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PRODUCTION OF COLOR PHOTOGRAPHIC IMAGES

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9 Claims. (Cl. 95—6)

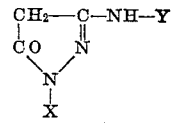
1

The present invention relates to a process for the production of color photographic images by color development in the presence of a color coupler, to photographic developers, and photographic material containing such couplers.

As known, a colored image may be formed by developing a reducible silver salt image in the presence of a compound which is referred to as a "color coupler" and which couples with the oxidation product of the developing agent during the development, forming a dyestuff which is deposited onto the developed silver grains.

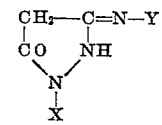
My co-pending application Serial No. 66,837, filed December 22, 1948, hereinafter referred to as the "co-pending application," discloses compounds which are useable as color couplers for the production of magenta images, said compounds corresponding to the following Formula I

FIG. I



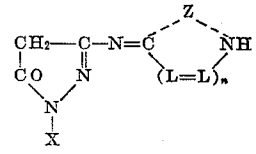
wherein Y is a heterocyclic radical; X is alkyl, aryl, acyl or a heterocyclic radical, these groups being either substituted or not, or H; and one or both H atoms of the CH_2 groups may be substituted by a substituent split off on development, and which formula may be written in a tautomeric form, for instance, as the following Formula II

FIG. II



or, when Y represents a nitrogen-containing heterocyclic ring, a further tautomeric form may be represented by the following Formula III

FIG. III



wherein Z is the non-metallic atoms necessary to complete the heterocyclic ring Y; L is a methine group or a substituted methine group; and n is 0 or 1.

2

On color development, these color couplers produce dyestuffs with an absorption maximum at about 550 $m\mu$ and an excellent blue-light transmission.

It is an object of the present invention to provide a new process for the production of a colored photographic image by developing a reducible silver salt image with a primary amino aromatic developing agent in the presence of a color coupler.

It is another object of the present invention to provide a photographic emulsion comprising a color coupler especially suited for the production of magenta images in three-color photographic processes.

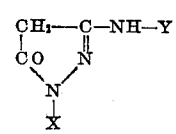
Still another object of the present invention is to provide a photographic color developer comprising a color coupler especially suited for the production of magenta images in three-color photographic processes.

Further objects will appear from the following description.

I have now found that dyestuffs which have a narrow absorption spectrum, as well as dyestuff-images with hard gradation, may be obtained by color development in the presence of compounds wherein the H atom, linked to one of the N atoms in Y, in the 3-amino substituent or in 2-position of the pyrazolone ring, is substituted by alkyl, aryl, acyl or a heterocyclic group, these substituents being either substituted or not.

According to my present invention, a reducible silver salt image is developed with a primary aromatic amino developing agent in the presence of a color coupler corresponding to Formula I

FIG. I



or a tautomeric form thereof, wherein the hydrogen atom of the 3-amino group or the corresponding H atom in the tautomeric form is substituted by alkyl, aryl, acyl or a heterocyclic group, these substitutents being either substituted or not.

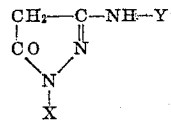
The group X or said groups replacing the hydrogen atom of the amino group or a corresponding hydrogen atom may be substituted by a group containing one or more pyrazolone nuclei, for instance, in such a manner that the coupler comprises two identical parts linked over the group

X or over said group replacing a hydrogen atom linked to a nitrogen atom.

The preparation of these couplers may be effected by any convenient method, for instance:

(*a*) A compound corresponding to Formula I

FIG. I



or its tautomeric forms is quaternated and treated with alkali during or after quaternating, e. g., said compound is treated in alkaline medium with dimethyl sulphate, ethyl bromide, di-bromo pentane, cetyl bromide or the like.

(*b*) A 3-amino-5-pyrazolone is reacted with a heterocyclic compound having a cyclic nitrogen atom quaternated by an acid residue and a substituent as defined above and a reactive halogen substituent, i. e., a halogen atom in 2- or 4-position, for example, 2-iodo-quinoline ethiodide, 2-bromo-6-methoxy - quinoline - ethyl bromide (Patent No. 2,231,659, Example 2), 2-iodo-4-methyl-thiazole-ethiodide (J. Chem. Soc. (1949) 1504), 2-iodobenzothiazole methiodide (J. Chem. Soc. (1949) 1505), 1-phenyl-3-chloro-5-pyrazolone-dimethyl sulphate (Ber. 46 (1913) 3604).

