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2,411,951

4,4'-BIS (PYRAZOLONE) COUPLERS FOR COLOR PHOTOGRAPHY

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12 Claims. (Cl. 95—6)

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This invention relates to the production of colored photographic images by color development, and more particularly to substituted and unsubstituted bis-pyrazolones as new color forming coupler compounds therefor.

The formation of colored photographic images by coupling the development product of an aromatic amino developing agent with color forming or coupling compounds is well known, and is generally referred to as color forming development. In these methods the subtractive process of color formation is ordinarily used and the image dyes are intended to be of the complementary primary colors, cyan or blue-green, magenta and yellow. The couplers which produce magenta dyes are ordinarily pyrazolones or cyano acetyl compounds. The dyes produced by coupling are azomethines, indamines or indophenols, depending upon the composition of the coupler and of the developer. The coupler or color former may be present in the emulsion or in the developing solution which during the development process couples with the oxidation product of the aromatic amino developer to form a dye image in the emulsion. The developed emulsion may then be bleached for removal of the silver image leaving the color image in the emulsion.

I have discovered that substituted and unsubstituted bis-pyrazolones are especially valuable color formers which couple with the oxidation product of an aromatic primary amino developer to form a magenta dye image in the emulsion. The substituted and unsubstituted bis-pyrazolones are permeable to blue rays and show a high transparency, with the result that a satisfactory color for subtractive color processes is obtained upon coupler development.

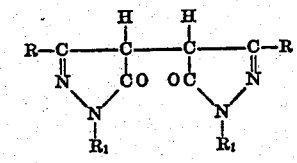
It is an object of the present invention to provide a new class of color formers for producing magenta dye images by color forming development.

A further object is to provide photographic developer solutions and emulsions which contain a new class of color formers for producing magenta dye images in situ with photographic images.

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A still further object is to provide finished photographs which contain stable dye images.

The above and other objects are accomplished according to the present invention by the use of substituted and unsubstituted bis-pyrazolones of the general formula:



wherein R represents hydrogen, or an alkyl group e. g., methyl, ethyl, propyl, butyl, octyl, decyl, heptadecyl, octadecyl, stearyl, or any other alkyl radical containing up to 24 carbon atoms, carbalkoxy alkyl, e. g., acetic ethyl ester and the like, alkylcarboxy, e. g., carbomethoxy, carbethoxy, carbopropoxy, etc., aryl, e. g., phenyl, naphthyl, anthranyl, diphenyl, etc., or aralkyl, e. g., benzyl, methyl benzyl, ethyl benzyl and the like, alkylamino, e. g., amylamino and the like, arylamino, e. g., anilino, anisylamino and the like, acetarylamido, e. g., acetanilido, acetanisido, acetdimethylanilido, acetnaphthylamido, etc., sulfamylphenylamino and the like, R_1 represents either hydrogen, alkyl, aryl, or aralkyl of the same value as R, or a heterocyclic nucleus, e. g., thiazolyl, benzothiazolyl, quinolyl, pyridyl, naphthiazolyl and the like. Said alkyl, aryl, aralkyl radicals given as values for R and R_1 may be substituted by a halogen such as chlorine, bromine or iodine, acetamido group, imino group, nitro group, alkoxy, e. g., methoxy, ethoxy, propoxy, butoxy, etc., amino group, e. g., primary amino, secondary amino such as methyl amino, phenyl amino and the like, or a tertiary amino such as dimethyl amino, diphenyl amino etc., sulfoamino, or solubilizing groups such as sulfonic or carboxylic acid groups.

Compounds representing this general classification are as follows:

4,4'-bis(1-phenyl-3-methyl-5-pyrazolone)

4,4'-bis(1-p-nitrophenyl-3-methyl-5-pyrazolone)

