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BIS-PYRAZOLONYL COLOR FORMER

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10 Claims. (Cl. 95—6)

This invention relates to color photography, more particularly it relates to color forming photographic emulsions; still more particularly it relates to photographic elements bearing emulsions which develop to form metallic silver and dyes in image areas in admixture with each other. The invention also relates to photographic developers and to finished colored photographs.

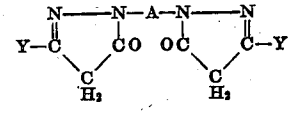
This invention has for an object the preparation of photographic emulsions containing novel and improved water insoluble dye-forming bodies or color-formers which yield colored dyes by coupling with the oxidation products of photographic developing agents. A further object is the preparation of photographic elements bearing an emulsion which contains novel color formers which do not migrate. A still further object is the preparation of multilayer photographic films containing color-formers which do not migrate from layer to layer or into the processing baths. A still further object is the preparation of finished photographs which contain stable dyed images which are formed of water insoluble dyes. Other objects include the preparation of color photographs and color forming emulsions upon opaque or transparent supports and a general advance in the art. Still other objects will appear hereinafter.

The above and other objects are accomplished by the following invention which involves the use of bis-pyrazolonyl aromatic organic compounds in which there is an active methylene group in the 4-position of each pyrazolone nucleus and the 1-position of each pyrazolone nucleus is directly attached to a benzene nucleus, as color-forming agents which couple with aromatic amino photographic developing agents to form dyes.

When a photographic emulsion, for example, a silver halide ebulsion containing a latent photographic image is developed, the silver halide is reduced to metallic silver and the developing agent is oxidized to form oxidation products which couple with coupling compositions to form dyes. In the case of the aromatic amino developing agents, the oxidation products of the same couple with the color-former and form a dye which is deposited in the gelatin or other binder or silver halide carrier adjacent to the metallic silver halide grain.

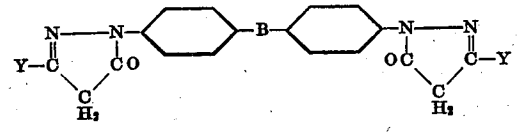
It has been found that the above-decribed bis-pyrazolonyl aromatic compounds are suitable color-formers, couple readily, and dyes therefrom do not readily migrate from their position. The bis-pyrazolonyl compounds as before stated, contain an active methylene group in the 4-position and the 1-position is attached to a benzene nucleus. The pyrazolone nuclei may contain various substituents, thus alkyl groups, e. g., ethyl, methyl, propyl, hexyl, aryl, e. g., phenyl, chlorphenyl, tolyl, naphthyl and aralkyl, e. g., benzyl, methyl benzyl, chlorbenzyl, heterocyclic, e. g., furoyl, etc., groups may be substituted in the 3-positions.

In one embodiment of the invention, the bis-pyrazolonyl compounds have the general formula:



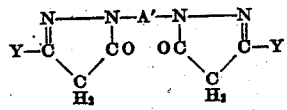
wherein A is a bivalent aromatic hydrocarbon radical, e. g., phenylene, naphthylene, biphenylene, biphenylene sulfone, and Y is a hydrocarbon radical of the type above described. The radicals A and Y may be further substituted by various radicals such as hydrocarbon radicals, e. g., methyl, ethyl, etc., phenyl, benzyl, halogen atoms, e. g., chlorine, bromine, etc., alkoxy, e. g., methoxy, ethoxy, etc., and nitro groups, and it is to be understood that the term "hydrocarbon" as used in the claim is intended to cover such substituted hydrocarbons. In general, substitution has only a slight effect upon the shade obtained.

In another embodiment of the invention, the bis-pyrazolonyl compounds have the general formula:



wherein B represents a bivalent element or radical which is connected to the benzene nuclei through a non-carbon atom. Thus, in a preferred instance, B may be oxygen or sulfur atom and Y has the above significance.

The compounds of the above formulae can be identified as having the general formula:



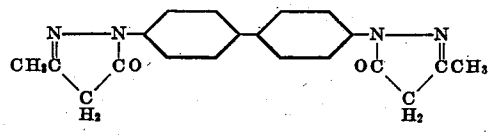
wherein A' is a bivalent hydrocarbon radical which contains one benzene nucleus or two benzene nuclei which are fused together, joined by a single bond or bridged by an ether group including a thioether group.

The above described classes of coupling components or color-formers may be incorporated in a photographic emulsion or they may be added to a developer solution. An exposed photographic element may then be developed in the usual manner.

The invention will be further illustrated but is not intended to be limited by the following examples:

Example I

To 100 ccs. of 2% by weight aqueous gelatin solution is added a solution consisting of 8 ccs. of ethyl alcohol and 0.4 gram of the compound of the following formula:

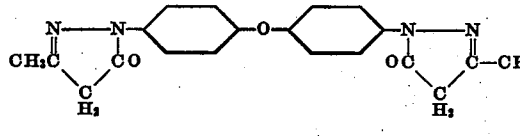


The total weight of the combined solution is then brought to about 150 g. with water after which the mixture is added to 100 g. of a gelatino-silver halide emulsion and mixed thoroughly. The resulting emulsion may then be coated upon a suitable photographic support such as paper or a cellulose derivative base, or upon another photographic emulsion layer which may or may not contain another color-forming dye component. After exposure directly in a camera or by printing through appropriate color records, the film is developed by means of an alkaline solution of diethyl-p-phenylenediamine, whereupon a magenta dye of good strength and color forms.

