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3,199,983

3-INDAZOLONE COLOR COUPLERS

Günther Koepke, Leverkusen, Willibald Pelz, Opladen, and Hans Schellenberger, Leverkusen, Germany, assignors to Agfa Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany

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A 36,629

9 Claims. (Cl. 96—55)

The present invention relates to indazolone color couplers in which the non-diffusing group comprises a long-aliphatic acyl radical substituted in the α -position to the carbonyl group by a sulpho group, to silver halide emulsions containing such couplers and to the production of colored photographic images in the presence of such couplers.

In the production of dyestuff images by color-forming development it is the practice to employ color formers containing non-diffusing groups such as a long aliphatic chain, the purpose of which is to prevent diffusion of the coupler in the silver halide emulsion. It is likewise common practice to provide such couplers with certain acid radicals such as a carboxy or sulpho radical, the alkali or ammonium salts of which are soluble in water or aqueous solutions such as photographic emulsions. It is, furthermore, customary to employ as the yellow coupler an open chain keto methylene compound such as benzoyl-acetanilide derivatives, as the cyan coupler a compound containing phenolic hydroxy groups such as α -naphthol derivatives and as the magenta coupler pyrazolone derivatives particularly those bearing an aryl radical on the nitrogen atom in the 1-position of the pyrazolone ring. These color couplers have a similar coupling intensity and speed of coupling with respect to the oxidation products of color developers formed upon development so that they can easily be employed for the production of multi-color images, for which purpose it is general practice to use multi-layer materials having three silver halide emulsion layers which are light-sensitive for different parts of the spectrum, the said emulsion layers having the said color couplers incorporated therein in a diffusion resistant form.

Since the pyrazolone derivatives do not meet all practical requirements as regards the absorption properties and stability, attempts have already been made to replace the pyrazolone derivatives by indazolone derivatives for the production of magenta color images. The indazolone derivatives and more especially those which are made diffusion-resistant by introduction of relatively long alkyl radicals, have, however, the disadvantage that the coupling intensity and the solubility thereof are too low. This refers also to octadecenyl succinoyl amino indazolone described in German Patent No. 814,996. These couplers precipitate on casting whereby matting of the resulting layers and flattening of the color gradation occur.

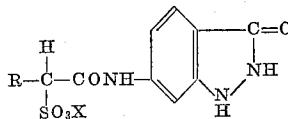
It is not possible to increase the solubility of such indazolone derivatives by introduction of sulpho groups into the benzene nucleus, because this is associated with an unacceptable displacement of the absorption maxima of the dyestuffs produced from these couplers towards longer wave lengths.

It is among the objects of the present invention to avoid the disadvantages described above.

We have now discovered a class of indazolone color couplers of the salt forming non-diffusing type in which a long aliphatic acyl radical contains the salt-forming function as a sulpho radical in α -position to the carbonyl group. The acyl radical is linked in the manner of carbon amide to an amino group which is substituted in the 6-position of the indazolone ring. Such indazolone

2

derivatives are characterized by the following general formula:



in which R represents an alkyl radical having 6–18 carbon atoms, preferably 12–18 carbon atoms and X stands for a cation such as hydrogen, alkali metal, for example lithium, sodium and potassium, alkaline earth metal, such as magnesium and calcium, ammonium or ammonium substituted with at least one alkyl radical having up to 4 carbon atoms.

These color couplers have extremely useful and valuable photographic properties. The amino derivatives according to the invention show an excellent solubility, even in the weakly acid range, and also a high coupling intensity, so that they can be used in conjunction with couplers which contain activated methylene groups or with α -naphthol derivatives, in single-layer or multi-layer materials. In contrast to known indazolone derivatives, the present couplers are resistant to digestion. The silver halide emulsions to which these couplers are added can be kept for a relatively long time in a molten condition without any precipitation of the coupler, which would lead to a change in the viscosity and the pH-value of the emulsion, a flattening of the gradation and a matting of the layers produced from these emulsions, as well as a decrease in the coupling intensity and thus a color tone displacement upon development of a multi-layer material. The couplers thus render possible the production of color materials with uniform and high-grade properties.

