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LIGHT-SENSITIVE EMULSIONS CONTAINING NON-MIGRATORY N-SUBSTITUTED 1-HYDROXY-2-NAPHTHAMIDE COLOR COUPLERS

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2 Claims. (Cl. 96—55)

This invention relates to a process for the manufacture of photographic color images by color development in the presence of a color coupler, to photographic material which contain such color couplers, and to photographic images obtained according to the process referred to.

It is known to obtain a photographic color image by developing a reducible silver salt image in the presence of a color coupler, i.e. a compound which during development couples with the oxidation product of the developing agent and forms a dyestuff on the area where the silver salt is reduced.

The modern methods of color photography are based upon the subtractive color principle according to which differently sensitized silver halide emulsion layers are superposed, each of them containing a color coupler which produces the subtractive yellow-, cyan- and magenta-dyestuff images by development in a solution containing a primary aromatic amine.

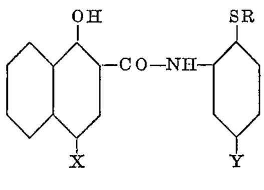
Different demands are made upon the color couplers according to whether they are designed for negative or for positive material. Thus it is known that 1-hydroxy-2-naphthamide color couplers, giving after the color development clear blue images, are preferably used for the manufacture of positive color materials. On the other hand it is desired to use in the manufacture of negative materials a 1-hydroxy-2-naphthamide color coupler which is developed to a cyan image, the absorption spectrum of which is brought as much as possible to the long wavelengths with side-absorptions as low as possible. But the disadvantage of the bathochromic shifting of the absorption centre is that this effect is almost always accompanied by an increase of unwanted side absorption viz. in the green and blue part of the spectrum.

To overcome this disadvantage there is a continuous research for cyan color couplers with a bathochromically shifted absorption spectrum whereby the side absorptions are kept as low as possible. In connection herewith we refer to the color couplers which are manufactured according to the British patent specification 831,731.

It is an object of the present invention to provide a photographic material containing a number of new color couplers.

It is another object of the present invention to provide a process to form a cyan dye color image in a light-sensitive silver halide emulsion.

Now it has been found that in the red light-sensitive silver halide emulsion of a photographic material, cyan color images are obtained with increased transparency in the green by incorporating in said emulsion an aromatic N-substituted 1-hydroxy-2-naphthoic acid amide color coupler corresponding to the following two formulae:



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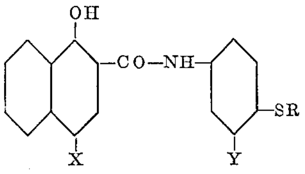


wherein

X is an halogen atom,

Y is a member selected from the group consisting of an hydrogen atom, a sulfonic acid group and a sulphonate group, and wherein

R is a non-migratory making radical consisting of a carbon chain with at least 5 carbon atoms and at most 20 carbon atoms.

The new color couplers can be prepared by condensation of a 1-hydroxy-2-naphthoic acid or a derivative thereof with the aromatic amine desired. For the preparation of color couplers which contain in the naphthol or the anilide group a sulfonic acid group it is advantageous to bring into the naphthol resp. anilide group before the condensation a sulfofluoride group which after condensation is saponified to the corresponding sulfonic acid, e.g. by application of the method described in Belgian patent specifications 584,152 and 590,934.

Hereinafter follows the preparation of some of these new color couplers.

