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2,964,402

MONO-ACETYL INDAZOLONE COLOR COUPLERS

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5 Claims. (Cl. 96—55)

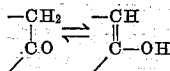
This invention relates to a process for the production of color photographic images by color development in the presence of a color coupler, to photographic developers, to photographic material containing such couplers, and to photographic images obtained by our process.

The present invention constitutes an improvement in and a modification of the subject matter disclosed in Patent 2,673,801 to Jacob Joseph Jennen, dated March 30, 1954.

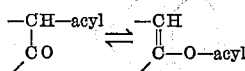
It is known that a colored image may be formed by developing a reducible silver salt image in the presence of a compound which couples during development with the oxidation product of the developing agent and forms a dyestuff. The dyestuff deposits onto the developed silver grains.

For developing magenta dyestuff images, compounds have been used until now which contain an active methylene group, such as pyrazolones and cyanacetic derivatives.

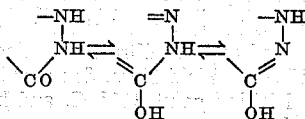
Many of the compounds used have a ring containing the following configuration:



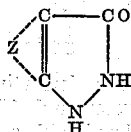
Compounds having a ring containing the following configuration are also known:



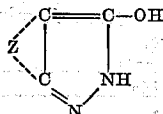
According to the referred to Patent 2,673,801, a magenta image may also be obtained when a compound containing no such active methylene group is used as a color coupler. These compounds have a pyrazolone-3 ring which is noted for the following configuration:



Further, according to the referred to patent a reducible silver salt image is developed with a primary aromatic amino developing agent in the presence of a compound corresponding to the following formula:

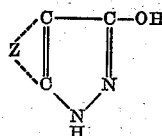


or to a tautomeric form thereof, for instance, the formula:



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or



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or

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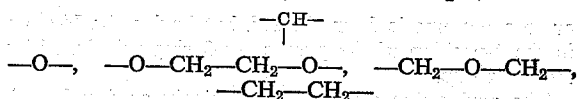
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In these three formulae, Z represents the non-metallic atoms required for completing a homo-, hetero-, or polycyclic nucleus.

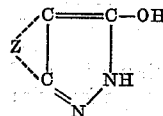
The polycyclic nucleus completed by Z may contain at least one further —NH—NH—CO— group to give a compound containing two pyrazolone-3 rings. The compound completed by Z may contain two or more nuclei as well, linked by a chemical bond or a bi- or polyvalent atom or a group, such as —CH₂—,



or

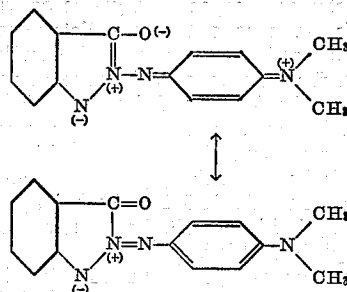


Assuming that these color couplers may be represented by the following formula:



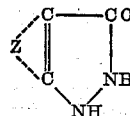
it is believed that the coupling with the oxidation products of the developing agent occurs at the N-atom in ortho position to the OH group. This assumption is supported by the coupling reaction of a diazo compound with para-cresol and beta-naphthol, which also takes place in ortho position to the OH group, and by the coupling reaction of a diazo compound with 3:4-dimethyl-5-hydroxypyrazole, which probably occurs in the same manner.

The dyestuff formed from these couplers may be written as follows:



which formulae are analogous to the formulae LV of Baker for 2-substituted indazole (cfr. J. Chem. Soc. (London), 1945, 267).

Now we have found that compounds corresponding to the following formula:



or a tautomeric form thereof, but having the H-atom in the 1-position of the pyrazolone-3 ring substituted by an acyl group, also couple with the oxidation product of an amino aromatic developing agent, yielding an image dyestuff which has the same structure as that obtained when a compound having no acyl substitution is coupled.

It is an object of our present invention to provide a

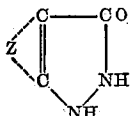
new process for the production of color photographic images by color development.

Another object of this invention is to provide new photographic developers containing a color coupler.

A further object is to provide new photographic material containing a color coupler.

Still further objects will become apparent from the following description.

According to our invention, a dyestuff having the same structure as that obtained with the compounds of Patent No. 2,673,801 is obtained by developing a reducible silver salt image with a primary aromatic amino developing agent in the presence of a compound corresponding to the formula



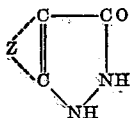
or to a tautomeric form thereof, but having the H-atom in the 1-position of the pyrazolone-3 ring substituted by an acyl group.

The acyl group may be bound singly or doubly. A double acyl, for instance, succinyl, is linked to two indazolone couplers. The compounds according to our present invention are monoacyl indazolones.

It is believed that the acyl group is split off by the action of the oxidation product of the developing agent.

The color coupler according to our invention may be obtained by acylating the color coupler of Patent 2,673,801.