(*c*) A 3-aryl- or -acyl-amino-5-pyrazolone or a 3-heterocyclic substituted amino pyrazolone according to the co-pending application is condensed with a heterocyclic compound having a reactive halogen substituent or a reactive mercapto group, as, for example, 2-bromo-pyridine, 2-chloro-pyridine, 2-chloro-quinoline, 2:4-dichloroquinazoline (J. Chem. Soc. (1947) 777), 2-bromo-6-methoxy lepidine (J. Org. Chem. 457), 6-methoxy-4-chloroquinoline (J. Am. Chem. Soc. 69 (1947) 1660), 2-chloro-4-anilino-quinoline (J. Chem. Soc. (1947) 904), cyanuric chloride, 2:4-dichloro-6-anisidino-1:3:5 - triazine (J. Chem. Soc. (1947) 158), 2-chloro-thiazole (Chem. Abstracts 40 (1946) 4059), 2-chloro-4:6-dimethyl-pyrimidine (Ber. 34 (1901) 3956), 2-chloro-benzselenazole (J. Chem. Soc. (1933) 1765), 1-phenyl-3-chloro-pyrazolone (Ber. 31 (1898) 3008), 9-bromo - di - benzoxanthene (Beilstein, XVII, 146) and 4:6-dihydroxy-2-methylmercapto-pyridine (J. Chem. Soc. (1947) 730).

(*d*) The thiourea derivative obtained by reacting a 3-amino-5-pyrazolone with an isothiocyanate is condensed with ethylene bromide, monochloro acetone or omega-bromo-acetophenone in order to obtain a thiazoline or a thiazole, or said derivative is condensed with mono-chloro-acetic acid to obtain a thiazolone.

As 3-amino-5-pyrazolone, any one of those mentioned in the co-pending application may be used as well as their condensation products with an aldehyde, a ketone or the like. Further, 3-amino-5-pyrazolones which may be used are, for instance, the bis-(3-amino-5-pyrazolones) described in Patent No. 2,411,951.

The color couplers according to my present invention may be used in the developing solution or in a colloid layer, in the latter case either in a light-sensitive layer, or in a non-light-sensitive layer adjacent to a sensitive layer, or separated therefrom by a water-permeable layer. When used in a colloid layer of a color photographic material, the color couplers generally have to be fast to diffusion. This fastness to diffusion is, for instance, obtained if for the preparation of the color couplers, compounds, such as 2-chloro-4-cetyl-amino-quinoline (which may be prepared by a method analogous to that described in the J. Chem. Soc. (1947) 904) are used, the compounds having a substituent known to possess the property of rendering them fast to diffusion.

Color couplers which are fast to diffusion may advantageously contain groupings that render them water-soluble. Such groupings may also be introduced into my heterocyclic substituted amino pyrazolones. For instance, a 3-amino-5-pyrazolone is condensed with the di-primary condensation product from the reaction of one equivalent of 4:4'-diamino-2:2'-stilbene disulphonic acid and two equivalents of a heterocyclic compound containing at least two halogen atoms. Any replaceable halogen atom still remaining may be removed by the reaction with a primary amine (British specification 578,014 and Chem. Abstracts 41 (1947) 6055).

The presence of color couplers according to the present invention during the development of a reducible silver salt image may result from adding to the photographic material, or to the developer, a compound capable of generating said color coupler, for instance, a compound differing from the color coupler only in that one or both of the hydrogen atoms of the reactive CH_2 group or the pyrazolone ring are substituted in a known manner by a substituent which splits off during development.

The aromatic amino compounds usable as developing agents in the present invention include the mono-, di- and tri-amino aryl compounds. Among the mono-amino developing agents may be mentioned amino phenols, amino cresols, the halogen derivatives of either of them, and amino naphthols.

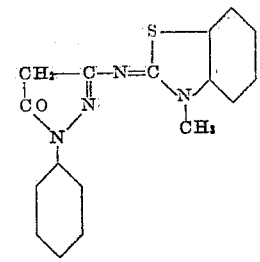
The developing agents preferably used and producing the best results in connection with the present invention are the aromatic ortho- and para-diamines, such as para-phenylene-diamine and its substitution products.

The following examples serve to illustrate my invention, without limiting, however, the scope thereof:

Example 1

15 g. 1-phenyl-3-(benzothiazolyl-2'-)amino-5-pyrazolone obtained as described in Example 3 of the co-pending application are dissolved in 250 ccm. of N/5 aqueous solution of NaOH. To this solution are added 5 ccm. dimethyl sulfate and the mixture is then heated for 20 minutes on the water bath. After cooling, filtering with suction, and washing the residue with water and drying, the product obtained is recrystallized from ethanol. The formula is as the following Formula IV

FIG. IV



or a derivative of a tautomeric form thereof. Melting point: 199–200° C. Analysis: N calculated 17.39%, found 17.29% and 17.33%. S calculated 9.93%, found 9.65% and 9.85%.