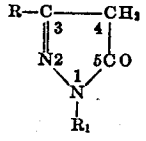
4,4'-bis(1-α-naphthyl-3-methyl-5-pyrazolone)
4,4'-bis(1 - p - bromophenyl - 3 - methyl - 5 - pyrazolone)
4,4'-bis-5-pyrazolone (unsubstituted)
4,4'-bis(3-phenyl-5-pyrazolone)
4,4'-bis(1-phenyl-3-acetic ethyl ester-5-pyrazolone)
4,4'-bis(1-phenyl-3-acetanilido-5-pyrazolone)
4,4'- bis(1 - phenyl - 3 - p - chlor - acetanilido - 5-pyrazolone)
4,4'- bis(1 - phenyl - 3 - acet - α - naphthyl - amido-5-pyrazolone)
4,4'-bis(1-β-naphthyl-3-acetic ethyl ester-5-pyrazolone)
4,4'- bis(1 - β - naphthyl - 3 - acet - o - anisido - 5-pyrazolone)
4,4'- bis(1 - phenyl - 3 - acet - α - naphthyl - amido-5-pyrazolone)
4,4'- bis(1 - p - tolyl - 3 - (acet - 2',4'- dimethyl - anilido) -5-pyrazolone)
4,4'-bis(3-anilino-5-pyrazolone)
4,4'-bis(1-acetyl-3-anilino-5-pyrazolone)
4,4'-bis(3-α-naphthylamino-5-pyrazolone)
4,4'-bis(3-o-bromanilino-5-pyrazolone)
4,4'-bis(3-n-amylamino-5-pyrazolone)
4,4'-bis(1-benzoyl-3-anilino-5-pyrazolone)
4,4'-bis(1-phenyl-3-anilino-5-pyrazolone)
4,4'- bis(1 - phenyl - 3 - p - anisyl - amino - 5 - pyrazolone)
4,4'- bis(1 - phenyl - 3 - p - sulfamylphenyl - amino-5-pyrazolone)
4,4'- bis(1 - phenyl - 3 - p - (p - tert. amyl - phenoxy) -phenylamino-5-pyrazolone)
4,4'- bis(1 - (3 - carboxyphenyl) - 3 - heptadecyl - 5-pyrazolone)
4,4'- bis(1 - (phenyl - 4'-sulfonic acid) - 3 - heptadecyl-5-pyrazolone)
4,4'- bis(1 - (phenyl - 3'-sulfonic acid) - 3 - heptadecyl-5-pyrazolone)
4,4'- bis(1 - (phenyl - 3'- carboxylic acid) - 3 - undecyl-5-pyrazolone)
4,4'-bis(1-ethane sulfonic acid-3-p-nitrophenyl-5-pyrazolone)
4,4'-bis(1-ethane sulfonic acid-3-methyl-5-pyrazolone)
4,4'-bis(1-ethane sulfonic acid-3-heptadecyl-5-pyrazolone)
4,4'- bis(1 - (phenyl - 4'-ethoxy) - 3 - methyl - 5-pyrazolone)
4,4'- bis(1 - (phenyl - 4'-nitro) - 3 - methyl - 5 - pyrazolone)
4,4'-bis(1 - (α - naphthyl - 4' - sulfo) - 3 - methyl-5-pyrazolone)
4,4'- bis(1 - (phenyl - 4'- sulfo) - 3 - methyl - 5 - pyrazolone)
4,4'- bis(1 - (2'- benzothiazolyl) - 3 - anilino - 5-pyrazolone)
4,4'- bis(1 - (α - quinolyl) - 3 - anilino - 5 - py - razolone)
4,4'- bis(1 - (α - pyridyl) - 3 - anilino - 5 - py - razolone)
4,4'-bis(3-methyl-5-pyrazolone)
4,4'-bis(1-phenyl-3-phenyl-5-pyrazolone)
4,4'-bis(1-p-tolyl-3-methyl-5-pyrazolone)
4,4'- bis(1 - (2'-methylphenyl - 5'-sulfonic acid) - 3-heptadecyl-5-pyrazolone)
4,4'-bis(1-(2'-methoxyphenyl-5'-sulfonic acid) - 3-(3'-stearylaminophenyl) -5-pyrazolone)
4,4'-bis(1-(2'-phenoxyphenyl-3'-sulfonic acid) sodium-3-heptadecyl-5-pyrazolone)
4,4'- bis(1 - (3 - carboxyphenyl) - 3 - hepta - decyl-5-pyrazolone)
4,4'- bis(1 - phenyl - 3 - (heptadecyl - 4'-sulfonic acid) -5-pyrazolone) and

4,4'- bis(1 - phenyl - 3 - (undecyl - 3'-carboxylic acid) -5-pyrazolone)

In general, the coupling compounds of the present invention which do not contain solubilizing groups, are water insoluble. Their solubility in water, however, is accomplished by the introduction of suitable solubilizing groups, e. g., sulfonic or carboxylic acid groups into the groups represented by R in the above general formula.

The condensation reaction is carried out by refluxing a substituted or unsubstituted pyrazolone in the presence of phenyl hydrazine according to the methods known in the art.

The substituted pyrazolones are prepared according to the methods described in U. S. Patents 2,200,306; 2,265,221; 2,334,495; 2,343,703; and U. S. Patent Re. 22,329. These substituted pyrazolones are characterized by having an active methylene group in the 4 position and have the general formula



wherein R and R_1 have the same values as above. The commonly accepted nomenclature is used and the positions from 1 to 5 are numbered as shown.