I. Preparation of N-(o-cetylmercaptophenyl) - 1 - hydroxy-4-chloro-2-naphthoic acid amide:

15.42 g. of o-cetylmercaptoaniline-hydrochloride (prepared according to Farmaco (Pavia), Ed. pract., Ed. sci. 12, 206–17 (1957)), and 8.08 g. of triethylamine are mixed with 100 cm.^{3} of anhydrous benzene whereby a gelatinous precipitate is formed. The reaction mixture is cooled off in ice and 7 g. of o-phenylene chlorophosphite (prepared according to Anschütz et al., Ber. 76, 1943/222) are dropwise added whereby the amount of precipitate increases. After stirring a certain time 8.9 g. of 1-hydroxy-4-chloro-2-naphthoic acid are added and the new mixture is refluxed for 20 min. This condensation is an application of the reaction type described in J. Am. Chem. Soc. 74 (1952), 5304–9. The benzene is removed by steam distillation. On cooling, the reaction mixture, a solid N-(o-cetylmercaptophenyl)-1-hydroxy-4-chloro-2-naphthoic acid amide is formed in the aqueous layer of the mixture. This product is sucked off and washed with a sodium bicarbonate solution. To purify the product it is recrystallized from isopropanol. Melting point: 83–84° C.

II. Preparation of N - (p-cetylmercaptophenyl)-1-hydroxy-4-chloro-2-naphthoic acid amide:

111 g. of p-mercapto-acetanilide (prepared according to J. Org. Chem. 15 (1950) 405) and 203 g. of cetylbromide are dissolved in 825 cm.^{3} of methyl Cellosolve. This mixture is refluxed whilst stirring whereafter 40 g. of potassium hydroxide dissolved in 175 cm.^{3} of methyl Cellosolve are dropwise added to the mixture. A potassium bromide precipitate is formed and after the addition of the potassium hydroxide the reaction mixture is still refluxed whilst stirring for 30 min. whereafter 250 cm.^{3} of water are added thereto. The formed p-cetylmercapto-acetanilide crystallizes and is recrystallized from a mixture of methanol and methyl Cellosolve. Melting point: 99–100° C.

29.3 g. of the synthetized (p-cetylmercapto-acetanilide) is refluxed for 3 h. in 500 cm.^{3} of absolute ethanol with 5 equivalent of dried hydrogen chloride gas. On cooling the mixture, crystals of p-cetylmercapto-aniline-hydrochloride are formed. These crystals are recrystallized from a mixture of methanol and methyl Cellosolve. Melting point: 130–132° C.

14.75 g. of the hydrochloride and 7.75 g. of triethylamine are mixed with 100 cm.^{3} of anhydrous benzene whereby a gelatinous precipitate of treiethylamine hydrochloride is formed. The reaction mixture is cooled by means of ice and 6.7 g. of o-phenylenechlorophosphite are dropwise added. The gelatinous precipitate of triethylamine hydrochloride increases and stirring is continued for a little while. Thereupon 8.5 g. of 1-hydroxy-4-chloro-2-naphthoic acid are added to the mixture, the new mixture is refluxed for 20 min., the reaction mixture is poured into hot water, the benzene layer is washed with a saturated sodium bicarbonate solution and hot water and the benzene is evaporated to dryness under vacuum till a precipitate is formed which is composed of N - (p-cetylmercaptophenyl)-1-hydroxy-4-chloro-2-naphthoic acid amide. By adding n-hexane, the naphthoic acid amide is completely precipitated. The product is sucked off whereafter it is purified by recrystallizing from a mixture of methanol and methyl Cellosolve. Melting point: 110° C.

III. The preparation of N - (2′ - cetylmercapto-5′-sulfophenyl)-1-hydroxy-4-chloro-2-naphthoic acid amide sodium salt is described in the Belgian patent specification 590,934 (preparation 6).

IV. The preparation of N - (2′ - cetylmercapto-5′-sulfophenyl-1-hydroxy-4-bromo-2-naphthoic acid amide sodium salt is described in the Belgian patent specification 590,934 (preparation 5).

V. The preparation of N-(3′-sulfo-4′cetylmercapto) phenyl-1-hydroxy-4-sulfo-2-naphthoic acid amide disodium salt is described in the Belgian patent specification 590,934 (preparation 8).