In place of the 4,4' bis-(3''-methylpyrazolonyl-1'')-biphenyl of this example can be substituted in similar amounts 4,4' bis-(3''-phenylpyrazolonyl-1'')-biphenyl, 4,4' bis-(3''-methylpyrazolonyl-1'')-3,3' dichlo-biphenyl, 4,4' bis-(3''-benzylpyrazolonyl-1'')-biphenyl, the corresponding meta bis-pyrazolonyl compounds, 2,7-bis-(3''-methylpyrazolonyl-1'')-3,6-dimethyl-biphenylene sulfone, etc.

Example II

To 100 ccs. of 2% by weight aqueous gelatin solution is added a solution consisting of 8 ccs. of ethyl alcohol and 0.8 gram of the compound of the formula:



The total weight of the combined solution is then brought to about 150 g. with water after which the mixture is added to 100 g. of a gelatino-silver halide emulsion and mixed thoroughly. The resulting emulsion may then be coated upon a suitable photographic support after the manner described in Example I. After exposure the photographic element is developed in an alkaline solution containing p-amino diethyl aniline hydrochloride, whereupon a magneta dye dark of shade and of good color is formed.

In place of the 4,4'-bis-(3''-methylpyrazolonyl-1'')-biphenyloxide of this formula may be substituted in similar amounts the corresponding thioether. The corresponding meta substituted pyrazolonyl compounds may be used. Other hydrocarbon radicals, e. g., ethyl, propyl, benzyl, phenyl, etc. may be used in the pyrazolone nuclei.

The following example illustrates the use of the novel coupling compounds of this invention in developer solutions.

Example III

To 100 ccs. of a developer having the following composition

Diethyl-p-phenylenediamine hydrochloride	g..	2
Sodium sulfite (anhydrous)	g..	5
Sodium carbonate (anhydrous)	g..	20
Water	cc..	1000

are added from 10 to 100 m. g. of 4,4'-bis(3-methylpyrazolonyl-1)-biphenyloxide dissolved in a few ccs. of ethyl alcohol. An exposed photographic element containing exposed silver salts are then developed in said developer solution.

A positive silver image which has been bleached to a silver salt image may be redeveloped in this solution. A suitable bleach may comprise a liter of water containing about 35 grams of potassium ferricyanide and 5 ccs. of 20% ammonia water. Thorough washing between treatments is essential. After color-development, the silver may be removed, leaving a pure dye image, by bleaching and fixing in plain hypo.

In place of the specific color-former of Example III, any of the specific color-formers listed in Examples I and II may be used in similar quantities. Likewise, any of the compounds falling within the scope of the above formulae may be similarly used.

The silver halide emulsions above described may form a single layer of a photographic element or may form one of a plurality of layers which may or may not contain another color-forming dye component. Alternatively, the silver halide emulsion may be coated on a plain or colored separating layer as one sensitive layer of a series of such layers on a monopack, multilayered film for use in color photography.

The photographic emulsions and emulsion layers may also contain the usual sensitizers such as the cyanine and carbocyanine salts and bases and the cyazines and carbocyazine salts and bases employed to extend the sensitivity of photographic emulsions.

In place of the specific aromatic amino developing agents of the above examples, others which may be used are the mono-, di- and tri-amino aryl compounds. The diamino aryl compounds such as para-phenylenediamine and its substitution products are preferred. These developers may be substituted in the amino groups as well as in the ring, preferably the former, to constitute compounds such as the alkyl arylenediamines including the alkyl naphthylenediamines, alkyl phenylenediamines and alkyl toluylenediamines. The compounds, of course, must have one free or unsubstituted amino group which enables the oxidation product of the developer to couple with the color-forming compounds. As examples of developers of the class described, there may be mentioned diethyl-p-phenylenediamine, dimethyl-p-phenylenediamine, monomethyl-p-phenylene diamine, naphthylenediamine-1,4, N-diethyl naphthylenediamine-1,4 and their acid salts. The salts of the bases, e. g. the hydrochloride and sulfate are preferred to the free bases since they are more soluble and more stable than the latter.

Among the advantages of the bis-pyrazolonyl aromatic compounds of this invention are:

A. When incorporated in a given photographic

layer they do not migrate or diffuse either in their dry state or when the film is subjected to bathing in water or alkaline solutions.

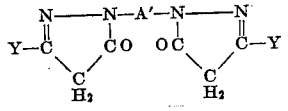
B. These compounds will react with the oxidation product of a p-phenylenediamine developer, as produced in the reduction of silver halides, to form reddish blue to bluish red dyes absorbing substantially in the green region so as to make them particularly useful in multicolor photography processes for the production of colored images.

