

1059,146



PATENT SPECIFICATION

NO DRAWINGS

1059,146

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Int. Cl.:—C 07 d 49/16 // G 03 c

COMPLETE SPECIFICATION

1-Aryl-3-Anilino-5-Pyrazolone Derivatives and their use in Colour Development Processes

We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America, of 343 State Street, Rochester 4, New York, United States of America, Assignees of ROBERT JOSEPH TUIITE, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention is related to colour photography and more particularly to magenta-forming couplers and their use in colour photographic development.

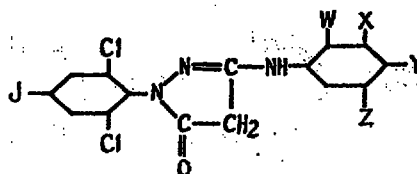
The formation of coloured photographic images by coupling oxidized primary aromatic amino developing agents imagewise with colour forming or coupling compounds is well known. In these processes, subtractive colours are usually produced and phenolic or naphtholic couplers are used to produce a cyan dye, 5-pyrazolone couplers are used to make a magenta dye, and compounds having an active methylene group separating two carbonyl groups are used to form a yellow dye.

In one well-known way of performing colour development, diffusible couplers are used in alkaline developer solutions containing primary aromatic amino colour developing agents. These solutions are used to colour develop exposed colour photographic materials which do not contain colour-forming couplers. During colour development, the coupler and developing agent diffuse into the colour photographic material with the imagewise formation of oxidized colour developer and its subsequent coupling to produce a non-diffusing dye image in the material.

It is desirable that couplers employed in colour photography should have good coupling activity, and produce dye images that have the desired spectral absorption characteristics and that have good stability on prolonged exposure to light. It is also desirable that the coupler and its reaction products do not produce yellow stain in the highlight or Dmin areas of the developed photographic materials.

Some of the magenta-forming couplers previously proposed for use have good activity and produce dyes with good absorption characteristics but the dyes do not have the desired light stability. Furthermore, the couplers may tend to produce undesirable yellow stain in the Dmin areas of the developed elements. Further, many previously described 3-anilino-5-pyrazolone magenta-forming couplers are unacceptable because of low coupling activity and undesirable spectral absorption characteristics of the dyes produced from them.

According to the present invention, there is provided a 1-aryl-3-anilino-5-pyrazolone of the following general formula:





wherein J represents chlorine, nitro or cyano, W represents hydrogen or chlorine, X represents hydrogen, cyano or nitro, Y represents hydrogen, chlorine, cyano or methylsulphonyl, and Z represents hydrogen or cyano, provided that at least one of W, X, Y and Z is not hydrogen.

We have found that couplers of this general formula have good coupling activity, do not cause a yellow stain in colour reproductions, and, on colour development, yield magenta dyes having good light stability and absorption characteristics. This combination of properties is unexpected in view of the prior art which includes descriptions of 1-aryl-3-anilino-5-pyrazolones similar to but outside the general formula of the present invention, which prior art pyrazolones do not show this combination of properties.

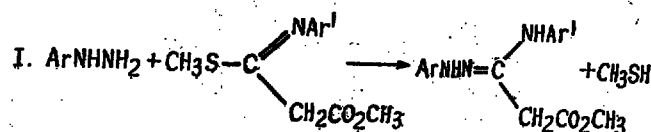
The 1-aryl-3-anilino-5-pyrazolones of the above formula are normally used in aqueous alkaline colour developer solutions containing primary aromatic amino developing agents to produce magenta dye images in imagewise exposed multicolour photographic materials.

