1–2 gms. of a solid which melted at 101°–103° C.

Developing Solution A when including this compound and used for the development of silver halide emulsions produced a mauve image in addition to the silver image.

Example 5

1-phenyl-3-methyl-4-m-nitrophenylmethylmethylene-5-parazolone



1.65 gms. m-nitro-acetophenone and 1.74 gms. 1-phenyl-3-methyl-5-pyrazolone were heated in an oil bath at 160° C. for 3 hours. The melt set to a pale yellow solid which was extracted with 20 ccs. ethyl alcohol; the addition of water to the alcoholic extract caused the precipitation of a yellow oily solid which melted at 150°–160° C.

Developing Solution A when including this compound and used for the development of silver halide emulsions produced a magenta image in addition to the silver image.

In each of the above examples, the dye image may be revealed by bleaching out the silver image with, for example, Farmer's Reducer or other known photographic bleaching agent.

In addition to the specific pyrazolone color-former described in the foregoing examples the following are examples of color-formers according to this invention:—

1-phenyl-3-methyl-4-(m - hydroxybenzal) -5-pyrazolone
1-phenyl-3-methyl-4-(p-hydroxybenzal) -5-pyrazolone
1-phenyl-3-methyl-4-(o-hydroxybenzal) -5-pyrazolone
3-methyl-4-benzal-5-pyrazolone
1-phenyl-3-methyl-4-(2'methyl dihydrobenzthiazolylidene) -5-pyrazolone
1-phenyl-4-benzal-5-pyrazolone
1-phenyl-3-methyl-4-resorcal-5-pyrazolone
1-phenyl-3-methyl-4-(p-bromo acetophenone-ω-formyl) -5-pyrazolone
1-phenyl-3-methyl-4-furfural-5-pyrazolone
1-phenyl-3-methyl -4- (dimethyl methylene) -5-pyrazolone
1-phenyl-3-methyl-4-(methyl-naphthyl methylene) -5-pyrazolone
1-phenyl-4-(phenyl-methyl methylene) -5-pyrazolone
1 - phenyl - 3 - methyl - 4 - (carbethoxy methyl-methyl-methylene) -5-pyrazolone
1-phenyl-3-methyl - 4 - (2'(1'hydroxy) naphthyl methyl methylene) -5-pyrazolone
1-phenyl-3-methyl -4- diphenylmethylene-5-pyrazolone
1-phenyl-3-methyl -4- (methyl-ω-styryl methylene) -5-pyrazolone
1-phenyl-3-methyl-4-cyclopentanyl-5-pyrazolone
1-phenyl - 3 - methyl-4-(methyl p-methylphenyl methylene) -5-pyrazolone

Example 6

This example illustrates the incorporation of the color formers of this invention in emulsion layers 20 ccs. of 1% solution in ethylene glycol mono-methyl ether of 1-phenyl-3-methyl-4-benzal-5-pyrazolone were added to 25 ccs. of 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, principally silver chloride, per pound weight of emulsion. The emulsion thus prepared was coated on a paper support and dried. The emulsion coated paper was exposed under a negative and was then developed with a developing solution of the constitution of developing Solution A excluding the color former but including an equivalent quantity of the water miscible liquid such as ethyl alcohol or ethylene glycol mono methyl ether. A magenta image was produced together with the silver image.

The compounds:

1-phenyl-3-methyl-4-paradimethyl aminobenzal-5-pyrazolone
1-phenyl-3-methyl-4-phenylmethylmethylene-5-pyrazolone
1-phenyl-3-methyl-4-phenylethylidene-5-pyrazolone
1-phenyl-3-methyl-4-m-nitrophenylmethylmethylene-5-pyrazolone

may be employed in a similar way in place of the

1-phenyl-3-methyl-4-benzal-5-pyrazolone

referred to above.

