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COLOR PHOTOGRAPHY UTILIZING 1-FLUOROALKYL - 2 - PYRAZOLINE - 5 - ONE COLOUR COUPLERS

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Int. Cl. G03c 7/32
U.S. Cl. 96—56.5 8 Claims

ABSTRACT OF THE DISCLOSURE

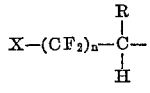
Color couplers of the 2-pyrazoline-5-one and bis(2-pyrazoline-5-one) type, which form azomethine dyestuffs when reacted with the oxidation product of aromatic primary amines, are disclosed. These color couplers contain a fluoroalkyl radical at the 1-position, and are capable of forming dyestuffs of unusually good light stability. The color couplers can be employed in photographic emulsions for use in photographic elements, particularly multi-layer photographic materials containing at least one green-sensitized silver halide emulsion layer. In such multi-layer materials, the silver halide layer and the color couplers cooperate to produce a magenta-colored photographic image upon exposure and color development.

This invention relates to 1-fluoroalkyl-2-pyrazoline-5-one colour couplers, to the preparation thereof, to photographic materials and developing compositions containing such colour couplers as well as to colour development processes wherein said colour couplers take part in the formation of a dyestuff image.

For improving the quality of photographic colour images there is a need for colour couplers yielding more light-stable dyes.

According to the present invention we provide 1-fluoroalkyl-2-pyrazoline-5-one colour couplers, which yield in the silver halide photographic process on colour development with aromatic primary amine developing agents azomethine dyes having an improved light-stability.

Especially good results are obtained with 2-pyrazoline-5-one colour couplers containing in the 1-position a fluoro-alkyl radical of the following structure:



wherein:

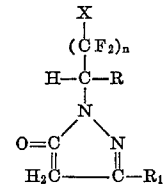
X represents a hydrogen atom or a fluorine atom,

R represents a hydrogen atom, an alkyl radical or an aryl radical, and

n represents a positive integer from 1 to 10 inclusive.

By 2-pyrazoline-5-one compounds there is not only meant the simple 2-pyrazoline-5-one compounds but also the bis-2-pyrazoline-5-one compounds, the pyrazoline nuceli of which are joined in the 4-position by a bivalent radical (cf. Pierre Glafkides, Photographic Chemistry, vol. II, Fontain Press, London (1960), p. 602).

More particularly we provide colour couplers corresponding to the general formula given below and bis-2-pyrazoline-5-one compounds derived therefrom by linking the 2-pyrazoline-5-one nuclei in the 4-position by means of a —CH_2— group.

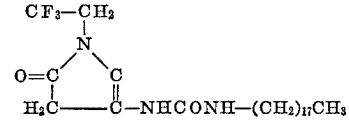


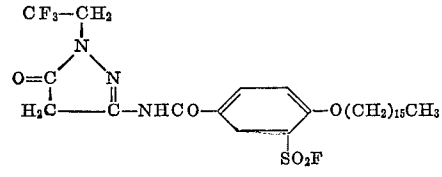
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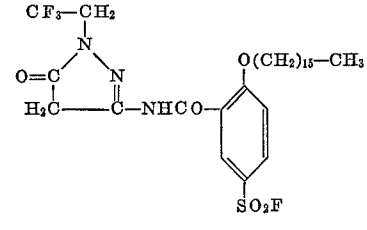
X, R and *n* have the same significance as set forth above, and

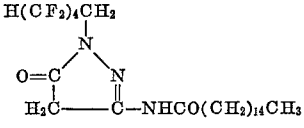
R_1 represents an alkyl radical, an aryl radical, a heterocyclic radical, a —NH-aryl radical, a —NHCO-alkyl radical, a —NHCO-aryl radical, a —NHCONH-alkyl radical or a —NHCONH-aryl radical, which radicals may be further substituted e.g. by a radical rendering the molecule fast to diffusion or by a group containing the latter radical, which is preferably an aliphatic radical containing from 5 to 20 carbon atoms in straight line.

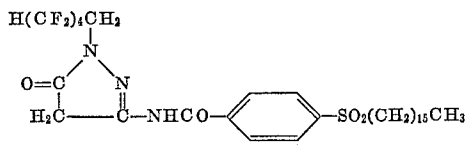
The following is a list of structural formulae of colour couplers according to the present invention:

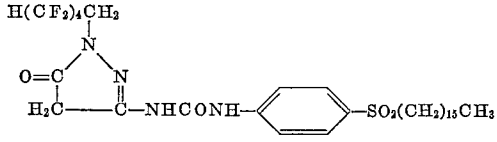
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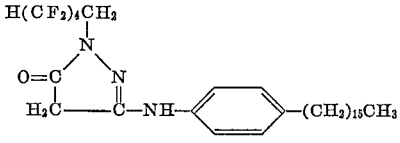
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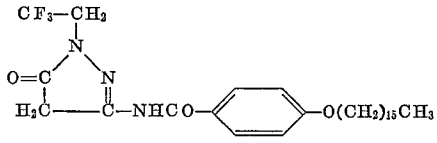
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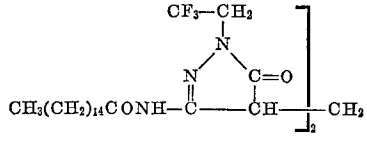
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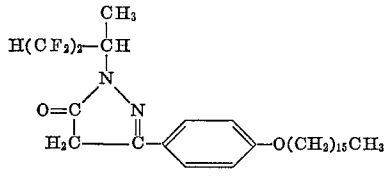
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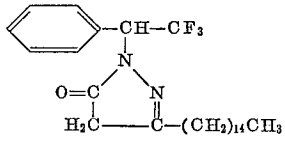
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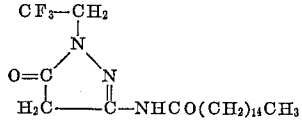
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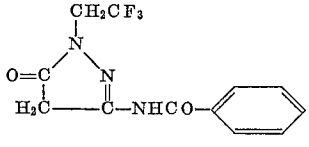
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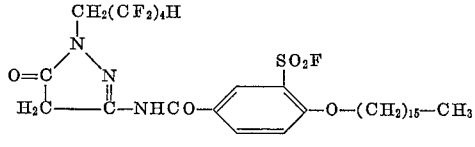
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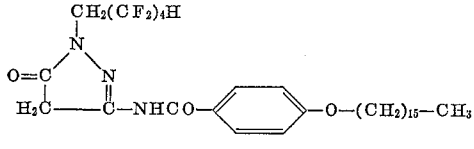
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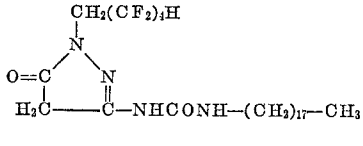
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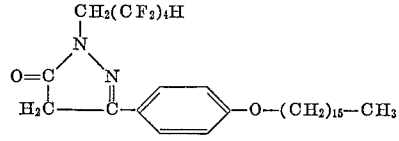
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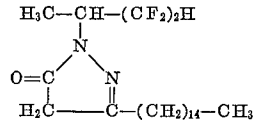
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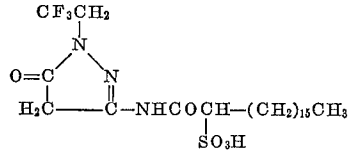
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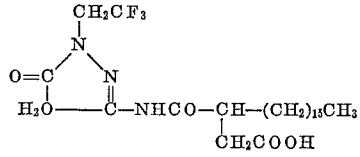
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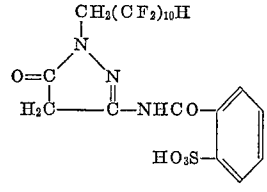
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The following description illustrates the preparation of colour couplers according to the present invention.

Preparation 1

The colour coupler 1-(2,2,2-trifluoro-ethyl)-3-(3-octadecyl-ureido)-2-pyrazoline-5-one having Formula 1 of the above list, is prepared according to the following steps:

(a) 114 g. of (2,2,2-trifluoro-ethyl)-hydrazine prepared as described in U.S. patent application Ser. No. 471,437 filed July 12, 1965, for "Fluoro-alkylhydrazines and process for the preparation thereof" and 159.5 g. of ethyl-β-ethoxy-β-iminopropionate are mixed in the presence of 2 cm.^{3} of acetic acid. The temperature of the reaction mixture rises to 45° C. After 1 hour a solid product precipitates. The reaction mixture is allowed to stand overnight, then the solid product is collected. It is recrystallized from a mixture of isopropyl ether and methyl acetate (50:50) yielding 1-(2,2,2-trifluoro-ethyl)-3-amino-2-pyrazoline-5-one as white crystals melting at 198° C.

(b) 18.1 g. of said pyrazoline compound and 29.5 g. of octadecyl isocyanate are allowed to react at 36° C. in 100 cm.^{3} of methylene chloride in the presence of 26.7 g. of aluminum chloride (this method is described in U.S. patent application No. 314,594).

After being washed with water the reaction product is recrystallized from methanol. The colour coupler is a white product melting at 147–148° C.

Preparation 2

The colour coupler 1-(2,2,2-trifluoro-ethyl)-3-(3-fluorosulphonyl-4-hexadecyloxybenzamido) - 2 - pyrazoline-5-one having Formula 2 of the above list is prepared as follows:

46.15 g. of m-fluorosulphonyl-p-hexadecyloxy-benzoyl chloride (prepared as described in U.S. patent application No. 381,230) is condensed with 18.1 g. of 1-(2,2,2-trifluoroethyl) - 3 - amino - 2 - pyrazoline-5-one (see Prepa-

ration 1) at 33° C. in 100 cm.³ of methylene chloride in the presence of 26.7 g. of aluminum chloride.