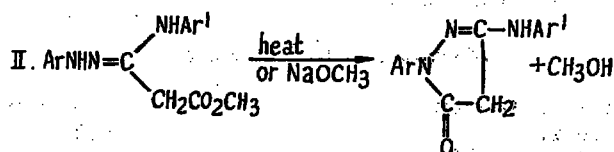
A reversal colour process well known in the art for the colour development of an imagewise exposed multilayer, multicolour photographic material comprising a support having coated thereon a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a blue-sensitive silver halide emulsion layer comprises the steps of:

- (1) developing a negative silver image in each of said silver halide emulsion layers,
- (2) washing in water,
- (3) selectively re-exposing the unexposed and undeveloped silver halide in the said red-sensitive layer,
- (4) colour developing the said re-exposed and undeveloped silver halide in said red-sensitive layer with a photographic colour developer containing a diffusible cyan-forming coupler,
- (5) washing in water,
- (6) selectively re-exposing the unexposed and undeveloped silver halide in the said blue-sensitive layer,
- (7) colour developing said re-exposed and undeveloped silver halide in said blue-sensitive layer with a photographic colour developer containing a diffusible yellow-forming coupler,
- (8) washing in water,
- (9) fogging the unexposed and undeveloped silver halide in the green-sensitive emulsion layer,
- (10) colour developing said fogged silver halide in the green-sensitive layer with a photographic colour developer containing a diffusible magenta-forming coupler,
- (11) washing in water,
- (12) bleaching to convert said silver images to silver halide,
- (13) fixing to remove silver halide,
- (14) washing in water and drying.

When performing this process in accordance with the present invention the magenta forming developer solution contains one of the 1-aryl-3-anilino-5-pyrazolone couplers of the above formula as the magenta-image-forming coupler.

The couplers of the invention are preferably prepared by a general synthesis for making 1-aryl-3-anilino-5-pyrazolone couplers. In this synthesis an arylhydrazine is mixed and heated with a methyl β -methylmercapto- β -aryliminopropionate. The reaction is believed to occur according to the following equations:





wherein Ar and Ar' are aromatic groups. This reaction can be stopped at the formation of the amide hydrazone, the product of equation I, but in general it is preferable to proceed without pause to the final cyclized 1-aryl-3-anilino-5-pyrazolone by further heating. However, when Ar is a 2,6-disubstituted phenyl group, as in the present invention, it is usually better to isolate the amide hydrazone, and cyclize in a separate step with sodium methylate. The methyl β -methylmercapto- β -aryliminopropionates used in this synthesis are prepared by a series of reactions in which ethyl acetoacetate is treated with an alkali metal methylate, such as sodium methylate, in a solvent, such as methyl alcohol, and the resulting sodio acetoacetic ester is then treated with an aryl isothiocyanate in methyl alcohol while heating.

The isothiocyanate should not be attacked irreversibly by the sodio acetoacetic ester at another substituent. The isothiocyanates used can be prepared by any of several methods, the most commonly used methods for making aryl isothiocyanates being the method described by Dyson, Organic Synthesis, Coll. Vol. 1, p. 165, and the method described by Dains, Brewster and Olander, Organic Synthesis, Coll. Vol. 1, p. 447.

Several arylhydrazines are commercially available, either as the free base or a salt. Others can be prepared by the reduction of the corresponding diazonium salts or, in the case of certain heterocyclic hydrazines, by direct replacement with hydrazine.

Included among the 1-aryl-3-anilino-5-pyrazolones of the invention are the following Couplers.

1. 1-(2,4,6-trichlorophenyl)-3-(4-methylsulphonylanilino)-5-pyrazolone
2. 1-(2,4,6-trichlorophenyl)-3-(4-cyanoanilino)-5-pyrazolone
3. 1-(2,4,6-trichlorophenyl)-3-(3-cyanoanilino)-5-pyrazolone
4. 1-(2,4,6-trichlorophenyl)-3-(2-chloro-5-cyanoanilino)-5-pyrazolone
5. 1-(2,4,6-trichlorophenyl)-3-(3-nitroanilino)-5-pyrazolone
6. 1-(2,4,6-trichlorophenyl)-3-(2,4-dichloroanilino)-5-pyrazolone
7. 1-(2,6-dichloro-4-nitrophenyl)-3-(2,4-dichloroanilino)-5-pyrazolone
8. 1-(2,6-dichloro-4-cyanophenyl)-3-(2,4-dichloroanilino)-5-pyrazolone