The examples of the substituted pyrazolones disclosed herein and in the above mentioned patents are exemplary only, it being understood that they may contain other substituent groups as well as those included in the above general formula.

During the experimentation with and the practicing of this invention, I have discovered that the nature of R and R_1 substituents in the above general formula is immaterial since any substituted or unsubstituted pyrazolone, having an active methylene group at the 4 position, will condense in the presence of phenyl hydrazine to give the corresponding bisymmetrical product, and such product will function as a color former.

The color formers may be added to the developer, providing they are not fast to diffusion in gelatin, or to the silver-halide emulsion in the form of a solution or a suspension in a suitable solvent, such as, 1-N-alcoholic sodium or potassium hydroxide, acetone, ethyl alcohol, isopropyl alcohol, etc. Dispersing agents such as isopropyl naphthalene sulfonic acid or any of the dispersing agents disclosed in U. S. 2,186,717 may be used in preparing the suspension of the water insoluble color formers for incorporation into developers or silver-halide emulsions. Instead of gelatin, the color formers may be incorporated in other colloidal materials such as, organic esters of cellulose, super-polyamides, polyesters or synthetic resins. The emulsion may be carried by a transparent medium such as cellulose esters, superpolyamides, synthetic resins 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 superposed layers containing the couplers may be coated on one or both sides of the support. The superposed layers may be differentially sensitized for the formation of a color image in the well known manner.

When incorporating the color formers into photographic silver-halide emulsions, it is essential that the substituents of R in the above gen-

eral formula be such that they will prevent the color formers from migrating from one layer to another, otherwise color distortion will result upon color-forming development. Several methods have been proposed to prevent migration of color formers from silver-halide emulsion layers by rendering such color formers "fast to diffusion in gelatin." This result may be accomplished in several ways, as for example, by substituting the 1 and/or 3 position of the pyrazolone nucleus with suitable groups which impart substantive characteristics to the color formers which combine permanently with the gelatin and other colloidal materials of the silver-halide emulsion, or by enlarging the substituent group of the color former with a long chain alkyl radical so that the color former is incapable of diffusing from the gelatin or other colloidal materials. Examples of such methods which render color formers fast to diffusion by imparting substantive characteristcs thereto are disclosed in U. S. 2,179,228. Examples of color formers which are rendered fast to diffusion by enlarging the substituent groups (R and/or R_1) are disclosed in U. S. Patents 2,175,-512; 2,179,238–9; 2,179,234; 2,178,612; 2,179,344; 2,179,244; 2,186,719; 2,186,851–2; 2,186,732–3–4; 2,186,849; 2,186,045; 2,200,306; 2,280,722; 2,292,-575; 2,303,928 and 2,307,399. By reference to the latter patents, it will be noted that the color formers are modified by the inclusion of radicals of resins, polypetides, hydrogenated ring systems, carbohydrates, long alkyl chains, and by having the substituent radical recur a number of times in the final molecule. It is to be understood that the substituent groups of the color formers of the present invention in addition to those previously mentioned, include substantive groups or molecular enlarging groups for the purpose of rendering the bis-pyrazolones fast to diffusion.

As examples of suitable aromatic primary amino developing agents which may be employed with the color coupling compounds of the present invention, there may be mentioned p-phenylene diamine, mono ethyl-p-phenylene diamine, diethyl-o-phenylene diamine, 4,4'-diamino-diphenylamine, p-amino dialkyl anilines, e. g., p-amino dimethyl aniline and p-amino-diethyl aniline. These developing agents are preferably used in the form of their salts such as the hydrochloride, since they are more soluble and stable than the free base. They are characterized by the presence of a free or primary amino group in the phenyl nucleus which enables the oxidation product of the developer to couple with the color former to form a dye image in the emulsion adjacent to the individual particles of the silver image. The silver image may be removed by bleaching in the well known manner to leave the color image in the emulsion.

A suitable developing solution is prepared as follows:

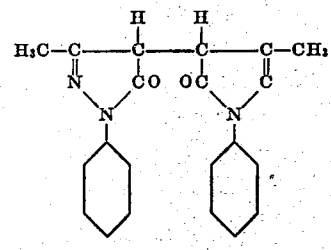
p-Amino-diethylaniline HCl	grams	2.0
Sodium carbonate (anhydrous)	do	50.0
Sodium sulfite (anhydrous)	do	2.0
Potassium bromide	do	0.2
Water to make	liter	1

The exposed silver-halide emulsions are developed in the above solution in the usual manner. A solution or suspension of the color former is only added to the developing solution where the color former is not present in the silver-halide emulsion.