To carry out the method according to the present invention, the color couplers must be incorporated into a photographic silver halide emulsion which in its turn is incorporated into a material having one or more layers. The color couplers can be incorporated into said emulsions by means of the usual colloids such as gelatin, polyvinyl alcohol, collodium or other natural or synthetic colloids such as e.g. those prepared according to the Belgian patent specification 568,153. The silver halide emulsions can be applied to a support consisting of paper, glass, nitrocellulose, cellulose esters such as cellulose triacetate, polyester, polystyrene or an other natural or synthetic resin. This multilayer material is usually composed of the following layers: a support, a red-sensitive emulsion layer having a color coupler for cyan, a green light-sensitive emulsion layer with color coupler for magenta and a blue-light sensitive emulsion layer having a color coupler for yellow. Between the blue-light sensitive and the green-light-sensitive emulsion layer, there is a yellow filter layer which in most cases consists of colloidal silver.

It is not only possible to incorporate the new color couplers into the light-sensitive silver halide emulsion layer itself but they can also be incorporated into an adjacent non-light-sensitive colloid layer or into a non-light-sensitive layer which is separated from the light-sensitive emulsion layer by a water-permeable colloid layer.

The following aromatic amino-compounds can be used as developers for such material: mono-, di- and triamino-aryl compounds, more especially N,N-dialkyl-p-phenylene diamine and its derivatives such as N,N-dialkyl-N′-sulphomethyl- or carboxymethyl p-phenylenediamine. As useful mono-amino-developer, aminophenols and amino-cresols, or their halogen derivatives and also the amino-naphthols are considered.

The following examples illustrate the present invention without limiting, however, the scope thereof. We draw the attention to the fact that all the amounts mentioned hereafter are parts of weight when no other indication is given.

Example 1

10 parts of N-[(2′-cetylmercapto-5′-sulfo)phenyl]-1-hydroxy-4-bromo-2-naphthoic acid amide sodium salt are wetted with 40 parts of ethanol. The whole is dissolved by adding 20 parts of water and by heating at 40° C. This solution is diluted with water up to 200 parts till obtaining a 5% solution. 200 parts of this color coupler solution and 260 parts of water are added to 500 parts of silver bromo-iodide gelatin emulsion (2% iodide). After adding the usual additives such as hardening agents and wetting agents the emulsion obtained is coated onto a photographic support. After drying, the photographic material is exposed and treated with a developing solution of the following composition:

	G.
N,N-diethyl-p-phenylenediamine hydrochloride	2.75
Sodium sulphite	2
Potassium carbonate	75
Potassium bromide	0.5
Hydroxylamine hydrochloride	1.2
Sodium hexametaphosphate	1.0
Water to 1000 cm.^{3}.	

This material is rinsed for 30 seconds and fixed in a fixing bath of the following composition:

	G.
Sodium thiosulphate (dry)	200
Borax	8
Sodium sulphite	25
Potassium alum	15
Boric acid	7.5
Water to 1000 cm.^{3}.	

Now the material is rinsed for 10 min. and bleached in a bath of the following composition:

	G.
Potassium ferricyanide	100
Potassium bromide	25
Borax	20
Boric acid	5
Water to 1000 cm.^{3}.	

Finally the material is rinsed for 5 min. and fixed in a bath of the following composition:

	G.
Sodium thiosulphate (dry)	130
Sodium sulphite	10
Sodium carbonate	14
Water to 1000 cm.^{3}.	

As a result of the foregoing treatments, an intense cyan image with low side-absorptions in the green range is obtained.

Example 2

10 parts of N - (2-cetylmercapto-5-sulfophenyl)-1-hydroxy-4-chloro-2-naphthoic acid amide sodium salt are wetted with 20 parts of ethanol dissolved into 180 parts of water. Now the color coupler solution is incorporated into the emulsion according to Example 1. The material is exposed and treated in the same way as described in Example 1. A cyan image is obtained which shows low side-absorptions.

Example 3

10 parts of N-(o-cetylmercaptophenyl)-1-hydroxy-4-chloro-2-naphthoic acid amide are wetted with 30 parts of ethanol and dissolved in 25 parts of 1 N sodium hydroxide and 145 parts of water. The color coupler solution is brought into the emulsion as described in Example 1. The emulsion is neutralized by 7.5 parts of acetic acid N/2 per 100 parts of color coupler solution. After exposure, the material is treated according to Example 1 whereby in the color developing bath 4-amino-N-ethyl-N - (β - methylsulfonamidoethyl)-m-toluidine - sesquisulphate monohydrate is substituted for N,N-diethyl-p-phen-

ylenediamine hydrochloride. A cyan image with low side-absorptions is obtained.