These and other 1-aryl-3-anilino-5-pyrazolone couplers falling within the formula of the invention may be employed in colour developing solutions to develop magenta images in light-sensitive materials (which do not contain a colour-forming coupler). Any of the well known primary aromatic amino colour-forming silver halide developing agents, such as, the phenylenediamines, e.g., N,N-diethyl-*p*-phenylenediamine hydrochloride, N-methyl-*p*-phenylenediamine hydrochloride, N,N-dimethyl-*p*-phenylenediamine hydrochloride, 2-amino-5-N,N-diethylaminotoluene hydrochloride, 2-amino-5-(N-ethyl-N-lauryl)toluene, N-ethyl- β -methanesulphonamidoethyl-3-methyl-4-aminoaniline sulphate, N-ethyl- β -methanesulphonamidoethyl-4-aminoaniline, and 4-N-ethyl-N- β -hydroxyethylamineaniline, and the *p*-aminophenols, and their substitution products when the amino group is unsubstituted may be used. As well-known in the art various other materials may be included in the developer solutions depending upon the particular requirements, for example, an alkali metal sulphite, carbonate, bisulphite, bromide or iodide.

The following Examples illustrate the results which may be obtained by performing the present invention.

EXAMPLE 1

A multilayer, multicolour photographic material comprising a support coated in succession with a red-sensitive cyan-forming silver halide emulsion layer, a green-sensitive magenta-forming silver halide emulsion layer, a yellow filter layer, and a blue-sensitive yellow-forming silver halide emulsion layer was exposed to a step wedge in a sensitometer. Pieces of this material were processed as follows: 1-minute treatment in a conventional alkali metal bisulphite-formalin prehardener, water washing, 2 1/2-minute development in a conventional *p*-methylaminophenol sulphate-hydroquinone black-and-white developer, water washing, fogging the unexposed and un-

h, washing, bleaching, fixing and washing.
The magenta colour developer solutions



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developed silver halide, 7-minute treatment in a number of magenta colour developer solutions had the general composition:

Magenta Colour Developer

Sodium hexametaphosphate	1.0 gram
Sodium sulphite	5.0 "
4-Amino-N-ethyl-N-(β-methanesulphon-amidoethyl)-m-foluidine sesqui-sulphate monohydrate	3.5 "
Trisodium phosphate	40.0 "
Potassium bromide	0.5 "
Sodium sulphate	50.0 "
Potassium iodide	.005 "
Citrazinic acid	1.5 "
Sodium thiocyanate	1.0 "
Coupler	.006 mole
Carbowax 4000	1.0 gram
Ethylenediamine sulphate	3.0 "
Water to	1.0 litre
pH adjusted to 10.8	

("Carbowax" is a registered Trade Mark).

The bleaching and fixing baths had the following compositions:

Bleach Formula

Sodium hexametaphosphate	1.0 gram
Sodium bromide	1.0 "
Sodium sulphate	150.0 "
Potassium ferricyanide	144.0 "
Water to	1.0 litre
pH 6.85	

Fixing Bath

Sodium hexametaphosphate	10.0 grams
Sodium sulphite	10.0 "
Sodium thiosulphate	320.0 "
Water to	1.0 litre
pH 7.2	

Separate pieces of the exposed multicolour photographic material were processed as described above, the magenta colour developer solution containing various magenta-forming couplers as indicated in the following table. The coupler 1-(2,4,6-trichlorophenyl)-3-(4-nitroanilino)-5-pyrazolone (claimed in Specification No. 950,676) which is not within the formula of the present invention was used as the control. The processed and dried elements were compared for yellow stain by determining the optical density in the Dmin areas with light through a blue filter having a cutoff point at 442 mμ. The optical density values of each of the processed strips were determined with light through a green filter. The strips were then exposed to a tungsten arc light for 3 days and the density values measured again with light through the green filter. The % fading of the magenta dye at a density of 1.0 and the yellow stain levels in each strip are tabulated with the magenta coupler used.