After being subsequently washed with water and methanol, the product obtained is recrystallized from ethanol. Melting point: 195–7° C.

Preparation 3

The colour coupler 1-(2,2,2-trifluoro-ethyl)-3-(2-hexadecyloxy-5-fluorosulphonylbenzamido) - 2 - pyrazoline-5-one having Formula 3 of the above list is prepared as follows:

(a) o-Hexadecyloxy-benzaldehyde is prepared by refluxing equimolecular amounts of salicyl aldehyde, hexadecyl bromide and sodium hydroxide in ethylene glycol monomethyl ether. On pouring the reaction mixture into methanol a white product precipitates. Melting point: 43–45° C.

(b) o-Hexadecyloxy-benzoic acid is prepared as follows: To a solution of 273 g. of o-hexadecyloxy-benzaldehyde in 1500 cm.³ of acetone are dropwise added at room temperature 261 g. of potassium permanganate dissolved in a mixture of 1100 cm.³ of acetone and 400 cm.³ of water. Thereupon the reaction mixture is refluxed for 30 min. The acetone is distilled off and sulphur dioxide is led through the solution until discolouration of the mixture. At 60° C. the reaction product separates as a supernatant oily layer which is collected and washed with water. After having dried and recrystallized it from n-hexane, o-hexadecyloxy-benzoic acid is obtained as a white product melting at 59° C.

(c) 3 - sulpho - 6 - hexadecyloxy - benzoic acid is prepared in the same way as 3-sulpho-4-hexadecyloxy-benzoic acid described in U.S. patent application No. 381,230.

(d) 3 - chlorosulphonyl - 6 - hexadecyloxy - benzoic acid is prepared analogously to 3-chlorosulphonyl-4-hexadecyloxy-benzoic acid described in said U.S. patent application 381,230. Melting point: 97° C.

(e) 3 - fluorosulphonyl - 6 - hexadecyloxy - benzoic acid is prepared analogously to 3-fluorosulphonyl-4-hexadecyloxy-benzoic acid described in said U.S. patent application 381,230 starting from the chlorosulphonyl compound. Melting point: 106° C.

(f) 3 - fluorosulphonyl - 6 - hexadecyloxy - benzoyl chloride is prepared analogously to 3-fluorosulphonyl-4 hexadecyloxy-benzoyl chloride described in U.S. patent application 381,260. Melting point: 31° C.

(g) The colour coupler of Formula 3 is obtained by allowing to react 9.05 g. of 1-(2,2,2-trifluoroethyl)-3-amino-2-pyrazolidine-5-one and 23.08 g. of 3-fluorosulphonyl-6-hexadecyl-benzoyl chloride for 2 h at reflux temperature in 50 cm.³ of acetonitrile. The precipitate formed on adding to water is recrystallized from n-hexane and isopropyl ether (50:50). Melting point: 110–112° C.

Preparation 4

The colour coupler 1-(2,2,3,3,4,4,5,5-octafluoropentyl) 3-pentadecylamido-2-pyrazoline-5-one having Formula 4 of the above list is prepared as follows:

(a) 24.6 g. (2,2,3,3,4,4,5,5-octafluoropentyl)-hydrazine (prepared as described in U.S. patent application Ser. No. 471,437 filed July 12, 1965, for "Fluoro-alkyl hydrazines and process for the preparation thereof") and 15.9 g. of ethyl - β - ethoxy - β - iminopropionate are mixed together with 0.5 cm.³ of acetic acid. The temperature of the reaction mixture rises to 42° C. After standing overnight at room temperature, the formed precipitate is sucked off, washed with isopropyl ether and recrystallized from a mixture of isopropyl ether and benzene. The 1-(2,2,3,3,4,4,5,5-octafluoropentyl)-3-amino - 2 - pyrazoline - 5 - one obtained melts at 101° C.

(b) By allowing to react at 50° C. 9.39 g. of 1-(2,2,3,3,4,4,5,5 - octafluoropentyl) - 3 - amino - 2 - pyrazoline 5-one and 8.25 g. of palmitoyl chloride in 30 cm.³ of nitrobenzene in the presence of 8.01 g. of aluminum chloride. The crude colour coupler obtained is subsequently washed with water and methanol and recrystallized from acetonitrile. Melting point: 118° C.