Many specific objects, features and advantages of my invention will become apparent to those skilled in the art from the specific examples appearing below. The following examples are not to be considered as limiting my invention but are merely illustrative of methods of carrying it out.

Example I

4,4'-bis(1-phenyl-3-methyl-5-pyrazolone)

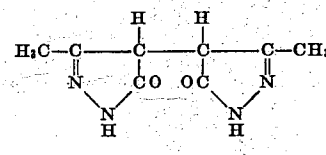


This compound was prepared according to the method given in Ann., 238, 167 and Ber., 17, 2044, by refluxing 5 grams of 1-phenyl-3-methyl-5-pyrazolone with 15 cc. of phenyl hydrazine for 1 hour. The reaction mixture was allowed to cool and the precipitated product was then filtered and recrystallized from ethyl alcohol.

1 gram of the above product was dissolved in 20 cc. of ethyl alcohol. 2 cc. of the solution were then added to the developing solution and used for the development of an exposed silver-halide emulsion. A magenta image was obtained together with the silver image.

Example II

4,4'-bis(3-methyl-5-pyrazolone)

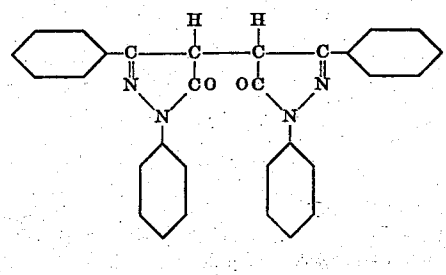


This compound was prepared according to the method of Max Edam, Dissertation Jena, 1893, pages 16 and 29, by refluxing 5 grams of 3-methyl-5-pyrazolone with 20 cc. of phenyl hydrazine for 1 hour. The reaction mixture was allowed to cool and the precipitated product was then filtered and recrystallized from ethyl alcohol.

1 gram of the above product was dissolved in 20 cc. of ethyl alcohol. 2 cc. of the solution were then added to the developing solution and used for the development of an exposed silver-halide emulsion. A magenta image was obtained together with the silver image.

Example III

4,4'-bis(1-phenyl-3-phenyl-5-pyrazolone)



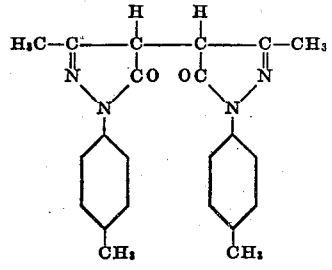
This compound was prepared according to the

directions given in Ber. 20, p. 2548, by refluxing 5 grams of 1-phenyl-3-phenyl-5-pyrazolone with 20 cc. of phenyl hydrazine for 1 hour. The reaction mixture was allowed to cool and the precipitated product was then filtered and recrystallized from ethyl alcohol.

1 gram of the above product was dissolved in 20 cc. of ethyl alcohol. 2 cc. of the solution were then added to the developing solution and used for the development of an exposed silver-halide emulsion. A magenta image was obtained together with the silver image.

Example IV

4,4'-bis(1-p-tolyl-3-methyl-5-pyrazolone)

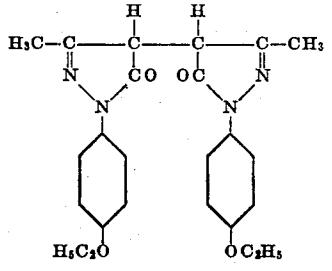


This compound was prepared according to the method of C. T. Sprague, Dissertation Gottinger, 1890, page 46 (can also be prepared according to the method of W. Hippmeir, Diss., Jena, 1894, s. 17), by refluxing 5 grams of 1-p-tolyl-3-methyl-5-pyrazolone with 15 cc. of phenyl hydrazine for 2 hours. The reaction mixture was allowed to cool and the precipitated product was then filtered and recrystallized from ethyl alcohol.

1 gram of the above product was dissolved in 20 cc. of ethyl alcohol. 2 cc. of the solution were then added to the developing solution and used for the development of an exposed silver-halide emulsion. A magenta image was obtained together with the silver image.

Example V

4,4'-bis(1-(phenyl-4'-ethoxy)-3-methyl-5-pyrazolone)

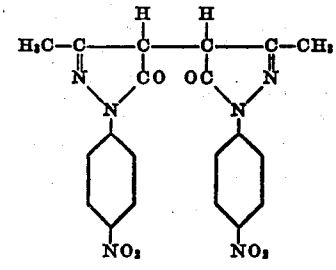


This compound was prepared according to the method of J. Grenzfelder, Dissertation Jena, 1894, page 17, by refluxing 5 grams of 1-(phenyl-4'-ethoxy)-3-methyl-5-pyrazolone with 20 cc. of phenyl hydrazine for 2 hours. The reaction mixture was allowed to cool and the precipitated product was then filtered and recrystallized from ethyl alcohol.