5
developer

10

15

5

10

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Coupler	Light Fade %	Yellow Stain Density	Reduction in Stain From Control
Control	38	.17	0
1	28	.11	0.06
2	32	.12	0.05
3	19	.13	0.04
4	16	.12	0.05
5	30	.12	0.05
6	20	.13	0.04
7	28	.13	0.04
8	20	.13	0.04



This table shows that the magenta dyes formed from the couplers of the invention were all more stable upon prolonged exposure to light than was the control. The yellow stain found in the Dmin areas of the processed strips was from 0.4 to 0.6 lower than the stain in the control strip. These improvements are unexpected, especially in the results from coupler 5 which is an isomer of the control coupler (that is, coupler 5 is 1-(2,4,6-trichlorophenyl)-3-(3-nitroanilino)-5-pyrazolone and the control is 1-2,4,6-trichlorophenyl)-3-(4-nitroanilino)-5-pyrazolone).

The couplers employed in Example 1 all exhibited good coupling activity, that is they formed good dye images having desirable sensitometric curves (curve relating developed dye density to log exposure).

In another test, the coupler 1-(2,4,6-trichlorophenyl)-3-anilino-5-pyrazolone which does not fall within the formula of the invention was used in the magenta developer composition described in Example 1 in the process described in Example 1. This coupler was found to have such low coupling activity that the magenta dye image formed was unusable, that is the Dmax and contrast of the dye image were too low. Similarly, other 1-aryl-3-anilino-5-pyrazolone couplers outside the formula of the invention have been found to have such low coupling activities that they cannot be used as desired for developing magenta dye images.

As stated above, the couplers are intended for use in reversal colour processes in which the coupler is incorporated in the developing solution such as those described in Specifications Nos. 447,092 and 507,841.

EXAMPLE 2

Two multilayer, multicolour photographic materials of the type employed in Example 1 were exposed as in Example 1 and given the reversal colour process described previously. This process included the steps: treatment in a conventional alkali metal bisulphite formalin prehardener, water washing, development in a conventional *p*-methylaminophenol sulphate-hydroquinone black and white developer, water washing, selective re-exposure of the red-sensitive layer with red light, treatment with an aqueous alkaline cyan developer solution containing a cyan-forming coupler and a primary aromatic amino developing agent, water washing, selective re-exposure of the blue-sensitive layer, treatment with an aqueous alkaline yellow developer solution containing a yellow-forming coupler and a primary aromatic amino developing agent, water washing, fogging the unexposed silver halide in the green-sensitive layer, treatment with an aqueous alkaline magenta developer solution containing a magenta-forming coupler and a primary aromatic amino developing agent, water washing, bleaching, fixing, water washing and drying. The magenta developer for one of the exposed photographic materials contained the control coupler 1-(2,4,6-trichlorophenyl)-3-(4-nitroanilino)-5-pyrazolone, the magenta developer for the second material contained coupler 5 in place of the control coupler. The processed strips were compared as in Example 1. The material containing dye from coupler 5 showed lower magenta dye fading upon exposure to light and about 30% less yellow stain in the Dmin area than did the control element.

Similarly, it can be shown that other couplers of the present invention give similar advantages over the control coupler. These advantages are not affected by the particular cyan and yellow dyes employed so that any desired cyan or yellow



forming coupler can be used in the reversal colour process of the invention as long as a magenta forming coupler of the invention is used.

The numbered couplers listed above may be prepared by the following procedures.

Coupler 1 may be prepared as follows. To a methanolic solution of sodium methoxide prepared from 2.3 grams (0.10 gram-atom) of sodium metal in 150 mls. of dry methanol were added 13 grams (0.10 mole) of acetoacetic ester. The solution was refluxed for 20 minutes, cooled slightly, and 19.3 grams (0.10 mole) of 4-methylsulphonylphenylisothiocyanate were added. The solution was refluxed for 5 minutes, cooled to 20° C. and 7 mls. (slight excess) of methyl iodide added. The solution was allowed to warm up to room temperature during 15 minutes, then was refluxed for 15—60 minutes. The solution was cooled slightly, 21.1 grams (0.10 mole) of 2,4,6-trichlorophenylhydrazine were added, and the solution was refluxed for 22 hours. The reaction mixture was cooled, the precipitated amide hydrazone was separated by filtration, washed well with methanol and dried.

