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CHEMICAL PROCESS AND COMPOSITION

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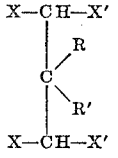
17 Claims. (95—6)

This invention relates to color photography. More particularly it relates to photographic emulsions and developer solutions containing novel dye-components. Still more particularly it relates to dye-components which contain two nuclei which are bridged by an alkylidene radical or a mono- or di- substituted alkylidene radical. The invention also relates to processes of producing photographic images in the presence of such compounds.

This invention has for an object the production of stable color-formers which form dyes of good tinctorial strength and color. A further object is the production of photographic developer solutions and emulsions which contain color formers which form haze-free, colored images which are of good stability and of improved spectral qualities. A still further object is to provide photographic compositions containing improved color formers which couple readily upon development of silver images to form water insoluble immobile dyes in situ with photographic images. Still further object is to provide color former compositions which do not affect the sensitivity of photographic emulsions, particularly gelatin silver halide and silver ferrocyanide emulsions. Still other objects will be apparent from the hereinafter described invention.

The above and other objects are accomplished by the preparation and use of color formers which contain two dyestuff component nuclei which are bridged by an alkylidene or a substituted alkylidene group. These bis- or dimeric compounds have the general formula:

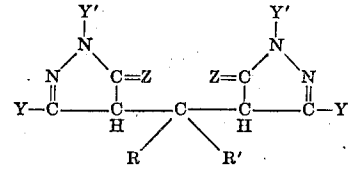
(1)



wherein X and X' are acidic groups, e. g. acyl, including aliphatic acyl such as acetyl, proprionyl, aromatic acyl such as benzoyl, naphthoyl and heterocyclic acyl such as the acyl radicals from N-heterocyclic and S-heterocyclic carboxylic acids, including nicotinic, iso-nicotinic and picolinic and thienyl carboxylic acids, cyano, sulfonyl or thiocarbonyl, etc. groups attached directly to the —CH— group or X and X' together form a ring; R and R' represent hydrogen, hydrocarbon or substituted hydrocarbon radicals, e. g. methyl, ethyl, phenyl, naphthyl, chlorophenyl, hydroxyphenyl, carboxyphenyl, sulfoxyphenyl, etc.

Among the classes of compounds falling under the above general formula are the alkylidene bis-pyrazolones which have the general formula:

(2)



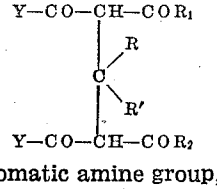
wherein R and R' have the same significance as in Formula 1, Y and Y' are hydrocarbon or heterocyclic radicals, e. g. ethyl, methyl, phenyl, furyl, wherein Y may be a solubilizing group, e. g. —COOH; and Z is oxygen or sulfur. Among the specific compounds falling in this class are 4,4' - methylene bis-(1-phenyl-3-methyl-5-pyrazolone), 4,4'-methylene bis-(3-methyl-5-pyrazolone), 4,4'-ethylidene bis-(1-phenyl-3-methyl-5-pyrazolone), 4,4'-isopropylidene-bis-(1-phenyl-3 - methyl-5-pyrazolone), 4,4'-benzylidene-bis-(1-phenyl-3-methyl-5-pyrazolone), 4,4'-methylene - bis - (p-chlorophenyl-methyl pyrazolone), 4,4' - methylene - bis-(m-stearoylaminophenyl-methyl pyrazolone), 4,4'-methylene-bis-(1,3-diphenyl pyrazolone), 4,4' - methylene bis - (1-phenyl - 3 - furyl-5-pyrazolone), 4,4'-methylene bis-(p-nitrophenyl-methylpyrazolone); and the corresponding sulfur analogues in which the

group in the above compounds would be a

group; and 4,4'-methylene-bis-(m-nitrophenyl methyl-pyrazolone). A number of these are new compounds and methods for their preparation are set forth below.