1 gram of the above product was dissolved in 20 cc. of ethyl alcohol. 2 cc. of the solution were then added to the developing solution and used for the development of an exposed silver-halide emulsion. A magenta image was obtained together with the silver image.

Example VI

4,4'-bis(1-(phenyl-4'-nitro)-3-methyl-5-pyrazolone)

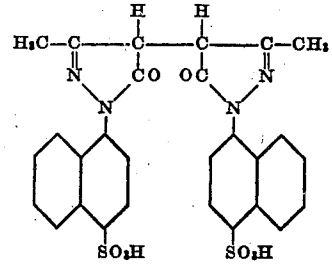


This compound was prepared according to the method of Example 5 by refluxing 5 grams of 1-(phenyl-4'-nitro)-3-methyl-5-pyrazolone with 20 cc. of phenyl hydrazine for 2 hours. The reaction mixture was allowed to cool and the precipitated product was then filtered and recrystallized from ethyl alcohol.

1 gram of the above product was dissolved in 20 cc. of ethyl alcohol. 2 cc. of the solution were then added to the developing solution and used for the development of an exposed silver-halide emulsion. A magenta image was obtained together with the silver image.

Example VII

4,4'-bis(1-(α-naphthyl-4'-sulfo)-3-methyl-5-pyrazolone)

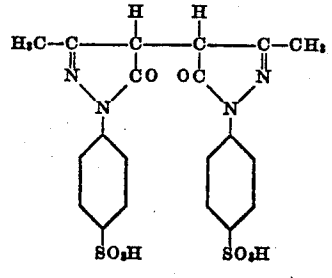


This compound was prepared according to the method of M. Mueller, Dissertation Jena, 1892, page 22, by refluxing 5 grams of 1-(α-naphthyl-4'-sulfo)-3-methyl-5-pyrazolone with 15 cc. of phenyl hydrazine for 2 hours. The reaction mixture was allowed to cool and the precipitated product was then filtered and recrystallized from ethyl alcohol.

1.8 grams of the above color former were dissolved in 2.0 cc. of 1-N-alcoholic KOH and added with thorough mixing to 100 cc. of a gelatin silver bromide-iodide emulsion. After coating the emulsion containing the color former onto a suitable support and drying, the film was exposed and developed to yield a magenta image together with the silver image.

Example VIII

4,4'-bis(1-(phenyl-4'-sulfo)-3-methyl-5-pyrazolone)



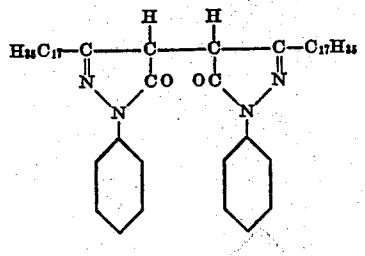
This compound was prepared according to the

method of Example 7 by refluxing 5 grams of 1-(phenyl-4'-sulfo)-3-methyl-5-pyrazolone with 15 cc. of phenyl hydrazine for 2 hours. The reaction mixture was allowed to cool and the precipitated product was then filtered and recrystallized from ethyl alcohol.

1.8 grams of the above color former were dissolved in 2.0 cc. of 1-N-alcoholic KOH and added with thorough mixing to 100 cc. of a gelatin silver bromide-iodide emulsion. After coating the emulsion containing the color former onto a suitable support and drying, the film was exposed and developed to yield a magenta image together with the silver image.

Example IX

4,4'-bis(1-phenyl-3-heptadecyl-5-pyrazolone)

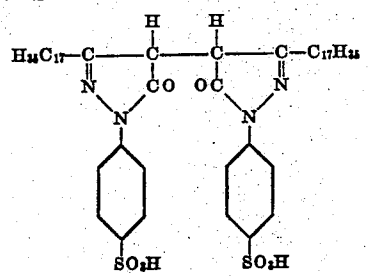


This compound was prepared by refluxing 5 grams of 1-phenyl-3-heptadecyl-5-pyrazolone with 20 cc. of phenyl hydrazine for 2 hours. The reaction mixture was allowed to cool and the precipitated product was then filtered and recrystallized from ethyl alcohol.

1.8 grams of the resulting product were dissolved in 2 cc. of water and the solution added to 100 cc. of a gelatin silver bromide-iodide emulsion. The emulsion was coated onto a cellulose acetate base and after drying, the film was exposed and developed. A dye image of excellent magenta color was formed in the emulsion.