The amide hydrazone (44.8 grams, 0.10 mole) was added to a solution of 10.8 grams (0.20 mole) of sodium methoxide in 350 mls. of methanol. The mixture was refluxed for about 1 hour (30—45 minutes after solution was obtained), cooled, 350 mls. of water added, and the solution acidified with acetic acid. The precipitate was separated by filtration, washed with water, and dried. After recrystallization from acetonitrile, the coupler 1 had a melting point of 267—269° C.

Coupler 2 was prepared by the method used to make coupler 1, except that 16.0 grams (0.10 mole) of 4-cyanophenylisothiocyanate were used in place of 4-methylsulphonylphenylisothiocyanate to make the amide hydrazone. The amide hydrazone, 40—45% yield, m.p. 206—208° C., was then cyclized to form the coupler which was recrystallized from acetic acid and dioxane to give a product with a melting point of 299—303° C.

Coupler 3 was prepared by the method used to make coupler 1 except that 16.0 grams (0.10 mole) of 3-cyanophenylisothiocyanate were used in place of 4-methylsulphonylphenylisothiocyanate to make the amide hydrazone. The cyclized coupler after recrystallization from dimethylacetamide and ethanol had a melting point of 290—292° C. (dec.).

Coupler 4 was prepared by the method used to make coupler 1 employing 19.5 grams (0.10 mole) of 2-chloro-5-cyanophenylisothiocyanate in place of 4-methylsulphonylphenylisothiocyanate to make the amide hydrazone. The coupler made by cyclization of the amide hydrazone was recrystallized from acetic acid to give a product with a melting point of 259—262° C. (dec.).

Coupler 5 was prepared by the method used to make coupler 1 employing 18.0 grams (0.10 mole) of 3-nitrophenylisothiocyanate in the reaction to make the amide hydrazone. The coupler made from the cyclization of the amide hydrazone was recrystallized from methanol to give a product melting at 250—251° C.

Coupler 6 was prepared by the method used for coupler 1 employing 20.4 grams (0.10 mole) of 2,4-dichlorophenylisothiocyanate and the final period of reflux was 72—96 hours. The reaction mixture was then filtered to remove a small amount of by-product (apparently the hydrazide formed by reaction of the uncyclized amide hydrazone and excess hydrazine). The filtrate was then added to a solution of 2 parts by weight of sodium methoxide in methanol, refluxed for 30 min. and an equal volume of water added. The reaction mixture was then extracted with ether to remove some dark tarry material. The aqueous solution was acidified with acetic acid, and the precipitate was separated by filtration, washed well with water, and dried. After three recrystallizations from acetonitrile there was obtained a 24% yield of product; m.p. 197—201° C.

Coupler 7 was prepared by the method used for coupler 1 employing equivalent amounts of 2,4-dichlorophenylisothiocyanate and 2,6-dichloro-4-cyanophenylhydrazine. The cyclized coupler was recrystallized from glacial acetic acid to yield the product; m.p. 229—231° C. (dec.).

Coupler 8 was prepared by the method used for coupler 1 employing equivalent amounts of 2,4-dichlorophenylisothiocyanate and 2,6-dichloro-4-cyanophenylhydrazine. The cyclized coupler was recrystallized from glacial acetic acid to yield the product; m.p. 258—261° C. (dec.).