A second class of compounds which constitutes an important embodiment of this invention are the alkylidene bis acylacetarylides which are new compounds. Methods of preparing them appear below. This class has the general formula:

(3)



wherein Y is an aromatic amine group, R and R' have the same significance as in Formula 1, and R_1 and R_2 are substituted or unsubstituted hy-

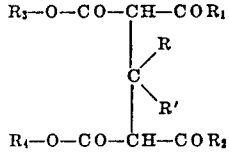
drocarbon radicals, e. g. alkyl, aryl, cycloalkyl, or heterocyclic, e. g. furyl, and thienyl. Thus, Y may be the substituted amine group corresponding to the following amines:

p-Aminophenyl morpholine
p-Anisidine
p-Phenetidine
p-Chloro-aniline
Alpha naphthylamine
Beta-naphthylamine
p-Aminophenyl piperidine
p-Amino dimethyl aniline
Benzoyl-p-phenylenediamine
N-ethyl-N-benzyl-p-phenylenediamine
N-ethyl-N-phenyl-p-phenylenediamine
2,5-dimethyl aniline
4-chloro-2,5-dimethyl aniline
2,3,5,6-tetramethyl aniline
2-chloro-5-methyl aniline
m-Toluidine
3-bromo-4-methyl aniline
3-nitro-4-methyl aniline
2,5-diethoxy-4-chloro-aniline
2,5-dimethoxy-4-chloro-aniline
2,5-diethoxy-4-furoylamine aniline
3-benzoylamino-4-methoxy aniline
4-benzoylamino-3-methoxy aniline
5-bromo-2-methoxy aniline
o-Phenoxy aniline
2,5-diethoxy-4-nitro aniline
m-Nitro aniline
p-Nitro aniline
p-Phenoxy aniline
o-Chloro aniline
p-Aminophenyl-benzyl ether
4-chloro-2-methoxy-5-isopropyl aniline
p-Fluoro-aniline
2-nitro-4,6-dimethyl aniline
p-Amino benzoyl-2-amino benzothiazole
2-methoxy-4-nitro aniline
p-Amino-p'-hydroxy-azobenzene
Benzylamine

As examples of alkyl radicals for R_1 and R_2, mention is made of methyl, ethyl, propyl, isopropyl, etc.; of cycloalkyl, cyclohexyl, abietyl, tetrahydroabietyl, menthanyl, etc.; or aryl, benzyl and naphthyl, phenyl, nitrophenyl, and aminophenyl.

A third class of compounds which constitute an important embodiment of this invention are the alkylidene bis acylacetic acid esters which may be represented by the general formula:

(4)



wherein R and R' and R_1 and R_2 have the same significance as in Formula 3, and R_3 and R_4 have the same significance as R_1 and R_2. It is to be distinctly understood, however, that the various Rs may be the same or different.

The invention is not to be limited to the three broad enumerated classes of compounds, although they represent the preferred embodiment hereof. On the contrary, many other classes of compounds which fall under the generic Formula 1 may be used. Practically any compound which contains an acidic group and an active methylene group and will react with aldehydes to form a dimeric dye component may be availed of to form the bis or dimeric compounds. Thus, malonic esters, acetyl acetone, benzoyl acetone, cyanacetophenone, desoxy benzoin, barbituric acid, nitrophenyl aceto nitrile, p-nitrobenzylcyanide, 3-hydroxythionaphthene, acetone dicarboxylic acid ester, 3-hydroxycoumarine, derivatives of p-nitrophenylacetic acid, phenacyl halides, etc., may be used to make bis alkylidene dye-components.

The color formers of this invention are in general prepared by reacting two mols of the dye component with one mol of an aldehyde or ketone. As examples of suitable agents mention is made of formaldehyde, acetaldehyde, propionaldehyde, acrolein, glyoxal, benzaldehyde, salicylaldehyde, p-hydroxybenzaldehyde, furfural, acetone, acetophenone, etc. In certain cases compounds containing active halogen atoms may be used in place of formaldehyde. Such compounds include chloroform, sulfur dichloride and phosphorous oxychloride. Dimethylol derivatives of phenols, amides, amines, etc., e. g. dimethyl urea, dimethylolguanidine, 2,6-dimethylol-4-methylphenol also have utility. When such compounds are used an alkylidene linkage is placed between the dye-component groups. By alkylidene is meant not only the hydrocarbon radicals, but the halogen, hydroxy, carboxylic and sulfonic acidic alkylidine radicals. Acid or basic condensing agents may be used, e. g. hydrochloric acid, p-toluenesulfonic acid, sulfuric acid, sodium hydroxide, ammonium hydroxide and potassium hydroxide. Readily hydrolyzed salts such as sodium acetate or ammonium chloride may be used.

