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ALKOXY PYRAZOLONE COUPLERS

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No Drawing. Original application December 22, 1944, Serial No. 569,428. Divided and this application June 15, 1945, Serial No. 599,742

5 Claims. (Cl. 260—310)

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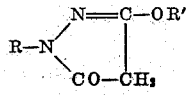
This invention relates to photographic color-forming compounds and particularly to coupler compounds which are derivatives of pyrazolones for color-forming processes of color photography.

This application is a division of our application, Serial No. 569,428, filed December 22, 1944, now abandoned.

The formation of colored photographic images by coupling the development product of aromatic amino developing agents with color-forming or coupling compounds is well known. In these processes, the color formation is ordinarily accomplished by the subtractive process and the image dyes are of the subtractive primary colors, cyan or blue-green, magenta, and yellow. The magenta dyes are frequently produced from pyrazolone or cyano acetyl couplers and the present invention relates to couplers of the former type.

Pyrazolone couplers have been described in Seymour U. S. Patent 1,969,479. Acylamino pyrazolone couplers and phenylamino pyrazolone couplers have been described respectively in Porter and Weissberger U. S. Patents 2,343,702 and 2,311,081. 3-amino pyrazolone couplers have been described in Porter and Weissberger U. S. Reissue Patent 22,329 and 3-acylamino pyrazolone couplers in Porter and Weissberger U. S. patent application Serial No. 457,276, now U. S. Patent 2,369,489.

We have discovered a class of pyrazolone couplers which possess valuable properties when used in color photography. These couplers have an alkoxy group in the 3-position of the pyrazolone ring and are represented by the following general formula:



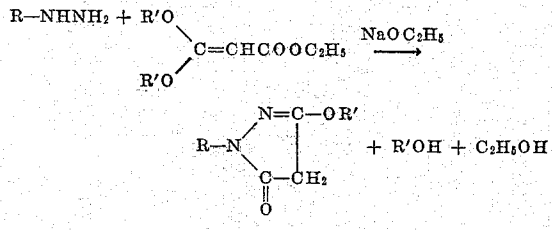
in which R is hydrogen, alkyl, aryl, heterocyclic, or thiocarbamyl, and R′ is alkyl.

In the general formula, the alkyl group may be methyl, ethyl, propyl, or butyl, the aryl group may be unsubstituted phenyl or substituted aryl group, such as nitrophenyl, sulfamyl phenyl, or chlorophenyl, and the heterocyclic groups may be radicals, such as benzothiazolyl or benzoxazolyl. The alkyl groups are lower alkyl groups, that is alkyl groups containing less than about five carbon atoms.

The couplers of our invention are made by a method which we believe to be novel. According to this method, hydrazine or a hydrazine de-

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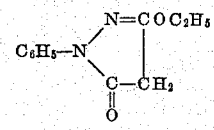
rivative is heated with an ethyl β,β-dialkoxyacrylate until the reaction is complete, as indicated by the evolution of alcohol or the solution of the hydrazine, and sodium ethylate in alcohol is then added and the mixture heated for a further short period. The desired coupler separates as the sodium salt and this is dissolved in water and the compound precipitated with acid. The general method of preparation is represented by the following equation:



In the equation, R and R′ have the same meaning as in the general formula above.

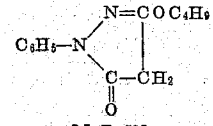
The following examples illustrate compounds which are suitable for use according to our invention:

1.



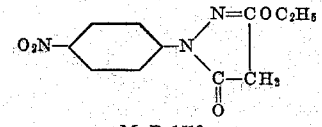
M. P. 116°
1-phenyl-3-ethoxy-5-pyrazolone

2.



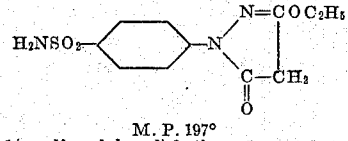
M. P. 59°
1-phenyl-3-butoxy-5-pyrazolone

3.



M. P. 151°
1-p-nitrophenyl-3-ethoxy-5-pyrazolone

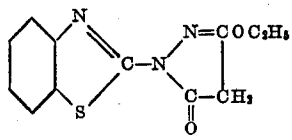
4.



M. P. 197°
1(p-sulfamylphenyl)-3-ethoxy-5-pyrazolone

p-sulfamylphenylhydrazine is prepared following Crippa and Maffei, Gazz. chim. Ital., 72, 97 (1942).

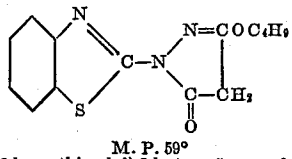
5.