The arylisothiocyanates used were prepared by reaction of the appropriate amine with thiophosgene in an aqueous suspension. The procedure included the use of high-speed stirring in a Morton flask, thus eliminating the need for an organic solvent.

nitrophenylhydrazine

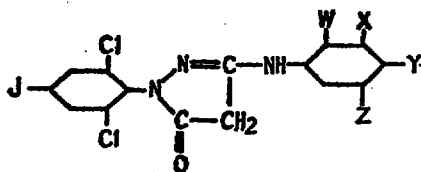
Consistently higher yields than are reported in the literature were obtained by this revised procedure. Most of these compounds have been described in the literature, for example, 4-methylsulphonylphenylisothiocyanate (L. Doub et al, J.A.C.S., 80, 2205 (1958)), 4-cyanophenylisothiocyanate (G.M. Dyson et al, J. Chem. Soc. 1927, 436), 2-chloro-5-cyanophenylisothiocyanate (Amine; J. J. Blanksma et al, Rec. Trav. Chim., 66, 365 (1947)), 3-nitrophenylisothiocyanate (G.M. Dyson et al, J. Chem. Soc., 125, 1702 (1924)), and 2,4-dichlorophenylisothiocyanate (G.M. Dyson et al, J. Chem. Soc., 1926, 3041). The 3-cyanophenylisothiocyanate had a melting point of 65.5—69° C.

2,4,6-Trichlorophenylhydrazine is available commercially. 2,6-Dichloro-4-nitrophenylhydrazine is prepared by chlorinating 4-nitroaniline by a conventional reaction then diazotizing the 2,6-dichloro-4-nitroaniline with nitrosyl sulphuric acid at 40° C. and reducing the diazo compound to the corresponding hydrazine compound by treating it with stannous chloride and hydrochloric acid. 2,6-Dichloro-4-cyanophenylhydrazine is prepared by chlorinating 4-cyanoaniline, diazotizing the amine with isoamyl nitrite at 0° C. and then reducing the diazo compound to the hydrazine derivative as described above.

The 1-aryl-3-anilino-5-pyrazolone couplers of the invention are valuable for use in colour photography, and are distinguished from other 1-aryl-3-anilino-5-pyrazolone couplers by having good coupling reactivity. They are further distinguished from other 1-aryl-3-anilino-5-pyrazolone couplers by producing up to 35.3% less yellow stain in Dmin areas of photographic materials processed through them. Finally, the magenta image dyes formed by the couplers have unexpectedly better light stability than couplers outside the invention.

WHAT WE CLAIM IS:—

1. A 1-aryl-3-anilino-5-pyrazolone of the following general formula:



wherein J represents chlorine, nitro or cyano, W represents hydrogen or chlorine, X represents hydrogen, cyano or nitro, Y represents hydrogen, chlorine, cyano or methylsulphonyl, and Z represents hydrogen or cyano, provided that at least one of W, X, Y and Z is not hydrogen.

2. A compound as claimed in Claim 1, being one of Couplers 1 to 8 hereinbefore listed.

3. An aqueous alkaline magenta forming colour developer solution containing a primary aromatic amino developing agent and a 1-aryl-3-anilino-5-pyrazolone according to either Claim 1 or 2.

4. A colour developer solution as claimed in Claim 3, in which the developing agent is 4-amino-N-ethyl-N-(β-methane sulphonamidoethyl)-*m*-toluidine sesquisulphate monohydrate.

5. A method of producing a magenta image in an exposed photographic silver halide emulsion layer which comprises treating the layer with an aqueous alkaline developing solution containing a primary aromatic amino developing agent, in the presence of a 1-aryl-3-anilino-5-pyrazolone according to either Claim 1 or 2.

6. A photographic reversal colour process which comprises subjecting an image-wise exposed photographic material comprising a support bearing three silver halide emulsion layers, respectively sensitive to red, green and blue light, to the following steps:

- (1) developing a negative silver image in each of the emulsion layers;
- (2) washing the material in water;
- (3) selectively re-exposing the unexposed and undeveloped silver halide grains in the red-sensitive layer;
- (4) colour developing the re-exposed silver halide grains in the red-sensitive layer with a photographic colour developer containing a diffusible cyan-forming coupler;
- (5) washing the material in water;
- (6) selectively re-exposing the unexposed and undeveloped silver halide grains in the blue-sensitive layer,