Example X

4,4'-bis(1-(phenyl-4'-sulfo)-3-heptadecyl-5-pyrazolone)

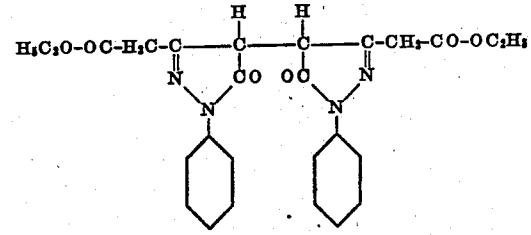


This compound was obtained by sulfonating the product of Example 9 with sulfuric acid containing 30% SO_3 with cooling.

After recrystallization from water, 1.8 grams of the resulting product were dissolved in 2.0 cc. of water and the solution added to 100 cc. of a gelatin silver bromide-iodide emulsion. The emulsion was coated onto a cellulose acetate base and after drying, the film was exposed and developed. A dye image of excellent magenta color was formed in the emulsion.

Example XI

4,4'-bis(1-phenyl-5-pyrazolone-3-acetic ethyl ester)

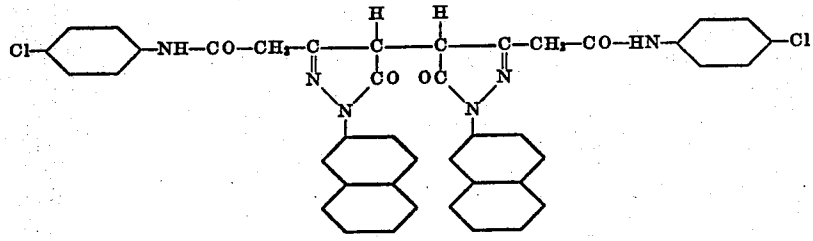


Five grams of 1-phenyl-5-pyrazolone-3-acetic ethyl ester, prepared according to Example I of U. S. Patent 2,334,495, were refluxed with 20 cc. of phenyl hydrazine for 2 hours. The reaction mixture was allowed to cool and the precipitated product was then filtered and recrystallized from ethyl alcohol.

1.8 grams of the above color former were dissolved in 2.0 cc. of 1-N-alcoholic KOH and added with thorough mixing to 100 cc. of a gelatin silver bromide-iodide emulsion. After coating the emulsion containing the color former onto a suitable support and drying, the film was exposed and developed to yield a magenta image together with the silver image.

Example XII

4,4'-bis(1-β-naphthyl-3-p-chloracetanilido-5-pyrazolone)

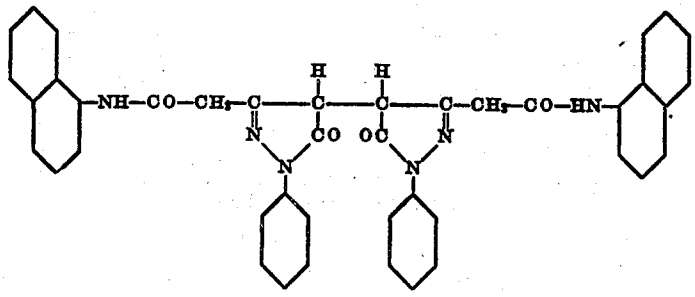


Five grams of 1-β-naphthyl-3-p-chloroacetanilido-5-pyrazolone, prepared according to Example 8 of U. S. Patent 2,334,495, were refluxed with 20 cc. of phenyl hydrazine for 2 hours. The reaction mixture was allowed to cool and the precipitated product was then filtered and recrystallized from ethyl alcohol.

1.8 grams of the resulting product were dissolved in 2 cc. of water and the solution added to 100 cc. of a gelatin silver bromide-iodide emulsion. The emulsion was coated onto a cellulose acetate base and after drying, the film was exposed and developed. A dye image of excellent magenta color was formed in the emulsion.

Example XIII

4,4'-bis(1-phenyl-3-acet-α-naphthylamido-5-pyrazolone)

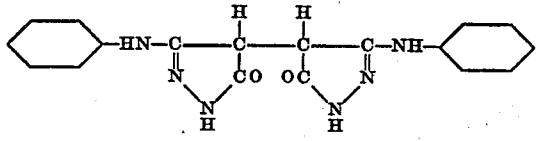


Five grams of 1-phenyl-3-acet-α-naphthylamido-5-pyrazolone prepared according to Example 6 of U. S. Patent 2,334,495, were refluxed with 20 cc. of phenyl hydrazine for 2 hours. The reaction mixture was allowed to cool and the precipitated product was then filtered and recrystallized from ethyl alcohol.