Preparation 5

The colour coupler 1-(2,2,3,3,4,4,5,5-octafluoropentyl) 3 - (p - hexadecylsulphonylbenzamido) - 2 - pyrazoline-5-one having formula 5 of the above list is prepared according to the following steps:

(a) p-Hexadecylthio-benzoic acid is prepared as follows: p-mercaptobenzoic acid (J. Am. Chem. Soc. 78, (1956) 89) and hexadecylbromide are allowed to react in boiling ethylene glycol monomethyl ether while adding 2 equivalents of sodium hydroxide. The collected precipitate is boiled in acetic acid and recrystallized from ethanol. The crystalline product melts at 111° C.

(b) p-Hexadecylsulphonyl-benzoic acid is prepared by oxidizing p-hexadecylthio-benzoic acid with 30% hydrogen peroxide in acetic acid medium at a temperature of 90° C. The reaction mixture is poured out into water and the precipitate is recrystallized from ethanol. Melting point: 166° C.

(c) p-Hexadecylsulphonyl-benzoyl chloride is obtained by allowing p-hexadecylsulphonyl-benzoic acid to react with thionyl chloride. After having distilled off the excess of thionyl chloride, the residue left is recrystallized from n-hexane. Melting point: 69° C.

(d) The colour coupler is obtained according to the method described in U.S. patent application 314,594 by allowing to react in 40 cm.³ of nitrobenzene at 80° C. 12.5 g. of 1-(2,2,3,3,4,4,5,5-octafluoropentyl)-3-amino-2-pyrazoline-5-one and 17.14 g. of p-hexadecyl-sulphonyl benzoyl chloride in the presence of 16.02 g. of aluminium chloride. After having washed the reaction product obtained with water and methanol, it is recrystallized from methyl acetate. A white crystalline product melting at 187° C. is obtained.

Preparation 6

The colour coupler 1-(2,2,3,3,4,4,5,5-octafluoropentyl) 3 - [3 - (p - hexadecyl - sulphonyl]phenyl) - ureido] - 2-pyrazoline-5-one having Formula 6 of the above list prepared as follows:

(a) p-Hexadecyl sulphonyl phenyl isocyanate is prepared by allowing to react at 50° C. p-hexadecyl sulphonyl aniline in ethyl acetate and an excess of phosgene. After the evaporation of the solvent, the reaction product is recrystallized from n-hexane. Melting point: 90° C.

(b) The colour coupler is obtained according to the method described in U.S. patent application 314,594 by allowing to react in 30 cm.³ of nitrobenzene at 87° C. and in the presence of 12.02 g. of aluminum chloride, 12.21 g. of p-hexadecyl sulphonyl isocyanate and 9.39 g. of 1-(2,2,3,3,4,4,5,5 - octafluoropentyl) - 3 - amino - 2 - pyrazoline-5-one.

The crude colour coupler is washed with water and recrystallized from methanol. Melting point: 174° C.

Preparation 7

The colour coupler 1-(2,2,3,3,4,4,5,5-octafluoropentyl) 3 - (p - hexadecylanilino) - 2 - pyrazoline - 5 - one having Formula 7 of the above list as follows:

Equimolar amounts of 1-(2,2,3,3,4,4,5,5-octafluoropentyl)-3-amino-2-pyrazoline-5-one and p-hexadecyl aniline (Chem. Abst. 55 (1961) 426) are refluxed in acetic acid medium. After having poured the reaction mixture into water, the precipitated solid product is collected and subsequently recrystallized from acetonitrile and methanol. Melting point: 125° C.

Preparation 8

The colour coupler 1-(2,2,2-trifluoro-ethyl)-3-(p-hexadecyloxy-benzamido)-2-pyrazoline-5-one having Formula 8 of the above list is prepared as follows:

38.05 g. of p-hexadecycloxy benzoyl chloride (United Kingdom patent specification 808,276) is condensed at 36° C. with 18.1 g. of 1-(2,2,2-trifluoroethyl)-3-amino-2-pyrazoline-5-one in 200 cm.³ of methylene chloride in the presence of 26.7 g. of aluminium chloride.

The condensation product obtained is washed with water and methanol and recrystallized from ethylene glycol monomethyl ether. Melting point: 226–228° C.

Preparation 9

The colour coupler 4.4'-{methylene-bis[1-(2,2,2-trifluoroethyl) - 3 - pentadecylamido - 2 - pyrazoline - 5-one]}having Formula 9 of the above list is prepared analogously to the method described in the United States Patent 2,294,909 starting from a mixture of 4.23 g. of 1-(2,2,2-trifluoroethyl)-3-palmitoyl-amino-2-pyrazoline-5-one, 0.5 cm.³ of a 40% aqueous formaldehyde solution and 0.4 cm.³ of piperidine in 15 cm.³ of dry ethanol. The solid product obtained is recrystallized from ethanol and dried. Melting point: 75° C.