2 g. of this product are dissolved in 50 ccm. ethanol and 10 ccm. of a 2 N aqueous solution of NaOH and added to a mixture of the following solutions:

(A)

N,N-diethyl-p-phenylene diamine sulfate	g--	3.2
Na_2SO_3	g--	5
Water to	ccm--	500

(B)

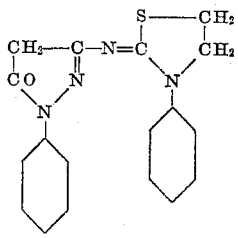
K_2CO_3	g--	75
KBr	g--	2.5
Water to	ccm--	500

An exposed positive ciné film is developed for three minutes at 20° C. in the bath thus obtained, washed for 30 minutes, bleached in order to remove the silver in a bath composed of 50 g. potassium ferricyanide and 3 g. potassium bromide in 1000 ccm. water, washed for 10 minutes, fixed for 20 minutes in a bath composed of 250 g. sodium thiosulfate in 1000 ccm. water, and finally washed for 30 minutes. A contrasting magenta image with an absorption maximum at 540 mμ is obtained.

Example 2

To 15 g. 1-phenyl-3-phenyl-thiocarbamylamino-5-pyrazolone, melting at 227° C. and obtained as described in Example 3 of the copending application are added 90 ccm. ethylene bromide. The mixture is boiled for one hour until the greater part of the hydrobromic acid is eliminated. After cooling and filtering with suction, glittering pellets melting at 253–254° C. are obtained. This product is dissolved in an N aqueous solution of NaOH. After treating with acetic acid, the precipitated product is filtered with suction, dried and recrystallized from ethanol. A product of the following Formula V

FIG. V



is obtained. Melting point: 197–198° C. Analysis: S calculated 9.52%, found 9.10%.

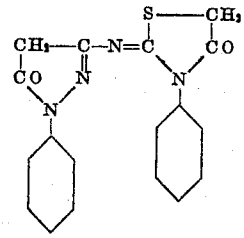
2 g. of this product are dissolved in 50 ccm. of an N solution of KOH in alcohol and added to a mixture of solutions as given above in Example 1.

An exposed positive ciné film is developed for three minutes at 20° C. in the bath thus obtained, washed for 30 minutes, bleached in order to remove the silver in a bath composed of 50 g. potassium ferricyanide and 3 g. potassium bromide in 1000 ccm. water, washed for 10 minutes, fixed for 20 minutes in a bath composed of 250 g. sodium thiosulphate in 1000 ccm. water, and finally washed for 30 minutes. A contrasting magenta image with an absorption maximum at 544 mμ is obtained.

Example 3

14 g. 1-phenyl-3-phenyl-thiocarbamylamino-5-pyrazolone and 28 g. mono-chloro acetic acid are melted togethed and heated on the water bath for 30 minutes. The product obtained is recrystallized from ethanol and corresponds to the Formula VI

FIG. VI



Melting point: 206–208° C. Analysis: N calculated 16%, found 15.75% and 15.80%.

2 g. of this product are dissolved in 50 ccm. ethanol and 25 ccm. of an N solution of KOH in methanol and added to a mixture of the solutions given in Example 1.

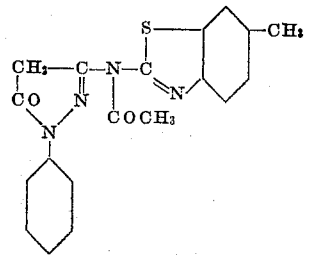
An exposed positive ciné film is developed for three minutes at 20° C. in the bath thus obtained, washed for 30 minutes, bleached in order to remove the silver in a bath composed of 50 g. potassium ferricyanide and 3 g. potassium bromide in 1000 ccm. water, washed for 30 minutes, fixed for 20 minutes in a bath composed of 250 g. sodium thiosulphate in 1000 ccm. water, and finally washed for 30 minutes. A contrasting magenta image with an absorption maximum at 546 mμ is obtained.

Example 4

26.5 g. 1-phenyl-3-amino-5-pyrazolone, 150 ccm. pyridine and 24 ccm. p-tolyl-isothiocyanate are refluxed for one hour. The reaction mixture is cooled to 50° C. and poured into one litre of a 2 N aqueous solution of hydrochloric acid whilst stirring. The precipitate formed is filtered off, washed with water and recrystallized from a mixture of equal parts of ethanol and methanol. Melting point: 257–258° C.

6.5 g. of the 1-phenyl-3-(toluthiazolyl-2'-)-amino-5-pyrazolone thus obtained and 30 ccm. acetic acid anhydride are boiled for fifteen minutes. The reaction mixture is poured into water. The precipitated product is separated by filtration with suction and recrystallized from ethanol. It corresponds to the following Formula VII

FIG. VII



or to a tautomeric form thereof. Melting point: 245–247° C. Analysis: N calculated 15.38%, found 14.90%.

2 g. of this product are dissolved in 40 ccm. ethanol and 20 ccm. of an N aqueous solution of KOH and added to a mixture of solutions given in Example 1.