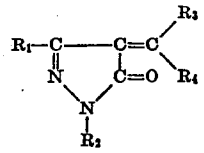
The process of development employing the color formers in accordance with the present invention may be applied either to a latent image in an emulsion of a silver halide which has been exposed to the action of light, for example, in a camera or behind a photographic negative image; or it may be applied to the residual silver halide left when an initial reduced silver image has been dissolved away as in the reversal process of development: or it may be applied to a developed photographic image in metallic silver which has been fixed by the removal of unchanged silver halide, and subsequently converted to a developable silver salt by means of known photographic bleaching agents. In the last two cases the residual silver halide and the silver salt respectively may be made developable by the action of light or in any other way, e. g., by treatment with sodium arsenite.

We claim:

1. A photographic color forming developer which comprises an aromatic amino developing compound and the condensation product of one molecule of a pyrazole-5-one having a reactive methylene group in the 4-position and one molecule of a compound selected from the group consisting of aldehydes and ketones.

2. A photographic color forming developer which comprises an aromatic amino developing

compound and a compound of the general formula:



in which R_1, R_2, R_3 and R_4 represent radicals taken from the group consisting of hydrogen, hydrocarbon and heterocyclic radicals.

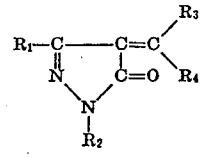
3. A photographic color forming developer which comprises an asymmetrical di-alkyl p-phenylene diamine and the condensation product of one molecule of a pyrazole-5-one having a reactive methylene group in the 4-position and one molecule of a compound selected from the group consisting of aldehydes and ketones.

4. A method of producing a colored image in a silver halide emulsion in which a latent image has been formed, which comprises developing the emulsion with an aromatic amino developing compound in the presence of the condensation product of one molecule of a pyrazole-5-one having a reactive methylene group in the 4-position with one molecule of a compound selected from the group consisting of aldehydes and ketones.

5. A method of producing a colored image in a silver halide emulsion in which a silver image has been produced and the residual silver halide removed by fixing, which comprises converting the silver image to a redevelopable silver salt by known photographic means and re-developing with an aromatic amino compound in the presence of the condensation product of one molecule of a pyrazole-5-one and one molecule of a compound selected from the group consisting of aldehydes and ketones.

6. A light sensitive silver halide photographic emulsion containing a color former which is the condensation product of one molecule of a pyrazole-5-one having a reactive methylene group in the 4-position with one molecule of a compound selected from the group consisting of aldehydes and ketones.

7. A light sensitive silver halide photographic emulsion containing a color former which is a compound of the general formula:



in which R_1, R_2, R_3 and R_4 represent radicals taken from the group consisting of hydrogen, hydrocarbon and heterocyclic radicals.

8. A process as set forth in claim 4 wherein the condensation product is 1-phenyl-3-methyl-4-benzal-5-pyrazolone.

9. A process as set forth in claim 4 wherein the condensation product is 1-phenyl-3-methyl-4-phenyl-methyl-methylene-5-pyrazolone.

10. A process as set forth in claim 4 wherein the condensation product is 1-phenyl-4-phenyl-methyl-methylene-5-pyrazolone.

11. A light sensitive silver halide photographic emulsion containing as a color former 1-phenyl-3-methyl-4-benzal-5-pyrazolone.

12. A light sensitive silver halide photographic emulsion containing as a color former 1-phenyl-3-methyl-4-phenyl-methyl-methylene-5-pyrazolone.

13. A light sensitive silver halide photographic emulsion containing as a color former 1-phenyl-4-phenyl-methyl-methylene-5-pyrazolone.

14. A developer as set forth in claim 3 wherein the condensation product is 1-phenyl-3-methyl-4-benzal-5-pyrazolone.

15. A developer as set forth in claim 3 wherein the condensation product is 1-phenyl-3-methyl-4-phenyl-methyl-methylene-5-pyrazolone.

16. A developer as set forth in claim 3 wherein the condensation product is 1-phenyl-4-phenyl-methyl-methylene-5-pyrazolone.

JOHN DAVID KENDALL.
RONALD BERNARD COLLINS.

CERTIFICATE OF CORRECTION.

Patent No. 2,213,986. September 10, 1940.

JOHN DAVID KENDALL, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 12, beginning with "Example 6" strike out all to and including the word and period "above." in line 45, and insert the same on same page 3, first column, after the paragraph ending with the words "silver image" in line 47; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 22nd day of October, A. D. 1940.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)