Preparation 10

The colour coupler 1-(1-methyl-2,2,3,3-tetrafluoropropyl) - 3 - (p - hexadecycloxyphenyl) - 2 - pyrazoline-5-one having Formula 10 of the above list is prepared by allowing to react for 5 min. at reflux temperature: 4.8 g. of 2,2,3,3-tetrafluoro-1-methylpropyl hydrazine and 12.54 g. of p-hexadecycloxy-benzoyl acetic acid methyl ester (described in United Kingdom patent specification 808,276) in 15 cm.³ of acetic acid. After having cooled the precipitate formed, it is collected and recrystallized from isopropylether. Melting point: 110° C.

Preparation 11

The colour coupler 1-(-α-trifluoro-methyl-benzyl)-3-pentadecyl-2-pyrazoline-5-one having Formula 11 of the above list is prepared by allowing to react for 5 min. at reflux temperature: 5.7 g. of (α-trifluoromethyl-benzyl)-hydrazine and 9.36 g. of palmitoyl acetic acid methyl ester in 15 cm.³ of acetic acid. After having cooled the precipitate formed, it is collected and recrystallized from 95% aqueous methanol. Melting point: 15° C.

Preparation 12

The colour coupler 1-(2,2,2-trifluoro-ethyl)-3-pentadecylamido-2-pyrazoline-5-one having Formula 12 of the above list is prepared analogously to the method of U.S. patent application No. 314,594 by condensing at 36° C./8.1 g. of 1-(2,2,2-trifluoro-ethyl)-3-amino-2-pyrazoline-5-one with 27.48 g. of palmitoyl chloride in 100 cm.³ of methylene chloride in the presence of 26.7 g. of aluminium chloride. The product obtained is washed with water and methanol and recrystallized from isopropyl ether. Melting point: 102° C.

Preparation 13

The colour coupler 1-(2,2,2-trifluoro-ethyl)-3-benzamido-2-pyrazoline-5-one having Formula 13 of the above list is prepared as follows: 18.1 g. of 1-(2,2,2-trifluoro-ethyl)-3-amino-2-pyrazoline-5-one and 14.05 g. of benzoyl chloride in 100 cm.³ of anhydrous acetonitrile are refluxed for 2 hours while stirring. The mixture is allowed to stand overnight at room temperature. Then 5 cm.³ of water are added and the precipitate formed is sucked off and washed with methyl acetate. The white product melts at 265° C.

Preparation 14

The colour coupler 1-(1H,1H,11H-eicosafluoro-undecyl)-3-(o-sulphobenzamido)-2-pyrazoline-5-one having Formula 21 of the above list is prepared as follows:

(a) 133.7 g. of 1H,1H,11H-eicosafluoro-1-undecylhydrazine (prepared as described in U.S. patent application Ser. No. 471,437 filed July 12, 1965, for: "Fluoroalkyl-hydrazines and process for the preparation thereof") and 40 g. of ethyl β-ethoxy-β-iminopropionate are dissolved in 70 ml. methanol and 0.75 ml. of acetic acid is added. The reaction temperature rises to 35° C. and the mixture is kept overnight at room temperature. The solidified reaction mixture is treated with 140 ml. of isopropylether, sucked off and the product washed with isopropyl ether. The 1-(1H,1H,11H-eicosafluoro-undecycl) - 3 - amino-2-pyrazoline-5-one obtained melts at 160° C.

(b) 11.9 g. of the above described product and 4 g. of o-sulphobenzoic anhydride are refluxed in 40 cm.³ of acetonitrile. After a few minutes a white product precipitates that is separated and washed with hot acetonitrile. Melting point: above 260° C.

The pyrazoline colour couplers according to the present invention containing a sulfonylfluoride radical can be allowed to react with alkali for transformation into the corresponding sulfonic acid derivatives, which without separation from the saponifying medium may be added to the emulsion. For that purpose, preferably 1 mol of sulfonylfluoride derivative is dissolved in an aqueous solution of 3 mol of sodium hydroxide whereupon the resulting clear solution is added to the silver halide emulsion as a 5 or 10% aqueous solution. The emulsion preferably is neutralized with diluted sulphonic acid.

For manufacturing an appropriate photographic multilayer colour material containing colour couplers for each colour separation image in the differently optically sensitized silver halide emulsion layers, the colour couplers ought to be present in the hydrophilic silver halide emulsion layers in a non-migratory form. This object can be accomplished e.g. by the use of a sufficiently water-soluble colour coupler comprising an organic radical which is sufficiently large to prevent the colour coupler from diffusing in the hydrophilic silver halide emulsion layer, or by the utilization of a lipophilic colour coupler, which in dissolved state in a high-boiling organic solvent is dispersed in the silver halide emulsion layer.