The above described classes of color-formers may be incorporated in a photographic emulsion or may be added to a developer solution in the known manners. In the event that their solubility is insufficient for the purpose they may be finely divided and dispersed with the aid of dispersing agents, if necessary. They may also be used in conjunction with the usual cyanine, carbocyanine, pseudocyanine, cyazine, carbocyazine salts and bases which are used to extend the sensitivity of silver halide emulsions.

Silver halide emulsions containing the above color formers may be worked up in the usual manner. One or more emulsion layers being superimposed on one or both sides of transparent supports as desired. The layers may be used for color photography and for such purposes the layers are sensitized respectively for different regions of the spectrum. Several color formers may be introduced into a single layer, being so selected that by development they give complementary colors.

The development process used in carrying out this invention may be applied either to a latent image in an emulsion of a silver halide which has been exposed to light and which may or may not contain the novel color formers hereof. The exposures having been made in a camera or by printing through a photographic negative image. Or it may be applied to the residual unaltered silver salt left where an initial reduced silver image has been dissolved away as in a reversal process of development. Or it may be applied to a developed photographic image in metallic silver which has been fixed by the removal of unaltered silver halides by means of solvents and subsequently converted to a developable silver salt by means of known photographic bleaching agents.

For instance, a silver halide emulsion layer containing one of the herein described color-formers which has been exposed and developed

to a silver image and fixed, is treated with a diezo or tetrazo salt and converted into a colored image by the process of Christensen, (1,517,049).

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

EXAMPLE I

An exposed plate or film is developed in a solution prepared by adding 0.5 gram of methylene bis-acetoacetic ethyl ester (Ann. vol. 332, page 10) dissolved in 10 ccs. of acetone to a developer of the following composition:

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

This treatment gives a certain amount of reduced silver image together with an image of a yellow dye formed by the color former. The silver may be removed by means of a bleaching solution such as Farmer's reducer or a bleach consisting of potassium ferricyanide and potassium bromide.

Similar results may be obtained by substituting other methylene bis-acyl acetic esters in similar results such as methylene-bis-benzoylacetic ester (Ann. vol. 281, page 57), ethylidene bis-acetoacetic ester, (Ann. vol. 323, page 99) or any of the esters described under Formula 4.

EXAMPLE II

To 100 ccs. of 2% by weight aqueous gelatine solution is added a solution consisting of 8 ccs. of ethyl alcohol and 1.5 grams of 4,4'-methylene bis-(1-phenyl-3-methyl-5-pyrazolone), together with 20% aqueous caustic soda solution in an amount equal to 1 mol of alkali for each mol of the compound. The total weight of the combined solution is brought to about 150 grams with water and then the mixture is added to 100 grams of a gelatino-silver halide emulsion and mixed thoroughly. The resulting emulsion may then be coated upon a suitable support such as paper, glass or a cellulose derivative or upon another photographic emulsion layer which may or may not contain another color-forming dye component. After exposure in a camera or 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 tinctorial strength and density and color forms. The film may be first developed in a black and white developer, re-exposed and developed.

Any of the methylene bis-pyrazolones herein described may be substituted in similar amounts.

EXAMPLE III

Solution A:		
Methylene bis-acetoacetanilide	g	0.5
Acetone	cc	10.
Solution B:		
p-Amino-dimethyl aniline	g	0.5
Sodium carbonate 10% aqueous sol.	cc	75.
Water	cc	175.

For use add solution A to solution B. The exposed plate or film is developed in the combined solution which gives a silver image together with a yellow dye image resulting from the development process. The silver is removed with Farmer's reducer.

Other bleaching agents may be used. It is, of course, requisite that the bleach used should not affect the colored image. Likewise, any of the herein described methylene bis-acylacetarylides may be substituted in a similar manner.

