

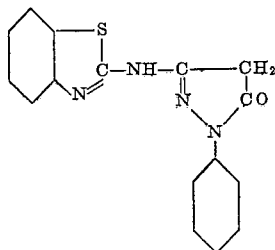
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the heterocyclic ring contains a nitrogen atom and is linked to the NH-substituent in the 3 position of the pyrazolone nucleus by its alpha or gamma position.

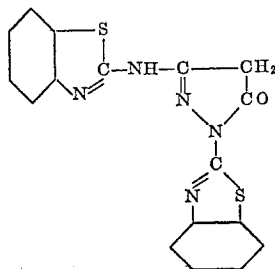
The preparation of the hetero-cyclic-amino-pyrazolone is very simple and may be carried out by reacting a 3-amino-5-pyrazolone with a heterocyclic compound having a reactive halogen substituent as, for instance, 2-bromo-pyridine, 2-chloro-pyridine, 2-chloro-quinoline, 2,4-dichloro-quinazoline (J. Chem. Soc. (1947) 777), 2-bromo-6-methoxy lepidine (J. Org. Chem. (1947) 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-p-anisidine-1,3,5-triazine (J. Chem. Soc. (1947) 158), 2-chlorothiazole (Chem. Abstracts 40 (1946) 4059), 2-chloro-4,6-dimethyl pyridine (Berichte 34 (1901) 3956), 2-chlorobenzoselenazole (J. Chem. Soc. (1933) 1765), 1-phenyl-3-chloro-pyrazolone, 9-bromo dibenzo-xanthene.

Also the corresponding heterocyclic compounds having a mercapto group in the alpha or gamma position as to the nitrogen, for instance, 4,6-dihydroxy-2-methylmercapto-pyridine (J. Chem. Soc. (1947) 730) may be condensed with a 3-amino-5-pyrazolone to give the 3-heterocyclic-amino-5-pyrazolones desired. The corresponding heterocyclic compounds having an alpha or gamma-amino group do not condense with a 3-amino-5-pyrazolone (compare Curd and Rose, J. Chem. Soc. (1946) 345). The reason would be that these compounds tend to behave as if they were alpha or gamma-imino-dihydro derivatives. As known, aromatic amines may be condensed with a 3-amino-5-pyrazolone, and this reaction is used to prepare the compounds claimed in Patent 2,343,703.

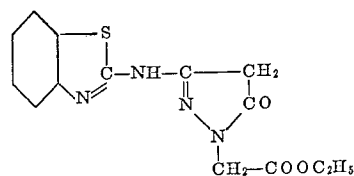
The preparation of the heterocyclic amino pyrazolones may also be effected by converting an amino pyrazolone into a compound which allows the formation of the heterocyclic amino pyrazolone desired by a simple ring closure, for instance, by condensation of the amino pyrazolone with an aromatic isothiocyanate and subjecting the thiourea derivative formed to a Hügershoff reaction. This method is illustrated by Example 3 hereinafter given. Besides, the coupler according to the following formula:



also the couplers represented by the following formulae:



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may be prepared by this method.

Said thiourea derivatives may also be converted by treatment with dimethyl sulphate into an isothiurea derivative which may be reacted with an amino thiophenol so as to form a 3-heterocyclic substituted amino pyrazolone. This method is described in the J. Am. Chem. Soc. 55 (1933) 4989.

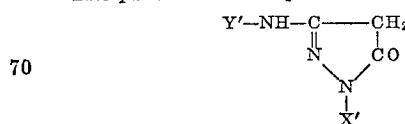
As 3-amino-pyrazolones, the following may be used: 3-amino-5-pyrazolone, 1-methyl-3-amino-5-pyrazolone, 1-phenyl-3-amino-5-pyrazolone, 1-m-tolyl-3-amino-5-pyrazolone, 1-m-chlorophenyl-3-amino-5-pyrazolone, 1-p-methoxyphenyl-3-amino-5-pyrazolone, 1-p-nitrophenyl-3-amino-5-pyrazolone, 1-(3-pyridyl)-3-amino-5-pyrazolone, 1-(4-pyridyl)-3-amino-5-pyrazolone, 1-(2-pyridyl)-3-amino-5-pyrazolone, 1-(2-benzothiazolyl)-3-amino-5-pyrazolone, 1-(2-benzoxazolyl)-3-amino-5-pyrazolone. The preparation of most of these pyrazolones is described in the J. Am. Chem. Soc. 66 (1944) 1850-55.