In the preparation of a light-sensitive colour material wherein non-migratory colour couplers are used these colour couplers are mixed homogeneously with the light-sensitive silver halide emulsion preferably immediately before the coating of the emulsion. They may also be added to the composition of a water-permeable non-light-sensitive layer, which is in direct contact with the light-sensitive silver halide emulsion layer, or they may be incorporated into a non-light-sensitive layer, which is separated from the light-sensitive layer by a water-permeable non-light-sensitive layer. The silver halide emulsion contains the usual colloids such as gelatin, poly(vinyl alcohol), collodion or other suitable natural or synthetic colloids. The photographic emulsion may further contain usual ingredients such as hardeners, chemical sensitizing agents, optical sensitizing agents, plasticizers, development accelerators, stabilizing agents and wetting agents.

The non-migratory colour couplers for magenta described in the present invention usually are added in dissolved form to a green-sensitive silver halide emulsion. According to a common procedure in the art this silver halide emulsion is coated as the second colour coupler containing layer of a photographic multilayer colour material. Such photographic multilayer colour material usually consists in the given sequence of a support, a red-sensitized silver halide emulsion layer with a colour coupler for cyan, a green-sensitized silver halide emulsion layer with a colour coupler for magenta and a blue-sensitive silver halide emulsion layer with a colour coupler for yellow. The support of this multilayer material may consist of paper, glass, cellulose nitrate, a cellulose ester such as cellulose triacetate, polyester, polystyrene or another synthetic or natural resin.

A yellow filter layer generally comprising colloidal silver dispersed in gelatin is provided usually between the silver halide emulsion layer containing a colour coupler for yellow and the green-sensitized silver halide emulsion layer.

The colour couplers for magenta according to the present invention may also be applied in so-called "droplet emulsions" (cf. U.S. patent specification 2,304,940) and if they are sufficiently soluble in an aqueous alkaline solution, they may be applied to the developing bath; an example of a colour coupler according to the present invention which can be applied to the developing bath is the colour coupler according to Formula 13.

For the production of photographic colour images according to the present invention an exposed silver halide emulsion layer is developed preferably with an aromatic primary amino developing substance in the presence of a colour coupler for magenta according to the present invention.

All colour developing agents capable of forming azomethine dyes can be utilized as developers. Aromatic primary amino compounds such as p-phenylenediamine and derivatives such as N-diethyl-p-phenylenediamine, N,N-diethyl-sulphomethyl-p-phenylenediamine and N,N-diethyl - N' - carboxymethyl-p-phenylenediamine are commonly used.

By varying the substituents, e.g. the substituent in 3-position, colour couplers can be obtained, which can yield azomethine dyes, some of which are suited for negative material and some others for positive material.

The dyes formed on colour development show good fastness to light. This is illustrated by comparative tests, the description and the results of which will be given hereinafter.

The following examples illustrate the preparation of light-sensitive emulsions and the processing of photographic material according to the present invention.

Example 1

To ½ kg. of a green-sensitive silver bromo-iodide (3 mol percent of iodide) emulsion containing 0.112 mol of silver halide is added at 45° C. 8 g. of the colour coupler of Preparation 1 dissolved by heating in a mixture of 16 cm.³ of ethanol, 24 cm.³ of N aqueous sodium hydroxide and 60 cm.³ of distilled water. After neutralization with sulphuric acid and after addition of the usual additives such as hardeners, wetting agents, stabilizers and the necessary amount of distilled water to obtain 1 kg. of emulsion, the latter is coated at a coverage of 10 sq. m. per kg. on a cellulose triacetate support and dried. After exposure through a grey-wedge with a constant 0.15, the photographic material is developed for 8 minutes at 20° C. in a colour developing bath of the following composition:

	G.
N,N-diethyl-p-phenylenediamine hydrochloride	2.75
Hydroxylamine hydrochloride	1.2
Anhydrous sodium hexametaphosphate	1
Anhydrous potassium carbonate	75
Anhydrous sodium sulphite	2
Potassium bromide	0.5
Water to make 1 l.	

The developed material is treated for 4 minutes in a stop-bath of the following composition:

	G.
Potassium alum	5
Acetic acid	10 cm.³
Borax	21
Water to make 1 l.	

The material is rinsed for 10 minutes with water and then treated in a fixing bath of the following composition:

	G.
Sodium thiosulfate-5-water	200
Anhydrous potassium metabisulfite	25
Potassium alum	15
Boric acid	7.5
Water to make 1 l.	

After having been fixed the material is treated in a bleaching bath of the following composition:

	G.
Borax	22
Anhydrous potassium bromide	14
Anhydrous sodium bisulphite	4
Potassium hexacyanoferrate (III)	100
Water to make 1 l.	

After the bleaching step, the material is rinsed with water for 6 minutes and fixed for another 6 minutes in a bath with the following composition:

	G.
Anhydrous sodium hexametaphosphate	1
Anhydrous sodium thiosulfate	130
Anhydrous sodium sulphite	10
Anhydrous sodium carbonate	6
Anhydrous sodium bicarbonate	14
Water to make 1 l.	

