

## UNITED STATES PATENT OFFICE

2,632,702

## PYRAZOLONE COUPLERS FOR COLOR PHOTOGRAPHY

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15 Claims. (Cl. 95-6)

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This invention relates to color-forming or coupler compounds for color photography and more particularly to pyrazolone coupler compounds.

The use of pyrazolone couplers in processes of color development in which the oxidation product of a primary aromatic amino developing agent couples with the pyrazolone to produce a dye image in situ with a developed silver image is well known in the art. The pyrazolone couplers are generally used to produce the magenta subtractive dye image, and their use has presented a number of problems particularly in color development processes of the type in which the coupler is incorporated into the emulsion layer of a multilayer element and color development is affected by a single developer solution free of coupler compounds. In such processes it is necessary that the pyrazolone coupler in the magenta layer react with the developing agent at the same speed as do the couplers in the other layers. Of course, the resulting dye image should have good stability and the coupler itself must be stable or residual coupler left in the emulsion layer will give rise to objectionable print-out under the influence of heat and light. The usual pyrazolone couplers are especially prone to yield magenta images of poor stability and objectionable print-out often accompanies their use. No clear explanation of the cause of these deficiencies is available but it has been suggested that poor dye image stability is due to a reaction of the unused coupler with the magenta dye image and print-out is probably due to the oxidation of unused pyrazolone coupler.

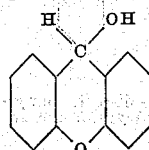
I have discovered that pyrazolone coupler compounds are readily reacted with certain hydriol and gem-diol compounds and the resulting monomolecular and bis-coupler compounds have good stability and the dye images obtained therefrom by means of color development are very stable. Furthermore, the coupler compounds have exceptionally good solubility in coupler solvents customarily used for dispersing the compounds in gelatino-silver halide emulsion layers.

The principal object of my invention is to provide pyrazolone couplers of good stability and solubility from which stable dye images may be obtained by means of color development. Another object is to provide photographic elements having the coupler dispersed in the emulsion layers. Other objects will be apparent from the following description of my invention.

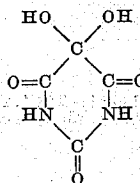
The couplers contemplated by my invention are obtained by condensation of either one or two mols of a pyrazolone with a compound, as for example, xanthidrol, or a gem-diol compound

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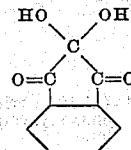
such as alloxan hydrate, or triketohydrindene hydrate. The latter compounds exist in the hydrate form wherein a molecule of water is firmly bound to a carbon atom which in turn is connected to two carbon atoms which are a part of a conjugated system. In these compounds, at least one hydroxyl group is attached to a carbon atom which is a part of a conjugated system, which structure appears to account for the unique properties of the compounds. The following structures have been assigned to the compounds mentioned:



Xanthidrol



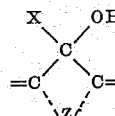
Alloxan hydrate



Triketohydrindene hydrate

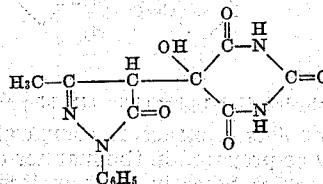
Alloxan hydrate and triketohydrindene hydrate are typical "gem-diol" compounds.

The compounds fall under the following general formula:



where X is either H or OH and Z represents the atoms necessary to complete a cyclic ring. The couplers of my invention are obtained by condensation of a pyrazolone coupler having a reactive methylene group in the 4-position with compounds of the above class. Monomolecular or bis-pyrazolone couplers are obtained depending upon the reaction conditions and the proportions of the reactants used. For example a monomolecular coupler can be obtained from alloxan hydrate by reacting it with approximately an equal molecular proportion of a pyrazolone whereas two mols of pyrazolone are used to produce the bis-compound. The following compounds are illustrative of those which may be used according to my invention:

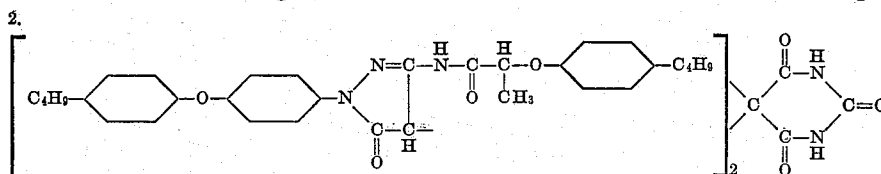
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4-allyloxan-1-phenyl-3-methyl-5-pyrazolone