As the color couplers of the aforementioned patent correspond to the following formula:



or a tautomeric form thereof, the acyl group, upon acylating, will be able to enter the 1-, 2- or 3-position so that several isomers are possible. As far as the monoacyl compounds are concerned, 1-, 2- or 3-acyl derivatives may be obtained.

The introduction of an acyl group in the 1-position may be effected with an acid anhydride or with an acid halide. It is, however, not easy to determine the position where an acyl group enters. Depending on the solvent used, for instance, with benzene or pyridine the acyl group may be driven to different positions. During the reaction, however, rearrangements may occur. The acyl group may move from the 2-position to the 1-position, as is known with respect to 2-acyl-7-nitro indazole (Ann., 451 (1927), 303). Such final change may be obtained by boiling in nitrobenzene, acetic acid, pyridine or simply by melting.

As regards the di-acyl compounds, the duration of the reaction plays a great part. We are of the opinion that by boiling with an acid anhydride for a long time, 1-3-di-acyl compounds are obtained, relying for support on the experience gained by Weissberger in the preparation of 2-acetyl-5-acetoxy pyrazoles (J.A.C.S., 65 (1943), 1495-99). It is advantageous to prepare first a diacyl indazolone, partial diacylation of which leads to 1-acyl indazolone.

1-acyl indazolone derivatives according to the present invention have the advantage over the indazolone couplers according to Patent 2,673,801 of being more soluble in water. This will be clear from a comparison of the examples of this patent and the present examples. The solubility of our present couplers may be further enhanced by introducing into the acyl group a group conferring solubility in water without enhancing the solubility of the image dyestuff since the acyl group is split off on development.

While the color couplers according to Patent 2,673,801 are converted into a yellow product when getting into contact with an alkaline oxidizing medium, such as a silver-removing bath, so that to the dyestuff image formed on color development a yellow reversal image is added, which results from the oxidation of the residual color coupler in the silver-removing bath, our present color couplers yield little or no yellow residual image.

The dyestuffs obtained upon color development with the color couplers according to the present invention are more stable to acid than those obtained with the known pyrazolones having a reactive methylene group.

The present dyestuffs that contain a substituent rendering them fast to diffusion are not removable from the emulsion layer even by prolonged washing.

Our new color couplers may be used in the developing solution or in a colloid layer, 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.

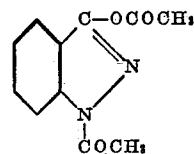
The aromatic amino compounds which may be used as developing agents in the present process include di- and tri-amino aryl compounds. Out of monoamino developing agents, we mention amino phenols, amino cresols and thier halogen derivatives, and amino naphthols.

The developing agents which we prefer to use and that give the best results in the present process are aromatic ortho and paradiamines, such as para-phenylene diamine and its substitution products.

The following examples of substituted indazolones are given to illustrate the invention without limiting, however, the scope thereof.

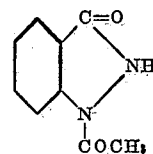
Example 1

5.9 gm. indazolone in 30 cc. acetic acid anhydride are refluxed for 3 hours. To this mixture ethyl alcohol is added. After evaporation to dryness in an open dish, the residue is recrystallized from alcohol (Ann., 212 (1882), 336). Melting point 111-112° C. Yield 5.6 gm. 1:3-diacetyl indazolone which corresponds to the following formula:



According to Ann., 212 (1882), 336, 1-2-diacetyl indazolone is obtained, but we are of the opinion that the formula just given is correct.

2 gm. of the 1:3-diacetyl indazolone in 800 cc. water are heated for 4 hours on a boiling water bath. The mixture is filtered and the filtrate is cooled in ice (Ber., 57 (1924), 1722). Yield 1 gm. fine needles of 1-acetyl-indazolone. Melting point 211° C. and having the following formula:



2 gm. of the indazolone derivative thus prepared are dissolved in 50 cc. water and 10 cc. of an aqueous solution of sodium hydroxide N, and added to 1 liter of a mixture of equal parts of the following solutions

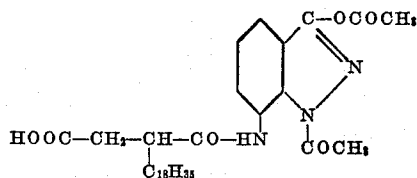
	Gm.
(A) N:N-diethyl-p-phenylene diamine hydrochloride	6
Water to 500 cc.	
(B) Potassium carbonate	75
Potassium bromide	2.5
Water to 500 cc.	

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An exposed positive cine film bearing a silver halide emulsion layer is developed in the developer thus prepared, washed, and further treated as usual in color development processes. A magenta image is formed.