On account of the good stability of the present color couplers, photographic silver halide emulsions containing these color couplers can also be cast in the acid pH-range, so that improved keeping properties are guaranteed in the layers so produced. Furthermore, these layers have the advantage that even after relatively long storage, they do not show any change in color tone and color intensity of the developed image, by comparison with layers developed immediately after manufacture, whereas with layers having known indazolone derivatives, occur a displacement of the color tone from magenta-red to magenta-blue shades and a decrease in the color intensity. It is also surprising that the indazolone derivatives according to the invention by contrast with corresponding known indazolone derivatives, are not transformed into yellow dyestuffs by the action of potassium ferricyanide solutions, which are used for the bleaching of photographic color materials being developed by means of color-forming developers. Consequently, the present color couplers can also be used for the production of those multi-layer films or papers which are employed for the production of positive color images by the use of potassium ferricyanide bleaching baths.

The color couplers to be used according to the invention are advantageously added to the silver halide emulsions in quantities of about 5 to 20 g./kg. Gelatine is preferably used as binder for the emulsion, but other binders known per se can also be used. Furthermore, it is also possible for the color couplers to be introduced into layers of multi-layer materials which are not sensitive to light, the said materials containing silver halide emulsion layers in addition to the said layers which are not light-sensitive.

The conventional color developers, in particular aromatic color developers with primary amino groups, can be used for the development of the present color materials.

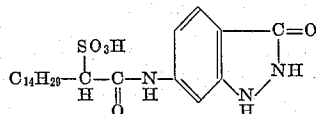
The present color couplers can be obtained by reaction of 6-amino indazolone with the mono-alkali metal salts

of α -sulpho fatty acids using phosphorus trichloride in the presence of tertiary amines, for example pyridine.

Example 1

22.2 g. of 6-amino-indazolone, 2 HCl and 35.8 g. of the mono-sodium salt of sulphopalmitic acid are suspended in 260 cc. of pyridine. From this mixture, 100 cc. of pyridine are distilled off with stirring, the suspension then being cooled to room temperature and a solution of 4.5 cc. of phosphorus trichloride in 25 cc. of absolute benzene is introduced dropwise over 30 minutes. The mixture is now boiled under reflux for 2 hours with stirring and about 70 cc. of solvent are then distilled off. The residue is then introduced into 500 cc. of cooled 2-molar hydrochloric acid, suction-filtered and the solid residue mixed twice with 2 n-hydrochloric acid, using 200 cc. on each occasion, and then suction-filtered. About 47 g. of crude product are obtained after drying, which product can be purified by dissolving it at about 60° C. in 220 cc. of water and about 45 cc. of 10 percent sodium hydroxide solution, followed by filtration and precipitation by introduction of the solution dropwise into a mixture of 570 cc. of water and 65 cc. of concentrated hydrochloric acid. It is then washed with dilute hydrochloric acid and thereafter with about 3 percent sodium chloride solution and dried.

37 to 40 g. of the compound of the following formula are obtained:

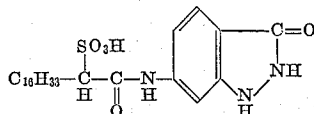


By neutralization with sodium hydroxide or potassium hydroxide the corresponding salts are formed.

Example 2

The preparation is carried out in a manner similar to that indicated in Example 1, except that 38.4 g. of the mono-sodium salt of α -sulphostearic acid are used instead of 35.8 g. of mono-sodium salt of sulphopalmitic acid.

The following indazolone derivative is obtained:



Suitable salts of said compound are obtained by reaction with carbonates or hydroxides of alkali metals or alkaline earth metals, ammonia or amines containing at least one alkyl radical having up to 4 carbon atoms.