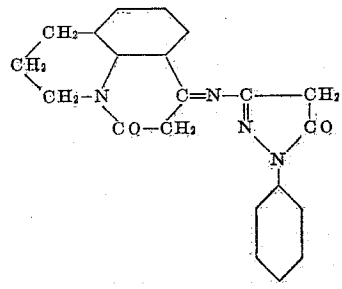
An exposed positive ciné film is developed for three minutes at 20° C. in the bath thus obtained, washed for 30 minutes, bleached in order to remove the silver in a bath composed of 50 g. potassium ferricyanide and 3 g. potassium bro-

mide in 1000 ccm. water, washed for 10 minutes, fixed for 20 minutes in a bath composed of 250 g. sodium thiosulphate in 1000 ccm. water, and finally washed for 30 minutes. A contrasting magenta image with an absorption maximum at 535 mμ is obtained.

Example 5

1.6 g. 1-phenyl-3-amino-5-pyrazolone and 2 g. 7-chloro-5-oxo-julolin (obtained as described in Berichte 25 (1892) 1198) are melted together at 140–150° C. in the presence of a few drops of a concentrated aqueous solution of HCl. The product obtained is dissolved in ethanol and precipitated with an aqueous solution of NaCl. This product corresponds to the following Formula VIII

FIG. VIII



2 g. of this product are dissolved in 50 ccm. ethanol and 25 ccm. of a normal solution of KOH in methanol and added to a mixture of solutions given in Example 1.

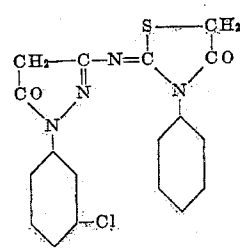
An exposed positive ciné film is developed for three minutes at 20° C. in the bath thus obtained, washed for 30 minutes, bleached in order to remove the silver in a bath composed of 50 g. potassium ferricyanide and 3 g. potassium bromide in 1000 ccm. water, washed for 10 minutes, fixed for 20 minutes in a bath composed of 250 g. sodium thiosulfate in 1000 ccm. water, and finally washed. A contrasting bluish-magenta image is obtained.

Example 6

11 g. 1 - m - chloro-phenyl-3-amino-5-pyrazolone prepared by the method described in the J. Am. Chem. Soc. 66 (1944) 1850, 8 ccm. phenyl-isothiocyanate and 60 ccm. pyridine are boiled for 1 hour. The reaction mixture is poured into a 2 N aqueous solution of hydrochloric acid. The hydrochloric acid is decanted and the viscous precipitate is purified by washing with water and suspending in ethanol. After filtration with suction, a product melting at 220–222° C. is obtained.

2.9 g. of this product and 5.8 g. mono-chloro acetic acid are heated on the boiling water bath for half an hour and next boiled with a little ethanol. A product according to the Formula IX

FIG. IX



is obtained. Melting point: 236–238° C.

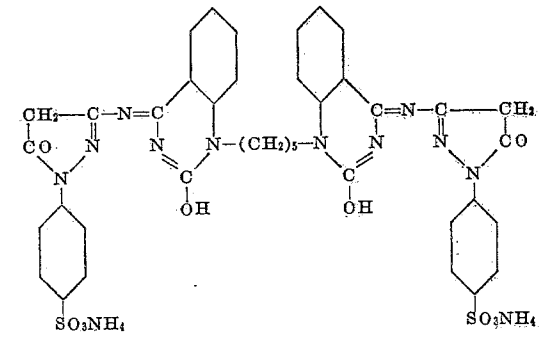
2 g. of this coupler are dissolved in 30 ccm. ethanol and 10 ccm. of a 2 N aqueous solution of NaOH and added to a mixture of the solutions as indicated in Example 1.

An exposed positive ciné film is developed for six minutes at 20° C. in the bath thus obtained, washed for 30 minutes, bleached in order to remove the silver in a bath composed of 50 g. potassium ferricyanide and 3 g. potassium bromide in 1000 ccm. water, washed for 10 minutes, fixed for 20 minutes in a bath composed of 250 g. sodium thiosulfate in 1000 ccm. water, and finally washed. A magenta image with an absorption maximum at 548 mμ is obtained.

Example 7

2.1 g. of the product obtained as described in Example 7 of the co-pending application and 1.3 g. dibromopentane are heated over night in a sealed tube at 120° C. After cooling, filtering with suction, washing with ether, and recrystallizing from a mixture of equal volumes ethanol and water, a product corresponding to the following Formula X

FIG. X



is obtained. This product, however, contains an amount of a similar product differing from that of Formula X in that the OH groups are replaced by chlorine atoms.

2 g. of this product are dissolved in a mixture of the solutions given in Example 1.

An exposed positive ciné film is developed for three minutes at 20° C. in the bath thus obtained, washed for 30 minutes, bleached in order to remove the silver in a bath composed of 50 g. potassium ferricyanide and 3 g. potassium bromide in 1000 ccm. water, washed for 10 minutes, fixed for 20 minutes in a bath composed of 250 g. sodium thiosulfate in 1000 ccm. water, and finally washed. A magenta image with an absorption maximum at 557 mμ is obtained.