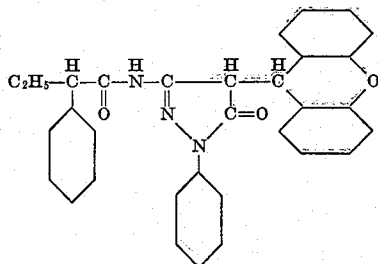
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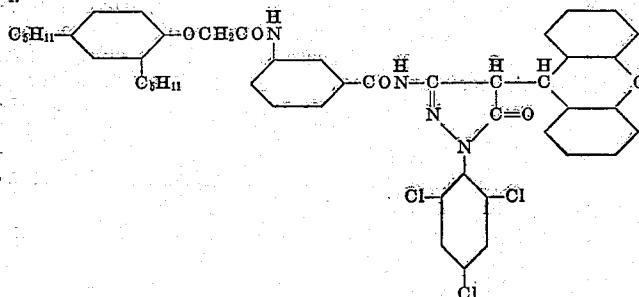
4,4'-alloxan-bis-1-(p-tert. butylphenoxy)phenyl-3-(p-tert. butylphenoxypropionylamino)-5-pyrazolone

3.



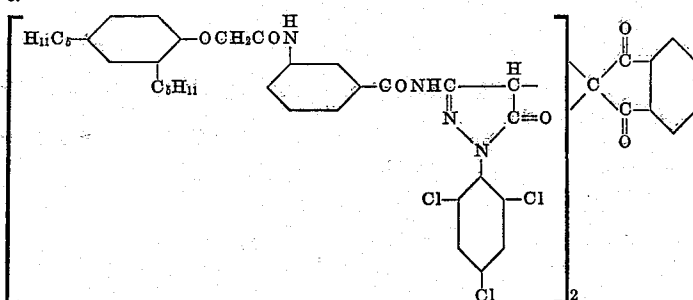
1-phenyl-3-( $\alpha$ -phenylbutyrylamino)-4-xanthidryl-5-pyrazolone

4.



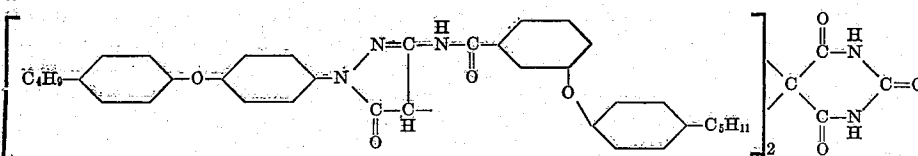
1-(2',4',6'-trichlorophenyl)-3-[3''(2''',4'''-di-tert. amylphenoxyacetamido)benzamido]-4-xanthidryl-5-pyrazolone

5.



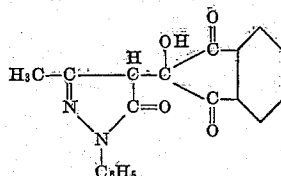
(4,4'-triketohydrindene-bis)1-(2',4',6'-trichlorophenyl)-3-[3''(2''',4'''-di-tert. amylphenoxyacetamido)benzamido]-5-pyrazolone

6.



Alloxan-bis-[1-(p-tert. butylphenoxy)phenyl-3-m-(p-tert. amylphenoxybenzoylamino)-5-pyrazolone]

7.



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

Other couplers of structure comparable to the above may be prepared in the manner of the following examples, wherein the substituent in the

1-position of the pyrazolone nucleus is either an aryl or substituted aryl group, and the 3-position may have for example an alkyl, aryl, amino or substituted amino substituent.

The method of preparation of the compounds of the invention will be understood by consideration of the following examples.

**Example 1.—1-phenyl-3-( $\alpha$ -phenylbutyrylamino)-4-xanthidryl-5-pyrazolone**

A mixture of 3.21 g. (.01 mole) 1-phenyl-3-( $\alpha$ -phenylbutyrylamino)-5-pyrazolone and 1.98 g. (.01 mole) xanthidrol in 25 cc. of acetic acid is heated at refluxing temperature for 1 hour.

The reaction mixture is poured into 200 cc. water and sufficient sodium hydroxide added to make

neutral to litmus. The white solid is collected by suction filtration and recrystallized from 1,4-

dioxane. The white crystalline powder had an M. P. of 220–222° C.