After a final rinsing the material is dried.

A magenta coloured wedge image is obtained.

Example 2

To ½ kg. of a green-sensitive silver bromo-iodide (3 mol percent of iodide) emulsion containing 0.115 mol of silver halide is added 8 g. of the colour coupler of preparation 2 dissolved by heating to 40° C. in a mixture of 16 cm.³ of ethanol, 44 cm.³ of N aqueous sodium hydroxide and 10 cm.³ of distilled water.

After neutralization with sulphuric acid and after addition of the usual additives such as hardeners, wetting agents, stabilizers, and the necessary amount of distilled water to obtain 1 kg. of emulsion, the latter is ready to be coated. After coating, the emulsion forms part of a multilayer photographic material comprising the following superposed layers in the indicated sequence: a support, an anti-halation layer, a gelatin insulating layer, a red-sensitized silver halide emulsion layer containing a cyan-forming colour coupler, a gelatin interlayer, a layer of the above-mentioned green-sensitized silver halide emulsion, a yellow filter layer, a blue-sensitive silver halide emulsion layer containing a yellow-forming colour coupler and at last a gelatin overcoat as antistress layer.

After exposure to a multicolour original the photographic material is developed and further treated as in Example 1. In the green-sensitized emulsion layer a negative magenta coloured image is obtained.

Example 3

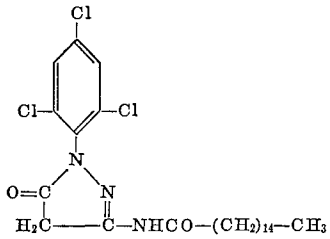
In a similar green-sensitized silver halide emulsion as described in Example 2, the colour coupler is replaced by half the amount of the colour coupler of Preparation 9 dissolved by heating in a mixture of 20 cm.³ of ethanol, 8 cm.³ of N aqueous sodium hydroxide and 12 cm.³ of distilled water. After neutralization and addition of the usual ingredients the emulsion is coated, exposed to a colour negative and processed as described in Example 1. In the green-sensitized silver halide emulsion layer a positive magenta coloured image is obtained.

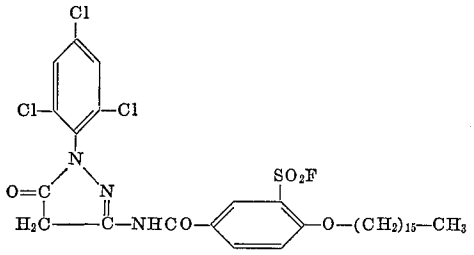
Results of comparative tests on light stability of azomethine dyestuffs formed with colour couplers according to the present invention and colour couplers according to the P.K. patent specification 630,488 are given in the following table. The colour couplers according to said U.K. patent specification are known as colour couplers with improved light stability. For the composition of the silver halide emulsions to be compared the same molar amounts of colour couplers in respect of the silver halide were used, the exposure of the test strips was carried out in the same circumstances of heat and humidity in a "Xenotest" (registered trademark) and the subsequent development was also executed in identical circumstances.

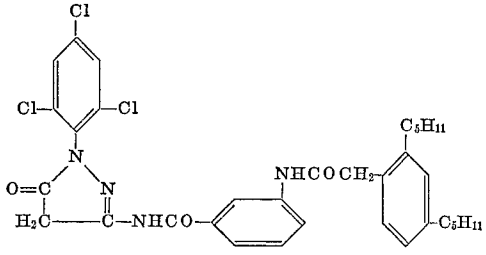
The stability to light of the dyestuffs formed on development with N-diethyl-p-phenylenediamine is determined from the procentual decrease in maximum density

after 15 hours of exposure to light of the Xenon-arc light sources of the "Xenotest" (daylight spectrum).

Colour coupler of formula	Percent decrease in max. density of the azomethine dyestuff after 16 hours of exposure in "Xenotest"
1	4
4	9
6	6
8	4
10	8
11	10
12	5
14	11
15	3
16	8
17	8
18	8
Colour couplers according to U.K. Patent Specification 680,488·	

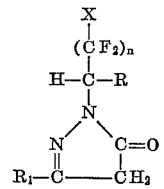






We claim:

1. A photographic emulsion for preparing a color photographic element comprising a water-permeable colloid as a carrier for light-sensitive silver halide grains and a 2-pyrazoline-5-one compound capable of forming a dye with the oxidation product of an aromatic primary amino silver halide developing agent, which compound has the structure



wherein:

X represents a member selected from the group consisting of a hydrogen atom and a fluorine atom;

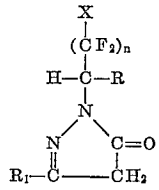
R represents a member of the group consisting of a hydrogen atom, an alkyl radical and an aryl radical;

n is a positive integer from 1 to 10 inclusive; and

R_1 represents a member selected from the group consisting of an alkyl radical, an aryl radical, a —NH-aryl radical, a —NHCO-alkyl radical, a —NHCO-aryl radical, a —NHCONH-alkyl radical or a —NHCONH-aryl radical.