Example 3

14.8 g. of the coupler described in Example 1 are formed into a paste with 20 g. of methanol and dissolved by adding 40 cc. of 5 n-sodium hydroxide solution and 150 cc. of water with heating to 65° C. The clear solution is added to 1 kg. of green sensitized silver halide emulsion. After addition of hardeners and wetting agents, the pH-value of the emulsion is adjusted by means of citric acid to pH 5.5. A photographic material produced with this emulsion mixture is exposed and then developed in a color developer containing N,N-diethyl-p-phenylene diamine, bleached and fixed or bleach-fixed. A negative magenta image is obtained with an absorption maximum of 560 m μ , which shows pure whites, even after being bleached and fixed.

Example 4

A cellulose acetate film support is cast with a red-sensitized silver halide emulsion containing, per kg. of emulsion, 15 g. of the color coupler 1-hydroxy-2-naphthoyl-3'-sulpho-6'-N-methyl-N-octadecylamino anilide. A separation layer of 3 percent gelatine solution is then cast thereon and above is a green-sensitized silver halide

emulsion, containing 15 g. of the color coupler described in Example 2 per kg. of emulsion. After casting a gelatine solution containing a yellow filter dyestuff a blue-sensitive silver halide emulsion is applied which contains, per kg. of emulsion 15 kg. of the color coupler 4-stearoylamido benzoyl-3',5'-dicarboxy acetanilide. After casting a protective layer consisting of a 3 percent gelatine solution, the film is dried.

After exposure, the film is developed in a color developer containing N,N-diethyl-p-phenylene diamine, and is then bleached and fixed.

A negative color image is obtained.

As color developer, it is for example possible to use the following solution:

	G.
N,N-diethyl-p-phenylene-diamine sulphate	3
Potassium carbonate	75
Anhydrous sodium sulphite	2
Potassium bromide	1
Water to make 1000 cc.	

The following baths can be used for bleaching the developed layers:

(1) K ₃ Fe(CN) ₆	g--	100
KBr	g--	15
Water to make 1000 cc.		
(2) KBr	g--	20
K ₂ Cr ₂ O ₇	g--	5
KAl(SO ₄) ₂	g--	21
CH ₃ COO.Na	g--	2.5
Glacial acetic acid	cc--	30
Water to make 1000 cc.		

A suitable bath for fixing the bleached layers has the following composition:

	G.
Na ₂ S ₂ O ₃ ·5H ₂ O	200
Na ₂ SO ₃	10
Na ₂ B ₄ O ₇ ·10H ₂ O	25
Sodium hexaphosphate	1
Water to make 1000 cc.	

For bleach-fixing, i.e., for simultaneously bleaching and fixing the layers, it is possible to use baths according to German patent No. 866,605.

Having thus described our invention, we now state that our invention is capable of numerous variation. It will be clear to those skilled in the art that the color couplers, according to our invention, can be used in any color photographic material such as mono-layer or multi-layer positive or negative material or reversal color films. The non-diffusing color couplers according to the invention can be used in combination with any sensitizers, anti-fog agents, stabilizers or the like which are known to be employed in color photographic material. With regard to the utility for multi layer color films it should be pointed out that the layer arrangement or sensitization-color-relationship are not especially critical. Although the binding agent of the layers in which the color couplers are to be used is preferably gelatine, other layer forming hydrophilic agents can be used such as carboxy cellulose, polyvinyl alcohol or the like. The processing of the exposed color material, containing in one layer a magenta coupler according to the invention, is accomplished in a manner well known by first developing the material with a developer composition containing a color forming developer. Said developers generally spoken are characterized by a content of a primary amino group or a substituted amino group, the substituent of which being split off during the development, e.g., as described in German Patent No. 926,713. Very useful color developers are for example, N,N-diethyl-p-phenylene-diamine, N-ethyl-N-hydroxy-ethyl-p-phenylene-diamine, N-butyl-N-sulpho-butyl-p-phenylene-diamine, N-ethyl-N-methyl sulfoamino-ethyl-p-phenylene-diamine, or derivatives thereof being substituted in the phenylene nucleus, furthermore,

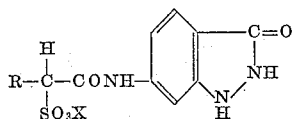
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4-aminopyrazolone and derivatives thereof. The developer composition may be alkalis by alkali carbonates, tertiary alkali phosphates or the like alone or in combination with small amounts of alkali hydroxides.