1.8 grams of the resulting product were dissolved in 2 cc. of water and the solution added to 100 cc. of a gelatin silver bromide-iodide emulsion. The emulsion was coated onto a cellulose acetate base and after drying, the film was exposed and developed. A dye image of excellent magenta color was formed in the emulsion.

Example XIV

4,4'-bis(3-anilino-5-pyrazolone)

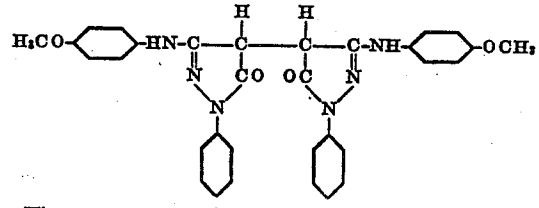


Five grams of 3-anilino-5-pyrazolone prepared according to the directions given in U. S. Patent Re. 22,329, were refluxed with 15 cc. of phenyl hydrazine for 1 hour. The reaction mixture was allowed to cool and the precipitated product was then filtered and recrystallized from ethyl alcohol.

1.8 grams of the resulting product were dissolved in 2 cc. of water and the solution added to 100 cc. of a gelatin silver bromide-iodide emulsion. The emulsion was coated onto a cellulose acetate base and after drying, the film was exposed and developed. A dye image of excellent magenta color was formed in the emulsion.

Example XV

4,4'-bis(1-phenyl-3-p-anisyl-amino-5-pyrazolone)

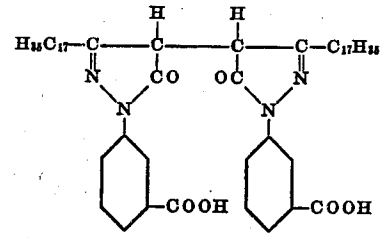


Five grams of 1-phenyl-3-p-anisyl-amino-5-pyrazolone prepared according to the directions given in U. S. Patent 2,343,703, were refluxed with 20 cc. of phenyl hydrazine for 2 hours. The reaction mixture was allowed to cool and the precipitated product was then filtered and recrystallized from ethyl alcohol.

1.8 grams of the above color former were dissolved in 2.0 cc. of 1-N-alcoholic KOH and added with thorough mixing to 100 cc. of a gelatin silver bromide-iodide emulsion. After coating the emulsion containing the color former onto a suitable support and drying, the film was exposed and developed to yield a magenta image together with the silver image.

Example XVI

4,4'-bis(1-(3-carboxyphenyl)-3-heptadecyl-5-pyrazolone)

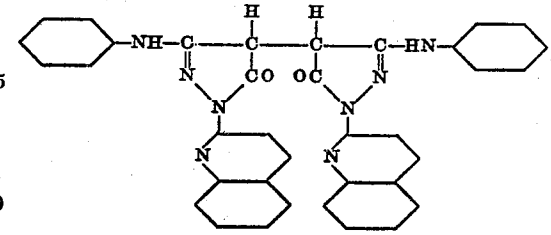


Five grams of 1-(3-carboxyphenyl)-3-heptadecyl-5-pyrazolone prepared according to Example I of U. S. Patent 2,200,306 were refluxed with 20 cc. of phenyl hydrazine for 2 hours. The reaction mixture was allowed to cool and the precipitated product was then filtered and recrystallized from ethyl alcohol.

1.8 grams of the above color former were dissolved in 2.0 cc. of 1-N-alcoholic KOH and added with thorough mixing to 100 cc. of a gelatin silver bromide-iodide emulsion. After coating the emulsion containing the color former onto a suitable support and drying, the film was exposed and developed to yield a magneta image together with the silver image.

Example XVII

4,4'-bis(1-(α-quinolyl)-3-anilino-5-pyrazolone)

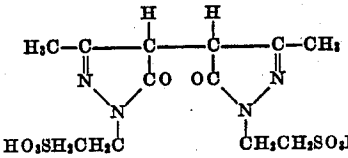


Five grams of 1-(α-quinolyl)-3-anilino-5-pyrazolone) prepared in the usual manner were refluxed with 20 cc. of phenyl hydrazine for 2 hours. The reaction mixture was allowed to cool and the precipitated product was then filtered and recrystallized from ethyl alcohol.

1.8 grams of the above color former were dissolved in 2.0 cc. of 1-N-alcoholic KOH and added with thorough mixing to 100 cc. of a gelatin silver bromide-iodide emulsion. After coating the emulsion containing the color former onto a suitable support and drying, the film was exposed and developed to yield a magneta image together with the silver image.