M. P. 200°
1(2-benzothiazolyl)-3-ethoxy-5-pyrazolone

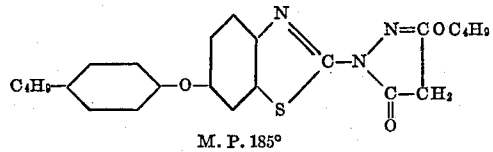
2-benzothiazolylhydrazine prepared following German Patent 614,327 (1935).

6.



M. P. 59°
1(2-benzothiazolyl)-3-butoxy-5-pyrazolone

7.

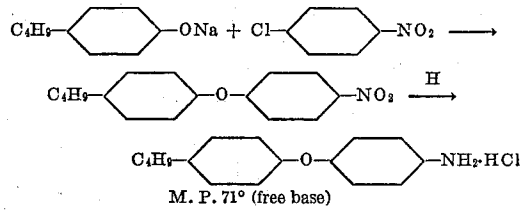


M. P. 185°

1-[6(p-tert. butylphenoxy)-2-benzothiazolyl]-3-butoxy-5-pyrazolone

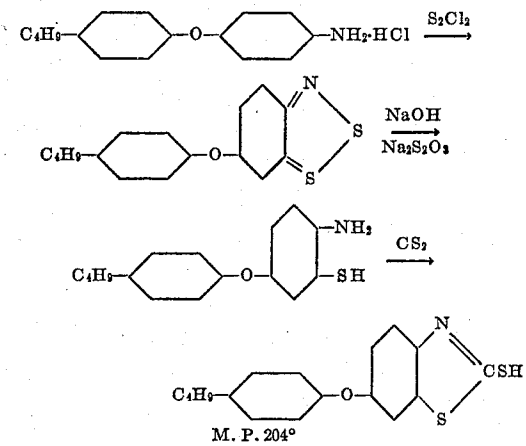
6(p-tert. butylphenoxy)-2-benzothiazolyl hydrazine was prepared by the following series of reactions:

a.



M. P. 71° (free base)

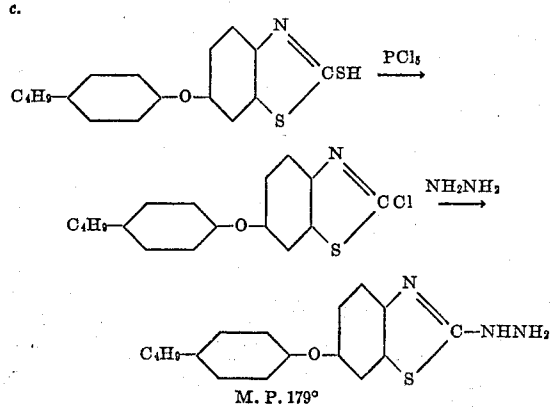
b.



M. P. 204°

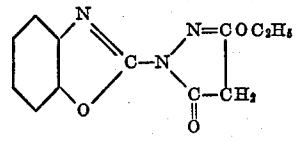
This preparation follows closely that given in J. Am. Chem. Soc., 53, 1891 (1931).

c.



M. P. 179°

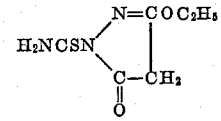
8.



M. P. 152° (heating rapidly)
1-(2-benzoxazolyl)-3-ethoxy-5-pyrazolone

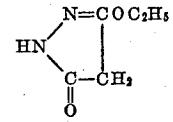
2-benzoxazolylhydrazine prepared following German Patent 614,327 (1935).

9.



M. P. 171°
1-thiocarbamyl-3-ethoxy-5-pyrazolone

10.



M. P. 177°
3-ethoxy-5-pyrazolone

Prepared by heating (9) in 5 parts of 10% sodium hydroxide for 1 hour.

As stated above, the couplers of our invention are prepared by reacting hydrazine or a hydrazine derivative with an ethyl β,β-dialkoxy-acrylate. The hydrazine derivative includes compounds such as phenyl hydrazine, p-nitrophenylhydrazine, p-sulfonylphenylhydrazine, 2-benzothiazolylhydrazine, 6-(p-tert. butylphenoxy)-2-benzothiazolylhydrazine, 2-benzoxazolylhydrazine and thiocarbamylhydrazine. The acrylate may include ethyl β,β-diethoxyacrylate, ethyl β,β-dipropoxyacrylate and ethyl β,β-dibutoxyacrylate.

The following example illustrates the preparation of 1-phenyl-3-ethoxy-5-pyrazolone, compound No. 1.

Example 1

Equal molecular weights of phenylhydrazine and ethyl β,β-diethoxyacrylate are heated together on the steam bath for ½ to 1 hour with or without solvent. A solution of sodium ethylate (one equivalent of sodium dissolved in 17 cc. per gram of absolute ethyl alcohol) is added and the mixture heated for another quarter to half hour. A clear solution is then formed by the addition of water and the product precipitated by acidification and is then filtered and recrystallized from a suitable solvent. The melting point is 116° C.