The following examples relate to the preparation of the novel color-former compounds of this invention.

EXAMPLE IV

Fifteen g. of ethyl-p-nitro-benzoylacetate is dissolved in alcohol (10 cc.) and treated with 3 cc. of 37% formaldehyde and 2 cc. of piperidine. After several days the crystalline solid is separated and recrystallized from alcohol, whereupon yellow crystals melting at 197° C. are formed.

EXAMPLE V

Methylene bis-furoylacetic ester

To 22 grams of ethyl furoylacetate (Am. Chem. J. 44, 407) are added 5 cc. of 37% formaldehyde and 4 cc. of piperidine. After standing several hours, the viscous mixture becomes crystalline. After washing with water and dilute alcohol the solid is crystallized from a mixture of alcohol and water. The pale yellow crystalline solid melts at 103–104° and is obtained in a yield of 15 grams. When crystallized from alcohol with zone-black, much of the color is removed and the melting point is raised to 109°.

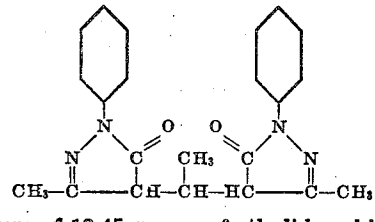
EXAMPLE VI

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

A smooth paste of 7 grams of phenyl methyl pyrazolone and 4 cc. of alcohol is treated with 1.5 cc. of 37% formaldehyde and .8 cc. of piperidine. Heat is evolved, solution takes place, and after standing a short time, a few cc. of acetic acid are added. Crystallization takes place shortly and after dilution with water the crystalline solid is filtered, washed with water and alcohol and recrystallized from alcohol. The melting point is 225°. It gives a powerful magenta color in the presence of oxidized diethyl p-phenylene diamine.

EXAMPLE VII

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



A mixture of 13.45 grams of ethylidene bis-acetoacetic ester (Example 4) and 10.89 grams of phenyl hydrazine is warmed one half hour on the water-bath. Alcohol is added and the solution is allowed to stand overnight to crystallize. The pure white product recrystallized from alcohol melts at 214–215°. A magenta color is obtained from this compound, but it is rather weak.

EXAMPLE VIII

4,4'-methylene-bis(p-chlorophenyl-methyl pyrazolone)

This compound is prepared as in Example VI, using piperidine as the condensing agent, and starting from p-chlorophenyl-methyl pyrazolone. The pure white crystalline product melts at 233° with decomposition to a turbid melt. A power-

ful magneta color is obtained from the compound with p-amino-diethylaniline.

EXAMPLE IX

4,4'-methylene-bis-(m-stearoylaminophenyl-methyl pyrazolone)

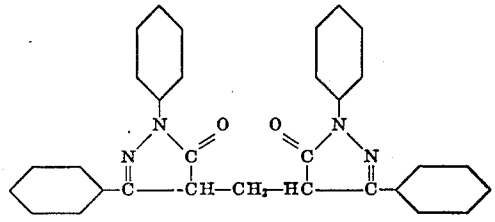
To a paste of 4.55 grams of m-stearoylamino-phenyl methyl pyrazolone and 15 cc. of alcohol, .5 cc. of 37% formaldehyde and .4 cc. of piperidine are added. The mixture is stirred and warmed very slightly. The suspended solid becomes a viscous liquid which separates from the solvent. After standing for a few minutes, however, this viscous liquid may be broken up mechanically into a crystalline solid which is suspended in the alcohol of the reaction mixture. The solid is filtered, washed with water and dried. The new compound is slightly soluble in alcohol or ether, and is readily soluble in a mixture of the two. It is likewise soluble in ethylene glycol mono-methyl ether, in diamethyl formamide, pyridine, and to some extent in glacial acetic acid. The compound may be purified by dissolving in aqueous alcoholic caustic soda and reprecipitating with HCl. The product is then filtered and washed well with water, dilute alcohol and finally with water again. The pale buff-colored solid melts in the range 130–135° when purified as above, whereas the mixed melting point with the starting material is 115–116°. The melting point of the starting material (purified by acid precipitation from caustic soda solution) is in the range 122–127°. It is of interest that the sodium derivative of the new compound in aqueous alcoholic solution is precipitated by dilution with water but remains homogeneous when alcohol is added. In the case of the starting material, such a solution may be diluted with water, but is precipitated by alcohol.