Example 8

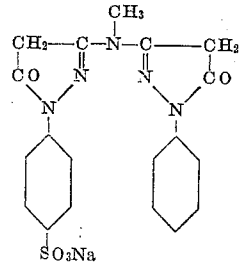
Raw 1-phenyl-3-amino-5-pyrazolone obtained according to the method described in the J. Am. Chem. Soc. 66 (1944) 1853 is recrystallized from ethanol. The non-dissolved residue is purified by boiling with water and recrystallizing from diethylene glycol mono-ethyl ether. Fine, glittering pellets melting at 282–285° C. are obtained. It is 3 - imino - bis (1 - phenyl - 5 - pyrazolone). Analysis: N calculated 21.02%, found 21.31% and 21.36%. On color development in the same manner as explained hereinafter, this product yields a violet dye image.

10 g. of this product are gradually added to 21 g. sulfuric acid. Next, 4 g. chloro-sulfonic acid are added. The mixture is slowly heated up to 100° C. and subsequently maintained at 130–140° C. for three hours. The reaction mixture is

poured into ice-water under stirring. After filtration with suction and recrystallization from water, 3 - (1'-phenyl-5'-pyrazolonyl-3')-imino-1 phenyl-5-pyrazolone-4''-sulfonic acid is obtained. Analysis: calculated N 16.24% (for the corresponding hydrate), found 16.24% and 16.12%.

2.15 g. of this product are dissolved on the water bath in 10 ccm. of an N aqueous solution of NaOH. Then, 0.6 ccm. dimethyl sulfate are added and the mixture is heated for half an hour on the water bath. The solution thus obtained is desiccated by evaporation. A product corresponding to the following Formula XI

FIG. XI



or to a tautomeric form thereof is obtained.

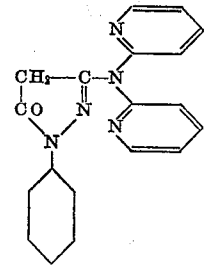
2 g. of this product are dissolved in a mixture of the solutions given in Example 1.

An exposed positive ciné film is developed for three minutes at 20° C. in the bath thus obtained, washed for 30 minutes, bleached in order to remove the silver in a bath composed of 50 g. potassium ferricyanide and 3 g. potassium bromide in 1000 ccm. water, washed for 10 minutes, fixed for 20 minutes in a bath composed of 250 g. sodium thiosulfate in 1000 ccm. water, and finally washed for 30 minutes. A magenta image is obtained.

Example 9

5.25 g. 1-phenyl-3-amino-5-pyrazolone, 3.4 g. chloropyridine and 15 ccm. glacial acetic acid are slightly boiled for 4 hours. After adding 2 g. sodium acetate, the reaction mixture is poured into water. After filtering with suction and boiling with ethanol, the residue not dissolved melts at 280° C. and is a product which corresponds to the following Formula XII

FIG. XII



2 g. of this product are dissolved in 50 ccm. ethanol and 10 ccm. of an N aqueous solution of NaOH and added to a mixture of the solution given in Example 1.

An exposed positive ciné film is developed for three minutes at 20° C. in the bath thus obtained, washed for 30 minutes, bleached in order to remove the silver in a bath composed of 50 g. potassium ferricyanide and 3 g. potassium bromide in 1000 ccm. water, washed for 10 minutes, fixed for 20 minutes in a bath composed of 250 g. sodium thiosulfate in 100 ccm. water, and finally washed. A bluish magenta image is obtained.

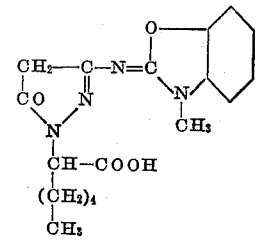
Example 10

2.5 g. ethyl-beta-amino-beta-ethoxy acrylate prepared according to the method described in the J. Am. Chem. Soc. 71 (1949) 983, footnote 2, 2.5 g. alpha-hydrazino-oenanthic acid prepared according to the method described in Jl. f. prakt. Chemie 146 (1936) 239 are thoroughly mixed and heated on the water bath for three hours. The reaction mixture is dissolved in an N aqueous solution of NaOH. This solution is extracted with ether. The aqueous fraction is acidified with a 2 N aqueous solution of acetic acid. The precipitate is filtered with suction. The product obtained is alpha-(3-amino-5-pyrazolonyl-1) oenanthic acid.

3 g. of this product and 2 g. 2-chloro-benzoxazole are melted together at 125° C. for 10 minutes. After cooling, a product which is alpha-3-(benzoxazolyl-2) amino-5-pyrazolonyl-1 oenanthic acid is obtained.