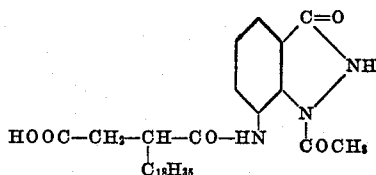
Example 2

10 gm. 7-octadecenyl succinyl amino indazolone, which may be prepared as described in Example 9 of Patent 2,673,801, in 40 cc. acetic anhydride are boiled for 15 minutes. The mixture is poured into water and recrystallized from alcohol. Yield 10 gm. 1:3-diacetyl-7-octadecenyl succinyl amino indazolone corresponding to the following formula:



Melting point 89-90° C.

To 10 gm. of this di-acetal indazolone are added 20 cc. of an aqueous solution of NaOH N. After left to stand overnight, the mixture is filtered, and the filtrate is neutralized with a normal aqueous solution of acetic acid. The product obtained is sucked off and recrystallized from alcohol. Yield 7 gm. 1-acetal-7-octadecenyl succinyl amino indazolone corresponding to the following formula:



Melting point 165-167° C.

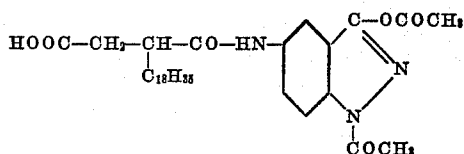
1 gm. of this indazolone is dissolved in 2 cc. of normal aqueous solution of potassium hydroxide, 4 cc. ethyl alcohol, and water to have a total volume of 25 cc., and is added to 100 cc. of a photographic silver halide emulsion prepared from 2.75 gm. silver nitrate. This emulsion is coated onto a support, exposed and developed with a solution obtained by mixing equal parts of the following solutions

	Gm.
(A) N:N-diethyl-p-phenylene diamine sulphate	3.2
Sodium sulphate	5
Water to 500 cc.	
(B) Potassium carbonate	75
Potassium bromide	2.5
Water to 500 cc.	

After washing and further treating as usual in color development processes, a bluish-magenta image is formed.

Example 3

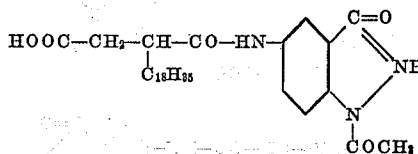
10 gm. 5-octadecenyl succinyl amino indazolone which may be prepared as described in Example 1 of Patent 2,823,998 to Jacob Joseph Jennen, dated February 18, 1958, in 40 cc. acetic anhydride are boiled for 15 minutes. The mixture is poured into water and recrystallized from alcohol. Yield 10 gm. 1:3-diacetyl-5-octadecenyl succinyl amino indazolone corresponding to the following formula:



To 10 gm. of this di-acetyl indazolone derivative are added 20 cc. of an aqueous solution of NaOH N. After

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left to stand overnight, the mixture is filtered and the filtrate is neutralized with a normal aqueous solution of acetic acid. The product obtained is sucked off and recrystallized from alcohol. Yield 7 gm. 1-acetyl-5-octadecenyl succinyl amino indazolone corresponding to the following formula:

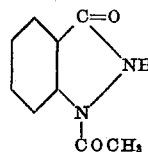


Melting point 150-152° C.

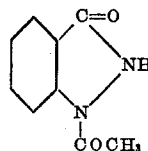
1 gm. of this derivative added to a silver halide emulsion and developed both as described in Example 2. A magenta image is formed.

We claim:

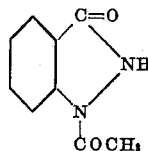
1. Process for the production of a colored photographic image, comprising developing a reducible silver salt image in a photographic element by means of a primary aromatic amino developing agent in the presence of a color coupler having the following formula



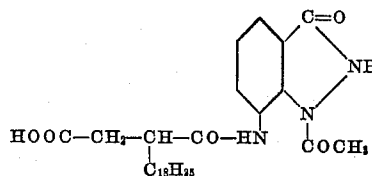
2. Photographic developer containing a primary aromatic amino developing agent and a color coupler having the following formula



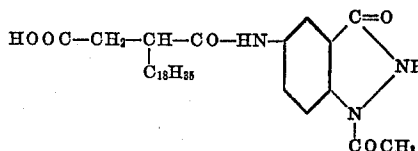
3. Photographic material comprising a silver halide emulsion layer and a colloid layer adjacent to the emulsion layer, the photographic material containing a color coupler having the following formula



4. Process for the production of a colored photographic image, comprising 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 of the group consisting of

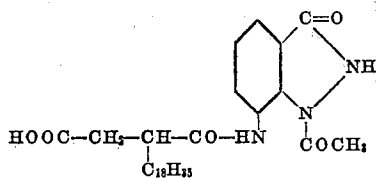


and

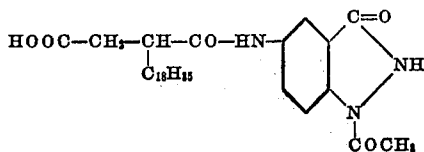


5. Photographic material comprising a silver halide emulsion layer and a colloid layer adjacent to the emul-

sion layer, the photographic material containing a color coupler of the group consisting of



and



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Berichte, 54 (1931), p. 1116.

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