Ethyl β,β-diethoxyacrylate is prepared according to the method of Reitler and Weindel, Berichte 40, 3359 (1907). The corresponding β,β-dipropoxy and β,β-dibutoxy esters are prepared analogously using n-propanol or n-butanol instead of ethanol. The boiling point of the dibutoxy ester is 150–160° at 7 mm. pressure.

The couplers of our invention may be incorporated in the developed solution or in the sensitive emulsion layer. When incorporated in the developed solution, the couplers may be used in processes such as those described in Mannes and Godowsky U. S. Patent 2,113,329 or Mannes, Godowsky and Wilder U. S. Patent 2,252,718. When incorporated in the sensitive emulsion layer, the couplers may be used in processes, such as those described in Fisher U. S. Patent 1,055,155, Mannes and Godowsky U. S. Patent 2,304,940 or Jelley and Vittum U. S. Patent 2,322,027.

The following examples illustrate developing solutions containing the couplers used according to our invention:

Example 2

A. 2 - amino-5-diethyl - aminotoluenehydrochloride	grams	2
Sodium sulfite anhydrous	do	2
Sodium carbonate anhydrous	do	20
Potassium bromide	do	1
Water to	liter	1
B. 1-Phenyl-3-ethoxy-5-pyrazolone	grams	2
Sodium hydroxide (10% solution)	cc	10

For use B is added to A.

Example 3

A. Dimethyl - p - phenylenediaminesulfate	grams	3
Sodium sulfite anhydrous	do	5
Sodium carbonate anhydrous	do	20
Potassium bromide	do	2
Water to	liter	1
B. 1-(2-benzothiazolyl) -3- ethoxy-5-pyrazolone	grams	3
Isopropyl alcohol	cc	100

For use B is added to A.

Certain of the coupler compounds of our invention, such as compound No. 7 are themselves non-diffusing and may be incorporated in the photographic layer without the use of additional compounds to prevent diffusion. Other couplers may be rendered non-diffusing in the emulsion layer by the use of special means as by causing the couplers to be absorbed or adsorbed to the sensitive silver salt.

In the development of exposed photographic silver halide emulsion layers using the couplers of our 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, such as alkylphenylenediamines and alkyltoluenediamines. These compounds are usually used 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-aminophenols and their substitution products may also be used where the amino group is unsubstituted. All of these developers have an unsubstituted amino group which enables the oxidation products of the developer to couple with the color-forming compound to form a dye image.

Our development process may be employed for the production of colored photographic images in layers of gelatin or other water-permeable colloidal carrier, such as collodion, organic esters of cellulose, or synthetic resins. The carrier may be supported by a transparent medium such as glass, a cellulose ester of 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 so that different colors may be recorded in the layers and differently colored images formed therein.

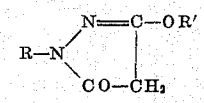
The examples and compounds set forth in the present specification are illustrative only and it is to be understood that our invention is limited only by the scope of the appended claims.

We claim:

1. The method of producing a 3-alkoxy-5-pyrazolone, which comprises heating a monosubstituted hydrazine in which the substituent is selected from the class consisting of hydrogen, alkyl, aryl, benzothiazolyl, benzoxazolyl and thiocarbamyl groups, and an ethyl β,β-dialkoxyacrylate in which the alkoxy is a lower alkoxy group on a steam bath until reaction is complete adding sodium ethylate and heating for a further period, precipitating the resulting product from solution and removing it from the solution.

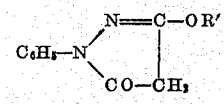
2. The method of producing 1-phenyl-3-ethoxy-5-pyrazolone, which comprises heating equal molecular weights of phenyl hydrazine and ethyl β,β-diethoxyacrylate on a steam bath for ½ to one hour, adding sodium ethylate and heating for a further period of ¼ to ½ hour, precipitating the resulting 1-phenyl-3-ethoxy-5-pyrazolone from solution and removing it from the solution.

3. A 3-alkoxy-5-pyrazolone selected from the group of 3-alkoxy-5-pyrazolones represented by the following general formula:



wherein R represents a member selected from the class consisting of hydrogen, alkyl, aryl, benzothiazolyl, benzoxazolyl and thiocarbamyl groups, and R′ represents a lower alkyl group.

4. A 1-phenyl-3-alkoxy-5-pyrazolone selected from the group of 1-phenyl-3-alkoxy-5-pyrazolones represented by the following general formula:



wherein R′ represents a lower alkyl group.

5. 1 phenyl-3-ethoxy-5-pyrazolone.

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ARNOLD WEISSBERGER.
WALTER A. GREGORY.

REFERENCES CITED

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

J. Am. Chem. Soc., vol. 65, pages 52–54, January 1943.