2 g. of this product dissolved in 6 ccm. of a 2 N aqueous solution of NaOH and 0.5 ccm. dimethyl sulfate are heated for half an hour on the water bath. The reaction mixture is cooled and poured into a 0.1 N aqueous solution of acetic acid. The precipitate formed is filtered with suction, washed with water, and dried in the air. A product corresponding to the following Formula XIII

FIG. XIII



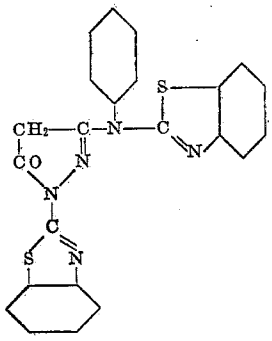
or to a tautomeric form thereof is obtained.

1 g. of this product is dissolved in 10 ccm. ethanol and added to 100 ccm. of a positive cinematographic silver halide emulsion. The emulsion is coated to a support, exposed to light, developed for three minutes at 20° C. in a bath obtained by mixing the solutions given in Example 1, washed for 30 minutes, bleached in order to remove the silver in a bath composed of 50 g. potassium ferricyanide and 3 g. potassium bromide in 1000 ccm. water, washed for 10 minutes, fixed for 20 minutes in a bath composed of 250 g. sodium thiosulfate in 1000 ccm. water, and finally washed for 30 minutes. A magenta image is obtained.

Example 11

3 g. 3-anilido-5-pyrazolone prepared according to the method described in J. Am. Chem. Soc. 65 (1943) 733 and 3 g. 2-chloro-benzthiazole are melted together at 180° C. A vigorous reaction occurs. When this reaction comes to an end, the whole is cooled, and as much of the reaction mixture as possible is dissolved in boiling ethanol. The solution is filtered. By adding ether, about 1 g. of a product is precipitated which is recrystallized from 100 ccm. of a mixture of 1 part by volume of water and 3 parts of ethanol. The product obtained corresponds to the following Formula XIV

FIG. XIV



Melting point 165–170° C. Analysis: N calculated 15.87%, found 16.35%.

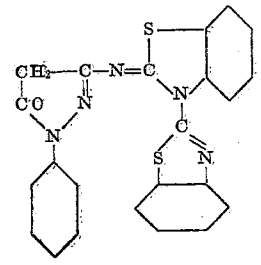
2 g. of this product are dissolved in 50 ccm. ethanol and 10 ccm. of an N aqueous solution of NaOH and added to a mixture of the solutions as given in Example 1.

An exposed positive ciné film is developed for three minutes at 20° C. in the bath thus obtained, washed for 30 minutes, bleached in order to remove the silver in a bath composed of 50 g. potassium ferricyanide and 3 g. potassium bromide in 1000 ccm. water, washed for 10 minutes, fixed for 20 minutes in a bath composed of 250 g. sodium thiosulfate in 1000 ccm. water, and finally washed for 30 minutes. A bluish magenta image is obtained.

Example 12

1 g. 1-phenyl-3-(benzthiazolyl-2')-amino-5-pyrazolone and 0.5 g. 2-amino-benzthiazole are melted together at 180° C. for one hour according to the method described for the preparation of 2-imino-3-(benzthiazolyl-2')-benzthiazoline in Ber. 75 (1942) 946. A product corresponding to the following Formula XV

FIG. XV



is obtained.

2 g. of this product are dissolved in 40 ccm. methanol and added to a mixture of the solutions given in Example 1.

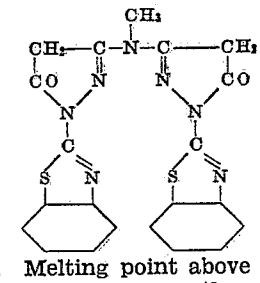
An exposed positive ciné film is developed for three minutes at 20° C. in the bath thus obtained, washed for 30 minutes, bleached in order to remove the silver in a bath composed of 50 g. potassium ferricyanide and 3 g. potassium bromide in 1000 ccm. water, washed for 10 minutes, fixed for 20 minutes in a bath composed of 250 g. sodium thiosulfate in 1000 ccm. water, and finally washed for 30 minutes. A magenta image is obtained.

Example 13

5 g. of the raw beta-[beta(benzthiazolyl-2)-hydrazino]-beta-imino-propionic acid ethyl ester prepared according to the method described in J. Am. Chem. Soc. 66 (1944) 1854 are dissolved in amylacetate. 0.5 g. of the product does not dissolve. It melts above 300° C. and is 3-imino-bis[1-(benzthiazolyl-2)-5-pyrazolone]. Analysis: N calculated 21.92%, found 22.18%.

0.4 g. of this product suspended in 3 ccm. of an N aqueous solution of NaOH and 0.1 ccm. dimethylsulfate are heated on the boiling water bath for 30 minutes. The reaction mixture is cooled. The precipitate obtained is filtered with suction. A product corresponding to the following Formula XVI

FIG. XVI



is obtained. Melting point above 300° C.