**Example 2.—1-(2',4',6'-trichlorophenyl)-3-[3''(2''',4'''-di-tert. - amylphenoxyacetamido)benzamido]-4-xanthidryl-5-pyrazolone**

A mixture of 6.72 g. (.01 mole) 1-(2',4',6'-trichlorophenyl)-3-[3''(2''',4'''-di-tert. - amylphenoxyacetamido)benzamido]-5-pyrazolone, 1.98 g. (.01 mole) xanthidrol, and 25 cc. of acetic acid is heated for 1 hour at refluxing temperature. The dark colored reaction mixture is poured with stirring into 200 cc. of water. Sufficient 10%

sodium hydroxide is added to make the mixture neutral to litmus. The precipitate is collected and recrystallized from methanol. The yield is 6 g. of greyish-white crystalline material melting at 120-125°. This is 70.4 per cent of the theoretical quantity 8.52 g.

**Example 3.** — (4,4 - triketohydrindene - bis) 1-(2',4',6' - trichlorophenyl) - 3 - [3''(2''',4''') - di-tert.-amylphenoxycetamido] benzamido]-5-pyrazolone

A mixture of 2.02 g. (.003 mole) 1-(2',4',6'-trichlorophenyl - 3 - [3''(2''',4''') - di-tert.-amylphenoxycetamido] benzamido]-5-pyrazolone, 2.67 g. (.0015 mole) triketohydrindene hydrate, 2.0 g. sodium acetate, and 25 cc. acetic acid is heated at boiling temperature for 2 hours. The resulting solution is poured into 300 cc. water with stirring. The precipitate is extracted with 100 cc. of boiling alcohol. The alcoholic extract is treated with decolorizing carbon and evaporated to crystallization. The yield of yellowish-brown crystals melting at 190-195° is 1.23 g., which is 55 per cent of the theoretical yield, 2.23 g.

**Example 4.** — 4,4'-alloxan-bis-1-(p-tert.butylphenoxy) phenyl - 3-a(p-tert.butylphenoxypropionylamino) - 5-pyrazolone

A solution of 5.27 g. (.01 mole) 1-(p-tert.butylphenoxy) - phenyl - 3-a(p-tert.butylphenoxypropionyl amino)-5-pyrazolone and .85 g. (.005 mole) alloxan monohydrate in 25 cc. pyridine is refluxed for 2 hours. After cooling somewhat, the mixture is poured into 200 cc. water and neutralized to litmus with acetic acid. The precipitate is collected and extracted with 200 cc. boiling ethyl alcohol. The alcohol extract is evaporated to crystallization. The yield of brownish crystals melting at 164-166° is 2.5 g., which is 42.1 per cent of the theoretical quantity, 5.94 g.

**Example 5.** — Alloxan-bis-[1-(p-tert.butylphenoxy) phenyl-3-m(p-tert.amylphenoxybenzoylamino) - 5-pyrazolone]

A mixture of 1.18 g. (.002 mole) 1-(p-tert.-butylphenoxy) phenyl-3-m (p-tert. amylphenoxybenzoylamino)-5-pyrazolone, 0.2 g. (.001 mole) alloxan monohydrate, 0.4 g. sodium acetate, and 50 cc. of acetic acid is refluxed for 2 hours. The reaction mixture is poured into water with stirring. The resulting precipitate is collected and recrystallized from ethylene chloride. The yield of yellowish crystalline powder is .02 g., which is 70 per cent of the theoretical quantity 1.31 g. The melting point is 225-227°.

**Example 6.** — 4-alloxan-1-phenyl-3-methyl-5-pyrazolone

Five grams (.29 mole) 1-phenyl-3-methyl-5-pyrazolone were suspended in 50 cc. distilled water. After heating to boiling the suspension was treated with 5 g. (.31 mole) alloxan monohydrate added in small portions. When the reaction was completed, the product was collected by suction filtration. Recrystallization from ethyl alcohol gave a white crystalline powder melting 196° dec. The yield was practically quantitative.

The compound No. 7 in the above list may be prepared in a similar manner by reacting triketohydrindene hydrate in place of alloxan with the pyrazolone in approximately equal molecular proportions.