The developers may contain any stabilizing agents, anti-fog agents and compounds protecting the composition against oxidation such as alkali sulphites or salts of hydroxylamine. The developing is followed by bleaching and fixing the color films. These procedures are well known to any person having ordinary skill in the art and need not to be described in detail.

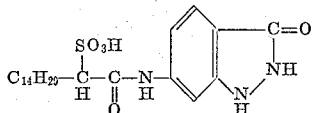
What is claimed is:

1. A process for the production of a photographic colored image which comprises exposing to an object to be reproduced a photographic material containing at least one silver halide emulsion layer and developing the said exposed silver halide emulsion layer with a primary aromatic amine developer in the presence of a substituted indazolone color coupler that is capable of forming a colored image with the oxidation product of a primary aromatic amine developer and has the following formula:

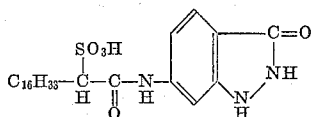


in which R is an alkyl radical having between 12 and 18 carbon atoms, X is a cation of the group consisting of hydrogen, alkali metals, alkaline-earth metals, ammonium, and alkyl-substituted ammonium radicals, the alkyl radicals of which contain between 1 and 4 carbon atoms.

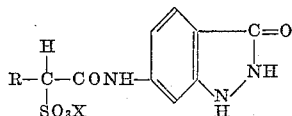
2. A process according to claim 1, wherein said color coupler is a compound having the following formula



3. A process according to claim 1, wherein said color coupler is a compound having the following formula



4. A light-sensitive silver halide emulsion containing a color coupler of the following general formula

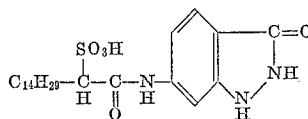


wherein R stands for an alkyl radical having from 12 to 18 carbon atoms, said coupler being capable of forming a colored image upon reaction with the oxidation product of said primary amine developer, and X is a cation selected from the group consisting of hydrogen, alkali metals, alkaline-earth metals, ammonium, and alkyl-

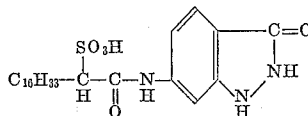
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substituted ammonium radicals the alkyl radicals of which contain between 1 and 4 carbon atoms.

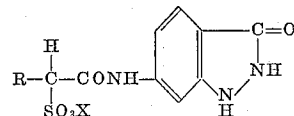
5. A light-sensitive silver halide emulsion according to claim 4 containing a color coupler having the following formula



6. A light-sensitive silver halide emulsion according to claim 4 containing a color coupler having the following formula

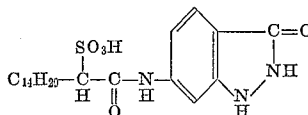


7. A photographic element having superimposed silver halide emulsion layers sensitive to different regions of the visible spectrum, one of said layers containing a color coupler capable of reacting with the oxidation product of a primary amine developer to form a dyestuff image, said coupler having the following general formula

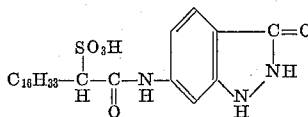


in which R is an alkyl radical having between 12 and 18 carbon atoms and X is a cation of the group consisting of hydrogen, alkali metals, alkaline-earth metals, ammonium, and alkyl-substituted ammonium radicals the alkyl radicals of which contain between 1 and 4 carbon atoms.

8. A photographic element according to claim 7, wherein said color coupler has the following formula



9. A photographic element according to claim 7, wherein said color coupler has the following formula



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LOUISE P. QUAST, *Examiner*.