1 g. is dissolved in 10 ccm. ethanol and 10 ccm. of an N aqueous solution of NaOH and added to a mixture of the solutions of Example 1.

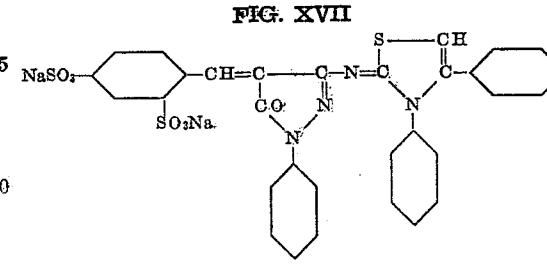
An exposed positive ciné film is developed for three minutes at 20° C. in the bath thus obtained, washed for 30 minutes, bleached in order to remove the silver in a bath composed of 50 g. potassium ferricyanide and 3 g. potassium bromide in 1000 ccm. water, washed for 10 minutes, fixed for 20 minutes in a bath composed of 250 g. sodium thiosulfate in 1000 ccm. water, and finally washed for 30 minutes. A magenta image is obtained.

Example 14

3 g. 1-phenyl-3-phenylthiocarbamyl-amino-5-pyrazolone melting at 227° C. and prepared as described in Example 3 of the co-pending application, 2 g. omega-bromo-acetophenone and 50 ccm. ethanol are boiled for 45 minutes. After cooling and filtering with suction, the filtrate is neutralized with a 2N aqueous solution of NaOH. After filtration with suction, a product melting at 116–118° C. is obtained.

4.1 g. of this product, 3.1 g. benzaldehyde-2,4-disodium sulfonate and 30 ccm. water contaning 0.1 g. of NaOH are heated on the water bath for about 1 hour. From the yellowish-brown reaction mixture obtained, a dye is precipitated by common salt. This product corresponds to the following Formula XVII

FIG. XVII

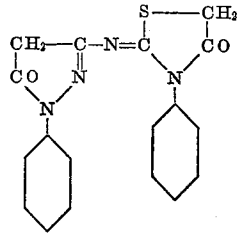


2 g. of this product are dissolved in a mixture of the solutions of Example 1.

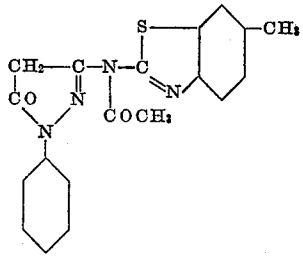
An exposed positive ciné film is developed for three minutes at 20° C. in the bath thus obtained, washed for 30 minutes, bleached in order to remove the silver in a bath composed of 50 g. potassium ferricyanide and 3 g. potassium bromide in 1000 ccm. water, washed for 10 minutes, fixed for 20 minutes in a bath composed of 250 g. sodium thiosulfate in 1000 ccm. water, and finally washed for 30 minutes. A nice magenta image is obtained.

I claim:

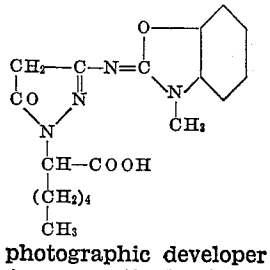
1. A color photographic developer containing a primary amino aromatic developing agent and a color coupler according to the formula



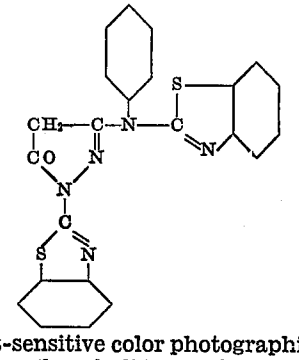
2. A color photographic developer containing a primary amino aromatic developing agent and a color coupler according to the formula



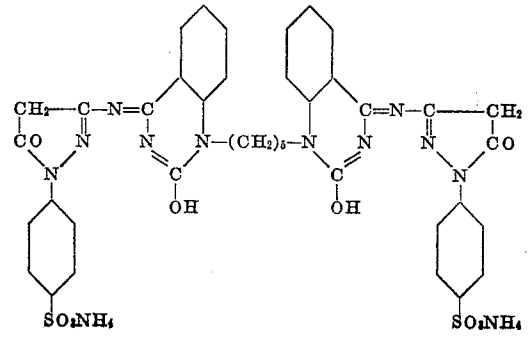
3. A color photographic developer containing a primary amino aromatic developing agent and a color coupler according to the formula



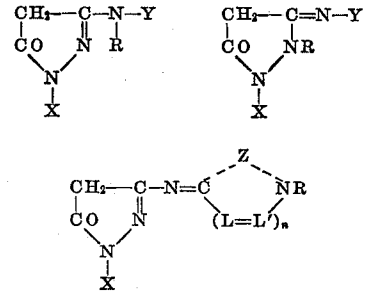
4. A color photographic developer containing a primary amino aromatic developing agent and a color coupler according to the formula