A solution of .8 grams of the material in 8 cc. of alcohol and .8 cc. of 20% aqueous caustic soda is added to 52.5 grams of a silver bromide emulsion. When this emulsion is coated on a support, dried, exposed and developed in alkaline diethyl p-phenylene diamine, a magneta type is deposited along with the silver.

EXAMPLE X

If in Example IX, an equivalent quantity of 1-(m-stearoylamino phenyl)-3-carboxy-5-pyrazolone is substituted, a product is obtained which produces a purple color when treated like the product of Example IX.

EXAMPLE XI



One mol of methylene bis-benzoylacetic ester and 4.32 grams of phenyl hydrazine (2 mols) plus one drop excess are heated at 80–85° for about 15 hours. The crystalline solid is crushed, washed with alcohol, boiled with a further quantity of alcohol, and filtered from the boiling liquid. The crystalline product melts at 213–214° with slight darkening and softening commencing at 210°. A bluish red color is obtained from the compound in color development.

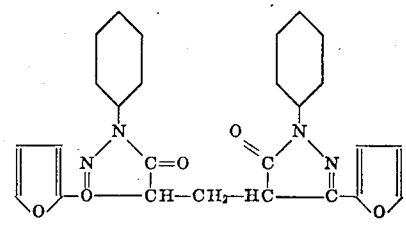
EXAMPLE XII

4,4'-methylene bis-(diphenyl pyrazolone)

A paste of 4.72 grams of 1,3-diphenyl pyrazolone and 7 cc. of alcohol is treated with .75 cc. of formalin solution (37%) and .4 cc. of piperidine. The mixture is warmed slightly. A sticky solid is formed, but this becomes fluid as the warming is continued. After cooling slightly, water is added and the mixture cooled further. The semi-crystalline solid is filtered, washed with alcohol and digested with more alcohol until only a pure-white, fine granular crystalline solid remains suspended in the liquid. The product is filtered hot and washed with cold alcohol. The compound is identical with that prepared as in Example XI, melting at 214–215°, and causing no depression of melting point when mixed with the compound of Example XI.

EXAMPLE XIII

4,4'-methylene bis-(1-phenyl-3-furyl-pyrazolone



A paste of 4.52 grams of 1-phenyl-3-furyl-pyrazolone (M. P. 182°) and 6 cc. of alcohol is treated with .75 cc. of 37% formaldehyde and .4 cc. of piperidine. The mixture is warmed and stirred until the solid becomes pasty. After cooling slightly, a few more cc. of alcohol are added followed by a few cc' of water. After cooling further, the solid is filtered, washed with cold alcohol and digested with more alcohol. When the sticky solid has become completely crystalline, the product is filtered hot and washed with cold alcohol. The pure white fine crystalline powder darkens somewhat at 200° and melts at 218°, with blackening and effervescence. The compound produces a bluish-red color in color-development.

EXAMPLE XIV

4,4'-methylene bis-(p-nitro-phenylmethyl-pyrazolone)

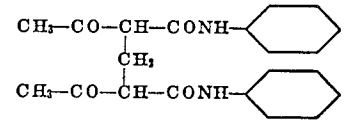
This is prepared by reacting methylene bis-aceto-acetic acid ethyl ester and p-nitrophenyl hydrazine after the manner of Example VII. The product has a melting point above 300° C. It gives an intense magenta color upon development of exposed images. If m-nitrophenyl hydrazine is substituted in a similar manner, the corresponding isomer having a melting point of 231° C. is formed.