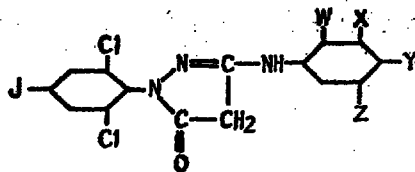
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2,4,6-Trichlorophenylhydrazine is available commercially. 2,6-Dichloro-4-nitrophenylhydrazine is prepared by chlorinating 4-nitroaniline by a conventional reaction then diazotizing the 2,6-dichloro-4-nitroaniline with nitrosyl sulphuric acid at 40° C. and reducing the diazo compound to the corresponding hydrazine compound by treating it with stannous chloride and hydrochloric acid. 2,6-Dichloro-4-cyanophenylhydrazine is prepared by chlorinating 4-cyanoaniline, diazotizing the amine with isoamyl nitrite at 0° C. and then reducing the diazo compound to the hydrazine derivative as described above.

The 1-aryl-3-anilino-5-pyrazolone couplers of the invention are valuable for use in colour photography, and are distinguished from other 1-aryl-3-anilino-5-pyrazolone couplers by having good coupling reactivity. They are further distinguished from other 1-aryl-3-anilino-5-pyrazolone couplers by producing up to 35.3% less yellow stain in Dmin areas of photographic materials processed through them. Finally, the magenta image dyes formed by the couplers have unexpectedly better light stability than couplers outside the invention.

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1. A 1-aryl-3-anilino-5-pyrazolone of the following general formula:



wherein J represents chlorine, nitro or cyano, W represents hydrogen or chlorine, X represents hydrogen, cyano or nitro, Y represents hydrogen, chlorine, cyano or methylsulphonyl, and Z represents hydrogen or cyano, provided that at least one of W, X, Y and Z is not hydrogen.

2. A compound as claimed in Claim 1, being one of Couplers 1 to 8 hereinbefore listed.

3. An aqueous alkaline magenta forming colour developer solution containing a primary aromatic amino developing agent and a 1-aryl-3-anilino-5-pyrazolone according to either Claim 1 or 2.

4. A colour developer solution as claimed in Claim 3, in which the developing agent is 4-amino-N-ethyl-N-(β-methane sulphonamidoethyl)-m-toluidine sesquisulphate monohydrate.

5. A method of producing a magenta image in an exposed photographic silver halide emulsion layer which comprises treating the layer with an aqueous alkaline developing solution containing a primary aromatic amino developing agent, in the presence of a 1-aryl-3-anilino-5-pyrazolone according to either Claim 1 or 2.

6. A photographic reversal colour process which comprises subjecting an image-wise exposed photographic material comprising a support bearing three silver halide emulsion layers, respectively sensitive to red, green and blue light, to the following steps:

- (1) developing a negative silver image in each of the emulsion layers;
- (2) washing the material in water;
- (3) selectively re-exposing the unexposed and undeveloped silver halide grains in the red-sensitive layer;
- (4) colour developing the re-exposed silver halide grains in the red-sensitive layer with a photographic colour developer containing a diffusible cyan-forming coupler;
- (5) washing the material in water;
- (6) selectively re-exposing the unexposed and undeveloped silver halide grains in the blue-sensitive layer,



- (7) colour developing the re-exposed silver halide grains in the blue-sensitive layer with a photographic colour developer containing a diffusible yellow forming coupler,
- 5 (8) washing the material in water,
- (9) fogging the unexposed and undeveloped silver halide grains in the green-sensitive silver halide emulsion layer,
- (10) colour developing the said fogged silver halide grains with a photographic colour developer containing a diffusible magenta-forming coupler being a solution according to either Claim 3 or 4;
- 10 (11) washing the material in water;
- (12) bleaching to convert said silver images to silver halide;
- (13) fixing to remove silver halide,
- (14) washing in water and drying.
- 15 7. An aqueous alkaline colour developing solution according to Claim 3 containing any component in any quantity as hereinbefore described.
8. A photographic colour development process according to Claim 5 employing any procedural detail hereinbefore specified.
9. A process of preparing a 1-aryl-3-anilino-5-pyrazolone according to either Claim 1 or 2, substantially as hereinbefore described.

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