5. A light-sensitive color photographic material containing a silver halide emulsion layer and a colloid layer comprising a color coupler having the formula

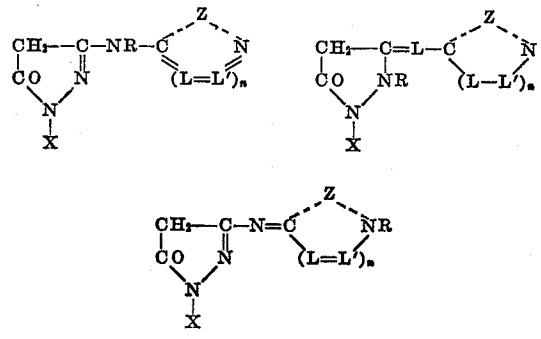


6. Process for the production of a color photographic image, which comprises developing a reducible silver salt image in a photographic element by means of a primary amino aromatic developing agent in the presence of a color coupler having a formula selected from the group consisting of the following three formulae:



wherein Y is a heterocyclic radical, X is a member selected from the group consisting of alkyl, aryl, acyl, a heterocyclic radical, and hydrogen, R is a member selected from the group consisting of alkyl, aryl, acyl, and a heterocyclic group, Z is the non-metallic atoms necessary to complete a heterocyclic radical, the heterocyclic radical in the definitions of Y, X, R and Z being a radical selected from the group consisting of 5 and 6-membered heterocyclic radicals containing at least one nitrogen atom and of such radicals having a fused-on ring, n is a value selected from the group consisting of 0 and 1, and L and L' are methine groups.

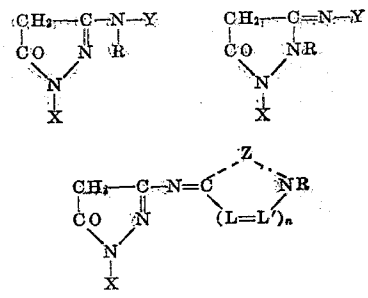
7. Process for the production of a color photographic image, which comprises developing a reducible silver salt image in a photographic element by means of a primary amino aromatic developing agent in the presence of a color coupler having a formula selected from the group consisting of the following three formulae:



wherein X is a member selected from the group consisting of alkyl, aryl, acyl, a heterocyclic radical, and hydrogen, R is a member selected from the group consisting of alkyl, aryl, acyl, and a heterocyclic group, Z is the non-metallic atoms necessary to complete a heterocyclic radical, the heterocyclic radical in the definitions of X, R and Z being a radical selected from the group consisting of 5 and 6-membered heterocyclic radicals containing at least one nitrogen atom and of such radicals having a fused-on ring, n is a value selected from the group consisting of 0 to 1, and L and L' are methine groups.

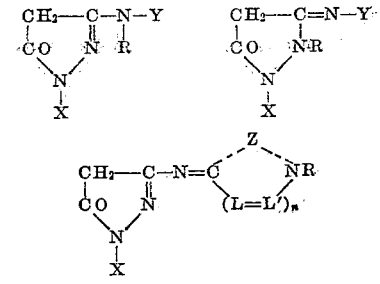
8. A light-sensitive photographic material comprising a silver halide emulsion layer and a colloid layer, containing a color coupler having a

formula selected from the group consisting of the following three formulae:



wherein Y is a heterocyclic radical, X is a member selected from the group consisting of alkyl, aryl, acyl, a heterocyclic radical, and hydrogen, R is a member selected from the group consisting of alkyl, aryl, acyl, and a heterocyclic group, Z is the non-metallic atoms necessary to complete a heterocyclic radical, the heterocyclic radical in the definition of Y, X, R and Z being a radical selected from the group consisting of 5 and 6-membered heterocyclic radicals containing at least one nitrogen atom and of such radicals having a fused-on ring, n is a value selected from the group consisting of 0 and 1, and L and L' are methine groups.

9. A color photographic developer containing a primary amino aromatic developing agent and a color coupler having a formula selected from the group consisting of the following three formulae:



wherein Y is a heterocyclic radical, X is a member selected from the group consisting of alkyl, aryl, acyl, a heterocyclic radical, and hydrogen, R is a member selected from the group consisting of alkyl, aryl, acyl, and a heterocyclic group, Z Z is the non-metallic atoms necessary to complete a heterocyclic radical, the heterocyclic radical in the definitions of Y, X, R and Z being a radical selected from the group consisting of 5 and 6-membered heterocyclic radicals containing at least one nitrogen atom and of such radicals having a fused-on ring, n is a value selected fom the group consisting of 0 and 1, and L and L' are methine groups.

JACOB JOSEPH JENNEN.

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