EXAMPLE XV

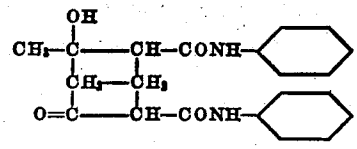
Methylene bis-acetoacetanilide

Acetoacetanilide was treated with formaldehyde in the presence of HCl and at a temperature of 100° in water. The pure white crystalline product (crystallized from alcohol) melted at 191°, gave a strong yellow color and apparently has the structure:

I



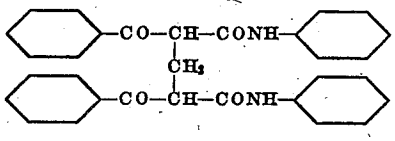
This compound upon standing seemed to change into a compound of the formula

II 

if piperidine is added. If piperidine is used as a condensing agent in the original reaction, a compound of formula II is formed.

EXAMPLE XVI

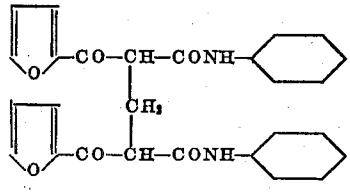
Methylene bis-benzoylacetanilide



Benzoylacetanilide (M. P. 107–109°) (4.76 grams) is worked into a smooth paste with 10 cc. of alcohol. .75 cc. of 37% formaldehyde is added followed by .3 cc. piperidine. The paste thins out, heat is evolved and the mixture soon thickens again and finally solidifies. After a short time, alcohol is added and the solid is broken up and filtered. After digesting several hours with alcohol, the pure white crystalline solid is filtered and washed with cold alcohol, M. P. 205°. The compound gives a strong yellow color, and probably has the structure given above.

EXAMPLE XVII

Methylene bis-furoylacetanilide

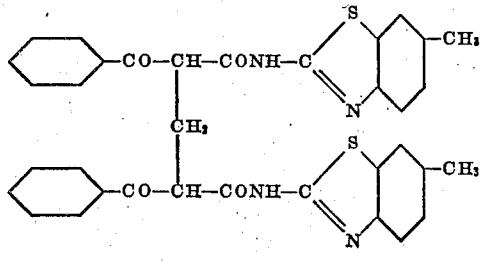


The compound is prepared as in Example XVI, the starting material being furoylacetanilide, Jennings and Middleton, Serial No. 215,702, (M. P. 105°). The product is worked up and purified as in the previous example. The structure is probably that indicated above. The pure white crystalline material melts at 218–220° and gives a brownish yellow color.

EXAMPLE XVIII

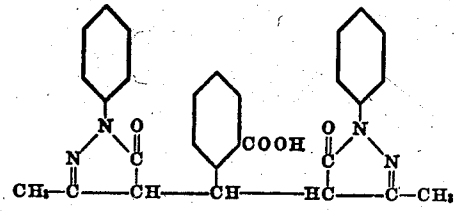
Methylene bis-(benzoylacet-2-amino-6-methyl benzothiazole)

This compound is prepared as in Example XVI by employing benzoylacet-2-amino-6-methyl benzothiazole. (M. P. 225–226°). The pure white product, crystallized from alcohol, melts at 170–172°, gives an orange color, and is of the following probable structure:



EXAMPLE XX

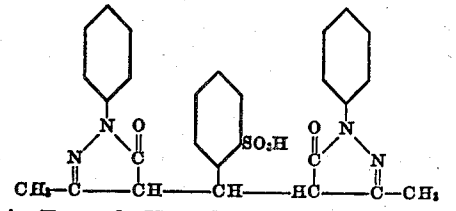
4,4'-o-carboxy-benzylidene-bis-(1-phenyl-3-methyl-5-pyrazolone)



To a solution of 15.9 grams of 1-phenyl-3-methyl-5-pyrazolone in 40 cc. of 95% ethanol is added a solution of 7.5 grams of phthalaldehydic acid in 20 cc. of 95% ethanol. The mixture is heated 15 minutes on a steam bath and precipitated by adding ether. The product is filtered and washed with ether. It probably has the structure indicated above. The material is readily soluble in dilute aqueous sodium carbonate solution and produces an intense magenta color when oxidized in the presence of diethyl p-phenylenediamine.

EXAMPLE XXI

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



If in Example XX, phthalaldehydic acid is replaced by o-sulfo-benzaldehyde, a product is obtained having the above probable structure.