Example 4

200 parts of a 5% solution of N-(p-cetylmercaptophenyl)-1-hydroxy-4-chloro-2-naphthoic acid amide in a mixture of ethanol and water (3:7) and 260 parts of water are added to 500 parts of a red-sensitized silver bromo-iodide emulsion (2% iodide). This emulsion is coated on a support. After exposure, color development and further treatment according to Example 1, an intense cyan image with low side-absorptions is obtained.

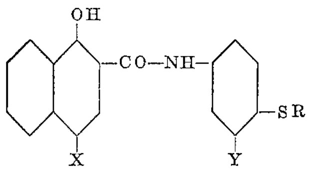
Example 5

200 cm.^{3} of a solution 5% of N-(4-cetylmercapto-5-sulfophenyl)-1-hydroxy-4-sulfo-2-naphthoic acid disodium salt (10 g. of color coupler dissolved in 20 cm.^{3} of ethanol and 30 cm.^{3} of sodium hydroxide N/2 diluted with water to 200 cm.^{3}) are added to 500 cm.^{3} of a red-sensitized silver bromo-iodide emulsion (2% iodide). After acidification with acidic acid N/2 to a pH 6.5, the total volume of the emulsion is brought to 1 l. This emulsion is coated onto a support which alreay is coated with an antihalation layer. To this emulsion layer is applied a gelatin intermediate layer on which is coated a green-light-sensitive emulsion layer with color coupler for magenta and covered with a yellow filter layer consisting of a thin gelatin layer containing colloidal silver. On this filter layer is then coated a blue-light-sensitive emulsion layer with a color coupler for yellow. This layer is coated with an antistress layer. The photographic material obtained is dried, exposed and color developed according to Example 1. In this way an image with a subtractive color reproduction of the original is obtained which has an increased transparency in the green.

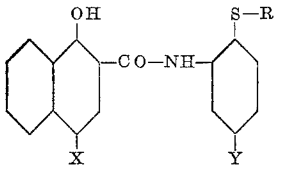
The term "methyl Cellosolve" is a registered trademark for (ethylene glycol monomethyl ether) manufactured by Union Carbide and Carbon, New York, and is used in the foregoing specification.

We claim:

1. Process for obtaining a colored photographic image in a red light-sensitive emulsion layer containing a reducible silver salt, comprising exposing said layer and developing same with a primary aromatic amino developing agent in the presence of 1-hydroxy-2-naphthoic acid anilide color coupler for cyan selected from the group consisting of compounds having the formulae:



and



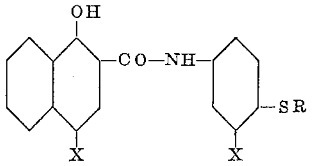
wherein

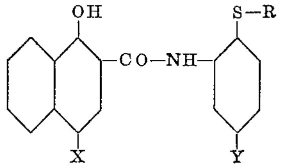
X is selected from the group consisting of a bromine atom and chlorine atom,

Y represents a member selected from the group consisting of a hydrogen atom, a sulfonic acid group and a sulfonate group, and

R is a hydrocarbon radical having a chain length of about 5–20 carbon atoms and sufficient to render said color coupler resistant to diffusion.

2. Light-sensitive element comprising a red light-sensitive silver halide emulsion layer and a 1-hydroxy-2-naththoic acid anilide color coupler for cyan for said layer, said color coupler being selected from the group consisting of compounds having the formulae:





wherein

X is selected from the group consisting of a bromine atom and a chlorine atom,

Y represents a member selected from the group consisting of a hydrogen atom, a sulfonic acid group and a sulfonate group, and

R is a hydrocarbon radical having a chain length of about 5–20 carbon atoms and sufficient to render said color coupler resistant to diffusion.

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