2. The photographic emulsion of claim 1 wherein R_1 includes a radical for rendering said compound fast to diffusion in a hydrophilic colloid medium.

3. A photographic element containing at least one silver halide emulsion layer and a 2-pyrazoline-5-one compound capable of forming a dye with the oxidation product of an aromatic primary amino silver halide developing agent, said compound having the structure



wherein:

X represents a member selected from the group consisting of a hydrogen atom and a fluorine atom;

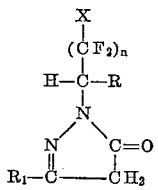
R represents a member of the group consisting of a hydrogen atom, an alkyl radical and an aryl radical;

n is a postive integrer from 1 to 10 inclusive; and

R_1 represents a member selected from the group consisting of an alkyl radical, an aryl radical, a —NH-aryl radical, a —NHCO-alkyl radical, a —NHCO-aryl radical, a —NHCONH-alkyl radical or a —NHCONH-aryl radical.

4. The photographic element of claim 3 wherein R_1 includes a 5–20 carbon aliphatic linear chain rendering said compound fast to diffusion in a hydrophilic colloid medium.

5. A photographic multi-layer material containing at least one green-sensitized silver halide emulsion layer, which contains a 2-pyrazoline-5-one compound corresponding to the following general formula:



wherein:

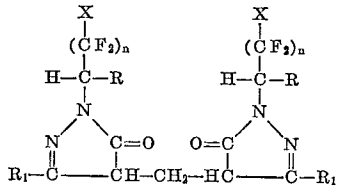
X represents a member selected from the group consisting of a hydrogen atom and a fluorine atom;

R represents a member of the group consisting of a hydrogen atom, an alkyl radical and an aryl radical;

n is a positive integer from 1 to 10 inclusive; and

R_1 represents a member selected from the group consisting of an alkyl radical, an aryl radical, a —NH-aryl radical, a —NHCO-alkyl radical, a —NHCO-aryl radical, a —NHCONH-alkyl radical or a —NHCONH-aryl radical.

6. A photographic multi-layer material containing at least one green-sensitized silver halide emulsion layer which contains a bis(2-pyrazoline-5-one) compound according to the following general formula:



wherein:

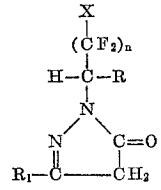
X represents a member selected from the group consisting of a hydrogen atom and a fluorine atom;

R represents a member of the group consisting of a hydrogen atom, an alkyl radical and an aryl radical;

n is a positive integer from 1 to 10 inclusive; and

R_1 represents a member selected from the group consisting of an alkyl radical, an aryl radical, a —NH-aryl radical, a —NHCO-alkyl radical, a —NHCO-aryl radical, a —NHCONH-alkyl radical or a —NHCONH-aryl radical.

7. A method of producing a magenta-colored photographic image in a silver halide-containing photographic material, which method comprises exposing said material and color developing it by reacting a 1-fluoro-alkyl-2-pyrazoline-5-one compound having the structure



wherein:

X represents a member selected from the group consisting of a hydrogen atom and a fluorine atom;

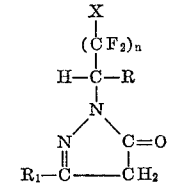
R represents a member of the group consisting of a hydrogen atom, an alkyl radical and an aryl radical;

n is a positive integer from 1 to 10 inclusive; and

R_1 represents a member selected from the group consisting of an alkyl radical, an aryl radical, a —NH-aryl radical, a —NHCO-alkyl radical, a —NHCO-aryl radical, a —NHCONH-alkyl radical or a —NHCONH-aryl radical,

with the oxidation product of an aromatic primary amino compound formed by the reduction of the exposed silver halide.

8. A method of producing a magenta-colored photographic image in a silver halide emulsion layer containing a 1-fluoro-alkyl-2-pyrazoline-5-one compound in diffusion fast form, said compound having the structure



wherein:

X represents a member selected from the group consisting of a hydrogen atom and a fluorine atom;

R represents a member of the group consisting of a hydrogen atom, an alkyl radical and an aryl radical;

n is a positive integer from 1 to 10 inclusive; and

R_1 represents a member selected from the group consisting of an alkyl radical, an aryl radical, a —NH-aryl radical, a —NHCO-alkyl radical, a —NHCO-aryl radical, a —NHCONH-alkyl radical or a —NHCONH-aryl radical.

which method comprises exposing said layer and color developing it.

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J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

96—74, 100