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 described in the preceding examples may be substituted various other specific agents of this type. These agents have an unsubstituted amino group which apparently enables the oxidation product to couple with the color-forming compound. Such agents include the mono-, di-, and tri-amino aryl compounds and the compounds formed therefrom by substitution in the amino group as well as in the ring. Thus, halogen, alkyl, alkoxy and aryl groups may be present.

The preferred developing agents in the process of dye coupling development are derivatives of p-phenylenediamine and particularly the asymmetric dialkyl p-phenylenediamines, e. g., p-aminodimethylaniline, p-aminodiethylaniline, p-aminodibutylaniline, etc. Other developing agents which may be used include p-phenylenediamine itself, p-methylaminoaniline, p-ethylaminoaniline and p-aminophenol, N,N-diethyl-o-phenylenediamine, chloro-p-phenylenediamine, 1,2,5-tolu-

ylenediamine, 2-amino-5-diethylaminotoluene, N-p-aminophenylpiperidine, N-methyl-N-hydroxyethyl-p-phenylenediamine, N-butyl-N-hydroxyethyl-p-phenylenediamine, 2-amino-5-hydroxyethyl-1-butylaminotoluene and its dihydrochloride, α-γ-dihydroxypropyl-p-phenylenediamine, etc. These aromatic amino-developing agents may be used in the form of their salts, which may be either inorganic or organic. The salts are in general more stable than the free bases. As examples of suitable salts mention is made of the hydrochloride, sulfates, acetates, etc.

Color-formers suitable for incorporation in emulsions which are polymeric and in some cases resinous in character and contain several dyestuff component groups which are bridged by aldehyde residues are known. The prior art color formers were obtained by reacting substantially equal molecular proportions of aldehydes and dyestuff component groups.

The "methylene bis-" color formers of this invention which are dimeric and non-resinous in character have the advantage that they may be obtained in a high degree of purity by crystallization from suitable organic solvents. They may be easily dispersed in colloidal emulsions and developer solutions.

The use of the "methylene bis"- compounds gives unexpected and surprising results in that the dyes formed upon development with aromatic amino developing agents, are greater in quantity than those obtained from monomeric compounds. For example, the bis-pyrazolone obtained from phenyl methyl pyrazolone upon development with aromatic amino developing agents gives a greater color density than the corresponding phenyl methyl pyrazolone. The bis-compounds and monomeric compounds just described when reacted with benzene diazonium chloride each gave 1-phenyl-5-oxo-4-phenylhydrazono-3-methyl-pyrazoline.

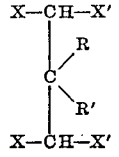
The methylene-bis-color formers hereof have other advantages, most important of which is the fact that a smaller amount of silver salt will produce the same dye density. Thus, the emulsion layers in a multilayer film may be thinner, or contain less silver salt. The resulting increase in transparency of the outer layers provides greater effective sensitivity of the film as a whole.

It is further surprising that the color-formers hereof absorb the shorter wave-lengths of light less than the dyes from prior art monomeric comounds. For example, the dyes from the bis-pyrazolones absorb blue less strongly than the dyes from the simple pyrazolones, producing therefore, better magentas for 3-color subtractive pigmentation. This phenomenon is probably due to a difference in the physical structure of the dye particles suspended in the colloid medium.

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 I do not limit myself to the specific embodiments hereof except as defined by the appended claims.

I claim:

1. A photographic silver salt emulsion layer containing a dye component of the general formula:



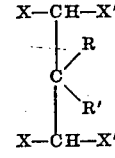
wherein X and X' are acidic groups taken from the class consisting of acyl, cyano and thiocarbonyl groups which are directly attached to the

radical, and which may form part of a ring, R and R' are members of the group consisting of hydrogen, halogen, hydrocarbon, halogenohydrocarbon, hydroxyhydrocarbon, carboxy hydrocarbon and sulfoxy-hydrocarbon groups.

2. A photographic emulsion layer as set forth in claim 1 wherein the silver salt is a silver halide.

3. A multilayer photographic element at least one layer of which comprises a gelatino silver halide emulsion containing a dye component of the type set forth in claim 1.