C. The dyes thus produced do not tend to migrate nor diffuse after their formation.

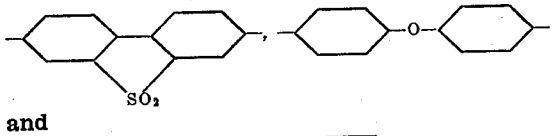
As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the invention described herein except as defined in the appended claims.

We claim:

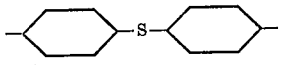
1. A photographic element bearing color-forming photographic emulsion layer comprising a binding agent, a silver halide and a compound of the general formula:



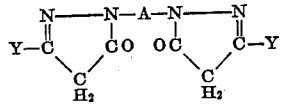
wherein Y is a hydrocarbon radical and A' is a bivalent radical taken from the class consisting of phenylene, naphthylene, biphenylene,



and

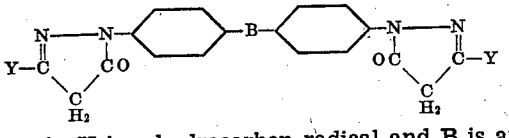


2. A photographic element bearing color-forming photographic emulsion layer comprising a binding agent, a silver halide and a compound of the general formula:



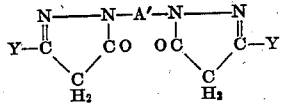
wherein Y is a hydrocarbon radical and A is a biphenylene radical wherein the nuclear carbon atoms are directly connected to the N-atoms of the pyrazolone nuclei.

3. A photographic element bearing color-forming photographic emulsion layer comprising a binding agent, a silver halide and a compound of the general formula:

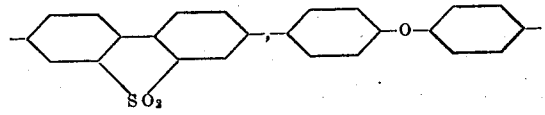


wherein Y is a hydrocarbon radical and B is an atom selected from the group consisting of oxygen and sulfur.

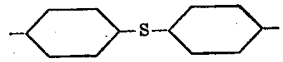
4. A color-forming photographic developer containing an aromatic amino developing agent and a compound of the general formula:



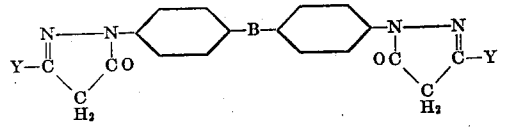
wherein Y is a hydrocarbon radical and A' is a bivalent radical taken from the class consisting of phenylene, naphthylene, biphenylene,



and

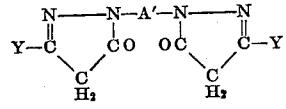


5. A color-forming photographic developer containing an aromatic amino developing agent and a compound of the general formula:

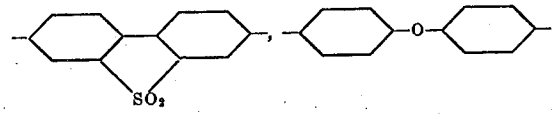


wherein Y is a hydrocarbon radical, and B is an atom selected from the group consisting of oxygen and sulfur.

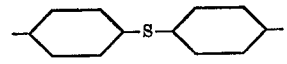
6. The process which comprises developing a photographic element containing exposed silver halides with an aromatic amino developing agent in the presence of a compound of the general formula:



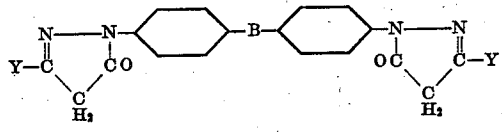
wherein Y is a hydrocarbon radical and A' is a bivalent hydrocarbon radical taken from the class consisting of phenylene, naphthylene, biphenylene,



and

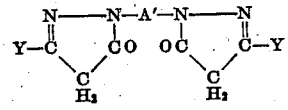


7. The process which comprises developing a photographic element bearing a silver salt image with an aromatic amino developing compound in the presence of a compound of the general formula:



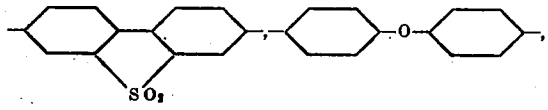
wherein Y is a hydrocarbon radical and B is an atom selected from the group consisting of oxygen and sulfur.

8. The process which comprises developing a photographic element containing exposed image with an arylene diamino developing agent in the presence of a compound of the general formula:

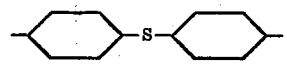


wherein Y is a hydrocarbon radical and A' is a

bivalent radical taken from the class consisting of phenylene, naphthlene, biphenylene,



and



9. A photographic element bearing at least one color-forming photographic emulsion layer comprising a binding agent, a silver halide and 4,4'-bis-(3-methyl-pyrazolonyl-1)-diphenyloxide.

10. A photographic element bearing at least one color-forming photographic emulsion layer comprising a binding agent, a silver halide and 4,4'-bis-(3-methyl-pyrazolonyl-1)-diphenylthioxide.

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