When the heterocyclic nucleus is a pyrazolone, the 3-heterocyclic amino pyrazolone may be obtained by condensing a hydrazine with a malonate imino ether, as described in the J. Am. Chem. Soc. 66 (1944) 1852. By this method an amino pyrazolone and an imino-bis-pyrazolone are simultaneously formed.

The 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 colloid layer. When used in a colloid layer of a color photographic material, the couplers generally have to be fast to diffusion. This fastness to diffusion is, for instance, obtained by using in the preparation of the 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), which have a substituent known to have the property of rendering fast to diffusion.

Couplers which are fast to diffusion contain advantageously groupings rendering them water-soluble. Such groupings may also be introduced in my heterocyclic substituted amino pyrazolones, for example, 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 reaction with a primary amine (British Patent No. 578,014, date of acceptance June 12, 1946; Chem. Abstracts 41 (1947) 6055).

The presence of couplers having the formula:



during the development of a reducible silver salt image may result from adding to the photo-

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graphic material or developer a compound capable of generating such couplers, for instance, a compound differing from one of formula II only in that one or both of the hydrogen atoms of the reactive CH₂ group of the pyrazolone ring are substituted in a known manner by a substituent split off during development.

The aromatic amino compounds which may be used as developing agents in accordance to my present invention include the mono-, di- and tri-amino aryl compounds. Among the mono-amino developing agents may be mentioned amino phenols and amino cresols and their halogen derivatives and amino naphthols.

The developing agents which I prefer to use and which give the best results in connection with my present invention are the aromatic ortho- and paradiamines, such as paraphenylenediamine and its substitution products.

A color developer which may be used to develop an exposed light-sensitive silver halide emulsion layer may have the following composition:

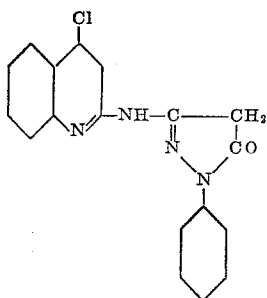
(A)	N,N - diethyl - p - phenylene - diamine hydrochloride	g	3
	Sodium sulphite (cryst.)	g	5
	Water	cc	500
(B)	Potassium carbonate	g	75
	Potassium bromide	g	2.5
	Water	cc	500
(C)	Color coupler	g	2
	Ethyl alcohol	cc	50
	Aqueous solution of sodium hydroxide (1N)	cc	10

For use, A and B are mixed together, and to this mixture C is added.

When the color coupler is added to the light-sensitive silver halide emulsion, development may be effected with a mixture of A+B.

The following examples are given to illustrate my invention without limiting, however, its scope.

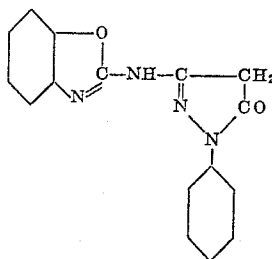
Example 1.—A transparent magenta image is obtained by developing an exposed light-sensitive silver halide emulsion layer with the developer mentioned above and containing a color coupler prepared as follows: 3 g. 1-phenyl-3-amino-5-pyrazolone, 3.5 g. 2,4-dichloro-quinoline and 12 cc. of glacial acetic acid are refluxed for 4 hours. The reaction mass is poured in water. The whole is filtered with suction. The residue is dissolved in ethyl alcohol. The latter is partially evaporated. The solution is cooled and filtered with suction. The filtrate is completely evaporated and the residue is recrystallised from a mixture of equal volumes of water and alcohol. A product melting at 224–228° C. is obtained. Probable formula:



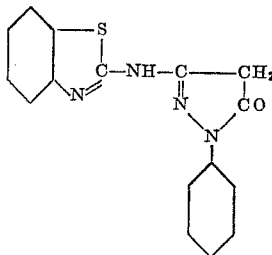
Example 2.—A bluish magenta image (absorption maximum at 539 m μ) is obtained by developing an exposed light-sensitive silver halide emul-

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sion layer with the developer mentioned above and containing a color coupler prepared as follows: 1.75 g. 1-phenyl-3-amino-5-pyrazolone and 1.53 g. 2-chloro-benzoxazole are treated for 20 minutes at 80° C. The product obtained is dissolved in ethyl alcohol. The solution is poured in water and the whole is filtered with suction. The residue is dissolved in a little methyl alcohol. The solution is filtered. The filtrate is cooled and the crystals formed are separated by vacuum filtration. A product melting at 227–228° C. is obtained. Probable formula:



Example 3.—A bluish magenta image (absorption maximum at 542 m μ) is obtained by developing an exposed light-sensitive silver halide emulsion layer with the developer mentioned above and containing a color coupler prepared as follows: 26.5 g. 1-phenyl-3-amino-5-pyrazolone, 150 cc. pyridine and 24 cc. phenyl-isothiocyanate are refluxed for one hour. The reaction mixture is cooled down to 50° C., poured in one litre HCl 2N whilst stirring. The precipitate formed is filtered off, washed with water and boiled with ethyl alcohol. A product melting at 227° C. is obtained. 4.2 g. of this product are dispersed in 40 cc. chloroform. To this dispersion 0.7 cc. bromine, dissolved in 7 cc. chloroform, are slowly added. The whole dissolves. The solution is heated for half an hour on the water bath and then evaporated. The residue is dissolved in an aqueous solution of caustic soda 2N by heating for about 15 minutes on the water bath. The solution is filtered. The product dissolved is precipitated with a concentrated acetic acid solution. The precipitate is filtered with suction, washed with water, dried and dissolved in a mixture of methyl alcohol and ethyl alcohol (1/1). The solution is evaporated till crystallisation sets in. A product melting at 245–246° C. and having the following probable formula is obtained:

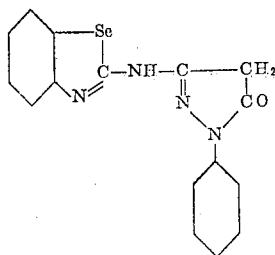


Analysis: N calculated 18.18, found 18.45 and 18.35; S calculated 10.39, found 10.20 and 10.26.

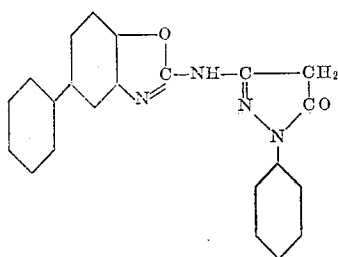
Example 4.—A bluish magenta image (absorption maximum at 556 m μ) is obtained by developing an exposed light-sensitive silver halide emulsion layer with the developer mentioned above and containing a color coupler prepared as follows: 3.5 g. 1-phenyl-3-amino-5-pyrazolone and 4.3 g. 2-chloro-benzoselenazole are melted together at 160° C. for 3 minutes. The product obtained is dissolved in ethyl alcohol. The solution is filtered. The filtrate is poured in water. The precipitate formed is dissolved in a solution

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of NaOH. The solution is filtered and acidified. The precipitate is separated by vacuum filtration, dried, dissolved in a little alcohol. The solution is treated with ether and filtered. The filtrate is treated with benzene. A product melting at 190–193° C. is obtained. Probable formula:



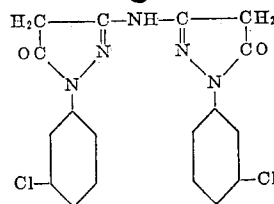
Example 5.—A magenta image (absorption maximum at 541 $m\mu$) is obtained by developing an exposed light-sensitive silver halide emulsion layer with the developer mentioned above and containing a color coupler prepared as follows: 4-hydroxy-3-amino-diphenyl is boiled with caustic potash and carbon sulphide in ethyl alcohol. The 2-mercapto-5-phenyl benzoxazole obtained after recrystallization from ethyl alcohol 50% melts at 210–212° C. This benzoxazole is heated with phosphorus pentachloride and phosphorus oxychloride on the water bath for 3 hours. The phosphorus oxychloride is distilled under reduced pressure and the residue is washed with petroleum ether and recrystallised from water-alcohol (1/1). 2.3 g. of the 5-phenyl-2-chloro-benzoxazole thus obtained and 1.75 g. 1-phenyl-3-amino-5-pyrazolone are refluxed for one hour in 10 cc. acetic acid containing 1 g. sodium acetate. The reaction mixture is poured in water. The precipitate formed is filtered off and recrystallised from ethyl alcohol. A product melting above 290° C. and corresponding to the probable formula:



is obtained.

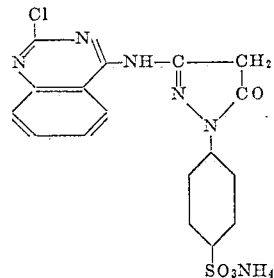
Example 6.—A bluish magenta image (absorption maximum at 563 $m\mu$) is obtained by developing an exposed light-sensitive silver halide emulsion layer with the developer mentioned above and containing a color coupler prepared as follows: 14 g. ethyl malonate mono-imido ether and 12.5 g. m-chloro-phenyl-hydrazine are heated for three hours on the water bath and 2.2 cc. methyl alcohol are added. The precipitate formed is filtered with suction, washed with methyl alcohol, dried and boiled in 350 cc. benzol. The solution is filtered and evaporated. The 1-m-chloro-phenyl-3-amino-5-pyrazolone obtained melts at 202° C. The residue on the filter after boiling with ethyl alcohol melts at 292–293° C. It is the 3-imino-bis-(1-m-chloro-phenyl-5-pyrazolone) corresponding to the probable formula:

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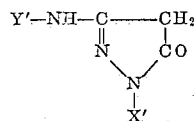
10 Analysis: N calculated 17.41, found 17.20 and 17.26; Cl calculated 17.66, found 17.23 and 17.00.

Example 7.—A bluish magenta image (absorption maximum at 557 $m\mu$) is obtained by developing an exposed light-sensitive silver halide emulsion layer with the developer mentioned above and containing a color coupler prepared as follows: 2.72 g. ammonium salt of 1-p-sulfo-phenyl-3-amino-5-pyrazolone, 2 g. 2,4-dichloro-quinazoline and 30 cc. of a mixture of ethyl alcohol and water (1/1) are heated on the water bath for 2½ hours. The reaction mixture is filtered with suction whilst yet warm, and the filtrate is cooled. The crystals formed in the filtrate are separated by filtering with suction. 1.1 g. of the desired product are thus obtained. On evaporating the last filtrate to one half its volume and filtering, further 1.5 g. are obtained. This product is a pale yellow powder. It is probably the ammonium salt of 1-p-sulfo-phenyl-3-(2'-chloro-4'-quinazolyl)-amino-5-pyrazolone corresponding to the following probable formula:



I claim:

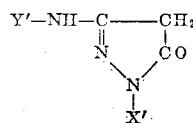
45 1. Process of color photography which comprises developing a reducible silver salt image in a photographic element by means of a primary aromatic amino developing agent in the presence of a color coupler having the following formula:



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wherein X' represents a member selected from the group consisting of hydrogen, alkyl, aryl, acyl and a heterocyclic radical, and Y' represents a radical resulting from the subtraction of a hydrogen atom from a carbon atom of a heterocyclic compound containing a nitrogen atom in the ring, said carbon atom being selected from the group consisting of the carbon atoms of the alpha and gamma position to the nitrogen atom.

2. Process of color photography which comprises developing by means of a primary aromatic amino developing agent a reducible silver salt image in a photographic element containing a color coupler having the following formula:



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