4. A photographic developer solution containing aromatic amino developing agent containing an unsubstituted amino group and a dye-component of the general formula:



wherein X and X' are acidic groups taken from the class consisting of acyl, cyano and thiocarbonyl groups which are directly attached to the

radical, and which may form part of a ring, R and R' are members of the group consisting of hydrogen, halogen, hydrocarbon, halogeno-hydrocarbon, hydroxyhydrocarbon, carboxy-hydrocarbon and sulfoxy-hydrocarbon groups.

5. A photographic element bearing at least one radiation sensitive silver salt emulsion layer containing an alkylidene bis-pyrazolone wherein the alkylidene radical is attached to the carbon atoms in the 4-position of the pyrazolone nuclei.

6. A photographic element bearing at least one radiation sensitive silver salt emulsion layer containing an alkylidene bis-acylacetarylide wherein the alkylidene radical is attached to the carbon atoms between the keto groups of the acylacetarylide nuclei.

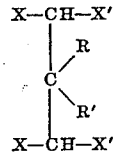
7. A photographic element bearing at least one radiation sensitive silver salt emulsion layer containing an alkylidene bis-acylacetic acid ester wherein the alkylidene radical is attached to the carbon atoms between the keto groups of the acylacetic acid ester nuclei.

8. A photographic developer solution containing an aromatic amino developing agent containing an unsubstituted amino group and an alkylidene bis-pyrazolone wherein the alkylidene radical is attached to the carbon atoms in the 4-position of the prazolone nuclei.

9. A photographic developer solution containing an aromatic developing agent containing an unsubstituted amino group and an alkylidene bis acylacetarylide wherein the alkylidene radical is attached to the carbon atoms between the keto groups of the acylacetarylide nuclei.

10. A photographic developer solution containing an aromatic amino developing agent containing an unsubstituted amino group and an alkylidene bis acylacetic acid ester wherein the alkylidene radical is attached to the carbon atoms between the keto groups of the acylacetic acid ester nuclei.

11. The process which comprises developing a photographic element containing an exposed silver salt image in the presence of a dye-component of the general formula:



wherein X and X' are acidic groups taken from the class consisting of acyl, cyano and thiocarbonyl groups which are directly attached to the

radical and which may form part of a ring, R and R' are members of the group consisting of hydrogen, halogen, hydrocarbon, halogeno-hydrocarbon, hydroxy-hydrocarbon, carboxy-hydrocarbon, and sulfoxy-hydrocarbon groups with a solution containing an aromatic amino developing agent containing an unsubstituted amino group.

12. A photographic element bearing at least one radiation silver salt emulsion layer containing 4,4'-methylene-bis-(p-nitrophenylmethylpyrazolone).

13. A photographic element bearing at least one radiation silver salt emulsion layer containing methylene-bis-benzoylacetanilide.

14. A photographic element bearing at least one radiation silver salt emulsion layer containing methylene-bis-ethyl-p-nitrobenzoylacetate.

15. The process which comprises developing a photographic element containing an exposed silver salt image in the presence of 4-4'-methylene-bis-(p-nitrophenylmethylpyrazolone) with a solution containing an aromatic amino developing agent having an unsubstituted amino group.

16. The process which comprises developing a photographic element containing an exposed silver salt image in the presence of methylene-bis-benzoylacetanilide with a solution containing an aromatic amino developing agent having an unsubstituted amino group.

17. The process which comprises developing a photographic element containing an exposed silver salt image in the presence of methylene-bis-ethyl-p-nitrobenzoylacetate with a solution containing an aromatic amino developing agent having an unsubstituted amino group.

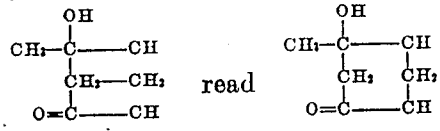
ANDREW B. JENNINGS.

Certificate of Correction

Patent No. 2,294,909. September 8, 1942.

ANDREW B. JENNINGS

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, line 1, for "diezo" read *diazo*; and second column, line 26, for "zone-black" read *bone-black*; page 5, first column, lines 3 to 9 inclusive, for that portion of the formula reading



read

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 12th day of January, A. D. 1943.

[SEAL]

HENRY VAN ARSDALE,
Acting Commissioner of Patents.