Monomolecular and bis-pyrazolone coupler compounds similar in structure to the compounds of my invention have previously been suggested

by the prior art for use in color-photography. Such couplers are obtained by reaction of an aldehyde or ketone with a pyrazolone compound but the reactants of my invention have not previously been used in this manner. One advantage of the instant couplers lies in their ease of preparation, the condensation of the pyrazolone with the hydrol compound being carried out with ease. Contrary to this, repeated attempts to react a prior art compound such as a cyclic ketone with a pyrazolone by the usual methods has not been productive of the monomolecular or bis coupler compounds. Similar couplers prepared from aldehydes are less soluble in coupler solvents than are the couplers of the invention, therefore, it is possible when using my couplers to decrease the coupler-solvent ratio which allows the coating of thinner emulsion layers, as a result of which valuable improvements in resolving power of the emulsion can be obtained.

Perhaps the chief advantage of the couplers of the invention aside from their stability and the stability of the dye images obtained therefrom, over the prior art compounds, lies in the ease with which coupling occurs in the color development process. As is apparent, in color processes the monomolecular or bis-pyrazolone coupler must split apart in the development step wherein the oxidized developer combines with the pyrazolone. The prior art compounds, for example, obtained by reaction of an aldehyde with a pyrazolone coupler, seem to be reluctant to split apart; at least the result is that color development utilizing such couplers is relatively sluggish. However, the couplers of the invention couple with the developing agent with surprising speed. This behavior of the couplers of the invention may be attributable to the conjugated system present in the molecule of the novel coupler.

The couplers of the invention are especially suitable for use in sensitive silver halide emulsion layers for use in processes such as those described in Fischer U. S. 1,055,155, Mannes and Godowsky, U. S. 2,304,940 and Jolley and Vittum, U. S. 2,322,027. Their usefulness in such processes is apparent, particularly since the couplers have little tendency to wander in emulsion layers. The couplers can be incorporated in the emulsion layers especially as described in the latter patent.

In the development of exposed silver halide emulsion layers using the couplers of my invention, any color-forming developer containing a primary amino group may be used. These include developers having two primary amino groups as well as those having one of the amino groups substituted or having substituents in the ring. These compounds are usually in the salt form such as the hydrochloride or the sulfate which are more stable than the amines themselves. Suitable compounds are diethyl-p-phenylenediamine hydrochloride, monomethyl-p-phenylenediamine hydrochloride, dimethyl-p-phenylenediamine hydrochloride, and 2-amino-5-diethylaminotoluene hydrochloride. The p-amino phenols and their substitution products may also be used where the amino group is unsubstituted.

We have found that when our couplers react with the oxidized developer, the same dye is formed which would be formed by reacting the parent methylene coupler with the oxidized developer. In certain cases, it has been found advantageous to use our new compounds instead of

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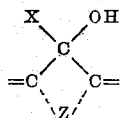
the parent methylene compound. For example, when the compounds are incorporated in a silver halide emulsion layer, the excess coupler which remains in the layer after processing does not confer heat instability upon the dye images as does the parent coupler.

My development process may be employed for the production of colored photographic images in layers of gelatin or other water-permeable colloidal carriers, such as albumen, collodion, or organic esters of cellulose or synthetic resins. The carrier may be supported by a transparent medium such as glass, a cellulose ester or synthetic resin or a non-transparent reflecting medium such as paper or an opaque cellulose ester. The emulsion may be coated as a single layer on the support or as superposed layers on one or both sides of the support. The superposed layers may be differentially sensitized to form natural color images.

The examples and compounds included herein are illustrative only and it is to be understood that my invention should be taken as limited only by the scope of the appended claims.

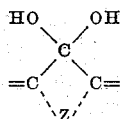
What I claim is:

1. A photographic emulsion layer comprising a carrier, silver halide and as a color-forming development component, the condensation product of a pyrazolone having a reactive methylene group in the 4-position and a compound containing the following group:



wherein X is a member of the group consisting of H and OH and Z represents the atoms necessary to complete a cyclic ring free of substituents reactive with said methylene group, the condensation taking place at said methylene group and at a hydroxyl group of said compound.

2. A photographic emulsion layer comprising a carrier, silver halide and as a color-forming development component, the condensation product of a pyrazolone having a reactive methylene group in the 4-position and a compound containing the following group:



wherein Z represents the atoms necessary to complete a cyclic ring free of substituents reactive with said methylene group, the condensation taking place at said methylene group and at a hydroxyl group of said compound.

3. A photographic emulsion layer comprising a carrier, silver halide and as a color-forming development component, the condensation product of a pyrazolone having a reactive methylene group in the 4-position and triketohydrindene hydrate, the condensation taking place at said methylene group and at a hydroxyl group of said hydrate.