Example XVIII

4,4'-bis(1-ethane sulfonic acid-3-methyl-5-pyrazolone)



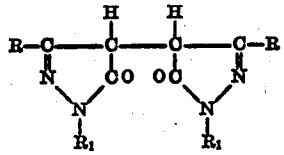
Five grams of 1-ethane sulfonic acid-3-methyl-5-pyrazolone prepared according to Example 2 of U. S. Patent 2,265,221 were refluxed with 20 cc. of phenyl hydrazine for 2 hours. The reaction mixture was allowed to cool and the precipitated product was then filtered and recrystallized from ethyl alcohol.

1.8 grams of the above color former were dissolved in 2.0 cc. of 1-N-alcoholic KOH and added with thorough mixing to 100 cc. of a gelatin silver bromide-iodide emulsion. After coating the emulsion containing the color former onto a suitable support and drying, the film was exposed and developed to yield a magenta image together with the silver image.

While I have disclosed the preferred embodiments of my invention and the preferred modes of carrying the same into effect, it will be readily apparent to those skilled in the art that many variations may be made therein without departing from the spirit thereof. Accordingly, the scope of my invention is to be limited solely by the following claims.

I claim:

1. A color forming photographic developer comprising an aromatic primary amino developing agent and a coupler compound having the general formula:



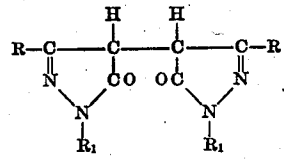
in which R is selected from the class consisting of hydrogen, alkyl, aryl, arylamino, acetarylamido, and aralkyl groups, and R_1 is selected from the class consisting of hydrogen, alkyl, aryl, aralkyl and heterocyclic groups.

2. A color forming photographic developer comprising an aromatic primary amino developing agent and 4,4'-bis(1-(α-naphthyl-4'-sulfo)-3-methyl-5-pyrazolone).

3. A color forming photographic developer comprising an aromatic primary amino developing agent and 4,4'-bis(1-phenyl-4'-sulfo)-3-methyl-5-pyrazolone).

4. A color forming photographic developer comprising an aromatic primary amino developing agent and 4,4'-bis(1-phenyl-3-heptadecyl-5-pyrazolone).

5. The method of producing a magenta color photographic image in a gelatino silver-halide emulsion layer which comprises exposing the layer and developing it with an aromatic primary amino developing agent in the presence of a coupler compound having the general formula:



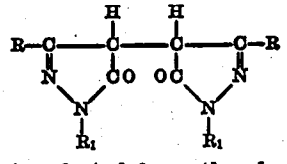
in which R is selected from the class consisting of hydrogen, alkyl, aryl arylamino, acetarylamido, and aralkyl groups, and R_1 is selected from the class consisting of hydrogen, alkyl, aryl, aralkyl and heterocyclic groups.

6. The method of producing a magenta color photographic image in gelatino silver-halide emulsion layer which comprises exposing the layer and developing it with an aromatic primary amino developing agent containing 4,4'-bis(1-(α-naphthyl-4'-sulfo)-3-methyl-5-pyrazolone).

7. The method of producing a magenta color photographic image in gelatino silver-halide emulsion layer which comprises exposing the layer and developing it with an aromatic primary amino developing agent containing 4,4'-bis(1-(phenyl-4'-sulfo)-3-methyl-5-pyrazolone).

8. The method of producing a magenta color photographic image in a gelatino silver-halide emulsion layer which comprises exposing the layer and developing it with an aromatic primary amino developing agent containing 4,4'-bis(1-phenyl-3-heptadecyl-5-pyrazolone).

9. A photographic silver-halide emulsion containing a coupler compound having the general formula:



in which R is selected from the class consisting of hydrogen, alkyl, aryl arylamino, acetarylamido, and aralkyl groups, and R_1 is selected from the class consisting of hydrogen, alkyl, aryl, aralkyl and heterocyclic groups.

10. A photographic silver-halide emulsion for forming color images comprising a colloidal carrier containing a sensitive silver-halide and 4,4'-bis(1-(α-naphthyl-4'-sulfo)-3-methyl-5-pyrazolone).

11. A photographic silver-halide emulsion for forming color images comprising a colloidal carrier containing a sensitive silver-halide and 4,4'-bis(1-(phenyl-4'-sulfo)-3-methyl-5-pyrazolone).

12. A photographic silver-halide emulsion for forming color images comprising a colloidal carrier containing a sensitive silver-halide and 4,4'-bis(1-phenyl-3-heptadecyl-5-pyrazolone).

ABRAHAM BAVLEY.