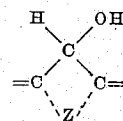
4. A photographic emulsion layer comprising a carrier, silver halide and as a color-forming development component, the condensation product of a 3-acylaminopyrazolone having a reactive methylene group in the 4-position and triketohydrindene hydrate, the condensation taking place at said methylene group and at a hydroxyl group of said hydrate.

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5. A photographic emulsion layer comprising a carrier, silver halide and as a color-forming development component, the condensation product of a pyrazolone having a reactive methylene group in the 4-position and alloxan hydrate, the condensation taking place at said methylene group and at a hydroxyl group of alloxan.

6. A photographic emulsion layer comprising a carrier, silver halide and as a color-forming development component, the reaction product of a 3-acylamino pyrazolone having a reactive methylene group in the 4-position and alloxan hydrate, the condensation taking place at said methylene group and at a hydroxyl group of alloxan.

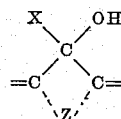
7. A photographic emulsion layer comprising a carrier, silver halide and as a color-forming development component, the condensation product of a pyrazolone having a reactive methylene group in the 4-position and a compound containing the following group:



wherein Z represents the atoms necessary to complete a heterocyclic ring free of substituents reactive with said methylene group, the condensation taking place at said methylene group and at a hydroxyl group of said compound.

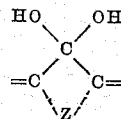
8. A photographic emulsion layer comprising a carrier, silver halide and as a color-forming development component, the condensation product of a pyrazolone having a reactive methylene group in the 4-position and xanthidrol, the condensation taking place at said methylene group and at the hydroxyl group of xanthidrol.

9. A photographic emulsion layer comprising a carrier, silver halide and as a color-forming development component, the condensation product of one molecule of a pyrazolone having a reactive methylene group in the 4-position and one molecule of a compound containing the following group:



wherein X is a member of the group consisting of H and OH and Z represents the atoms necessary to complete a heterocyclic ring free of substituents reactive with said methylene group, the condensation taking place at said methylene group and at a hydroxyl group of said compound.

10. A photographic emulsion layer comprising a carrier, silver halide and as a color-forming development component, the condensation product of two molecules of a pyrazolone having a reactive methylene group in the 4-position and one molecule of a compound containing the following group:



wherein Z represents the atoms necessary to complete a cyclic ring free of substituents reactive with said methylene group, the condensation taking place at said methylene group and the hydroxyl groups of said compound.

11. A photographic emulsion layer comprising

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a carrier, silver halide and as a color-forming development component, the condensation product of one molecule of a pyrazolone having a reactive methylene group in the 4-position and one molecule of xanthidrol, the condensation taking place at said methylene group and at the hydroxyl group of xanthidrol.

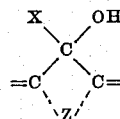
12. A photographic emulsion layer comprising a carrier, silver halide and as a color-forming development component, the condensation product of two molecules of a pyrazolone having a reactive methylene group in the 4-position and one molecule of alloxan hydrate, the condensation taking place at said methylene group and at the hydroxy groups of said hydrate.

13. A photographic emulsion layer comprising a carrier, silver halide and as a color-forming development component, the condensation product of two molecules of a pyrazolone having a reactive methylene group in the 4-position and one molecule of triketohydrindene hydrate, the condensation taking place at said methylene group and at the hydroxy groups of said hydrate.

14. A photographic emulsion layer comprising a carrier, silver halide and as a color-forming development component, the condensation product of a pyrazolone having a reactive methylene group in the 4-position and a compound selected from the class consisting of xanthidrol, alloxan hydrate and triketohydrindene hydrate, the condensation taking place at said reactive methylene group and at a hydroxyl group of a compound of said class.

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15. The method of producing a colored image in an exposed silver halide emulsion layer, which comprises developing said layer with a primary aromatic amino developing agent in the presence of a color-forming development component which is the condensation product of a pyrazolone having a reactive methylene group in the 4-position and a compound containing the following group:



15 wherein X is a member of the group consisting of H and OH and Z represents the atoms necessary to complete a cyclic ring free of substituents reactive with said methylene group, the condensation taking place at said methylene group and at a hydroxyl group of said compound.

GEORGE W. SAWDEY.

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25 The following references are of record in the file of this patent:

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