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1-HYDROXY-2-NAPHTHAMIDE COUPLERS FOR COLOR PHOTOGRAPHY

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4 Claims. (Cl. 96—100)

This invention relates to color photography and to compounds which form dyes on coupling with a developing agent to produce colored images. In particular my invention relates to coupler compounds for forming cyan dye images and to photographic emulsions containing such couplers.

It is known to produce colored photographic images wherein a color former or coupling component reacts with the oxidation product of a primary aromatic amino developing agent. In processes of this type the subtractive method of color formation is ordinarily employed with the result that the photographic images so obtained are composed of the subtractive primary colors, i.e., cyan, magenta and yellow. It is the common practice to use phenols or naphthols for producing cyan images and pyrazolones for magenta images, whereas open chain reactive ketomethylene compounds serve as a source of the yellow dye images.

The present invention is concerned with naphthol couplers and with cyan images produced on color development therefrom.

In a multilayer color photographic element the red sensitive layer contains a color former which on color development produces a cyan dye image. Since the function of the cyan dye image is to filter or regulate the amount of the red absorption in a color transparency or print, it is obvious that the cyan image should not absorb significantly in the blue and green portions of the spectrum. Ideally, a cyan dye should have a spectral absorption which lies at 660–670 mμ with virtually no absorption in the blue and the green.

There have been numerous proposals of coupler structures which on color development yield cyan dye images approximating the aforedescribed spectral characteristics. For instance, cyan dye forming couplers are known which are derivatives of 1-hydroxy-2-naphthamide in which the hydrogen atoms on the amide linkage have been replaced by a wide variety of substituents. For example, an aryl-1-hydroxy-2-naphthamide coupler yields on color development a dye that absorbs around 690 mμ and is therefore too far in the red portion of the spectrum. The alkyl naphthanilides on the other hand fall short of the desired spectral absorption and the structures form dyes, the absorption of which usually falls within the range of 630–640 mμ. Mixed substituents of alkyl and aryl groups have likewise been prepared, but these couplers give rise to dye images absorbing too much light in the shorter wave lengths.

Aside from their spectral properties, dyes composing photographic images must also possess other properties peculiar to the photographic art. Thus, it is essential that photographic dye images endure varying conditions of light, heat and humidity and the couplers themselves must possess stability and not give rise to various stains or discoloration of the final prints or transparencies. It can thus be seen that a color coupler and the dyes produced therefrom must be possessed of certain specific properties before they are suitable for use in color photography.

It is, therefore, a primary object of this invention to provide novel photographic coupler compounds capable of producing cyan dye images on color development.

It is a further object of this invention to provide coupler

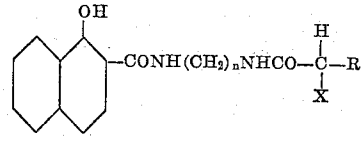
compounds which produce cyan dye images characterized by a high degree of red absorption while simultaneously displaying little or no absorption in the blue or green portions of the spectrum. It is a still further object to provide coupler compounds which produce dyes having a high degree of resistance to light, heat and excessive humidity.

Other objects will appear as the description proceeds.

The aforesaid objects are accomplished according to my invention by the use of certain 1-hydroxy-2-naphthamide coupler compounds containing in the amide portion thereof a long aliphatic chain for rendering the couplers non-diffusing in photographic emulsions.

Couplers of this type can be depicted by the following general formula:

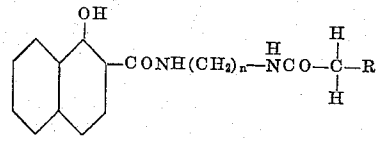
(I)



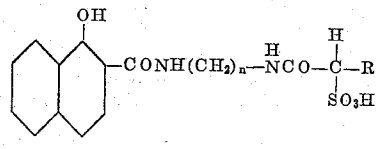
wherein n is an even integer such as 2, 4, 6 etc. and R represents a non-diffusing aliphatic group of from 8 to 20 carbon atoms and X represents hydrogen or a solubilizing or salt forming group such as a sulfo radical, a carboxylic acid radical etc.

Couplers falling within the ambit of the above general formula can be further divided into two sub-generic structural types: (1) hydrophilic couplers characterized by the presence of a solubilizing group; and (2) lipophilic couplers soluble in oily solvents. These sub-generic structures can be represented by the following two general formulas:

(II)



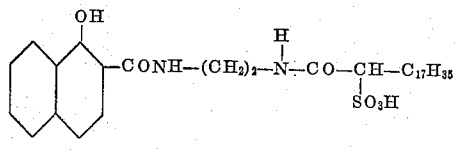
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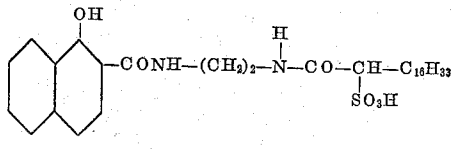
wherein n has the values given above. It is to be understood that Formula III also includes the ammonium and alkali salts thereof.

Couplers falling within the ambit of the formula include the following structures:

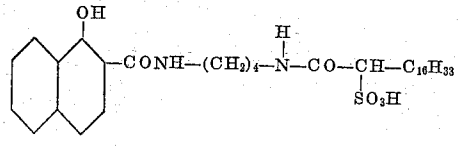
(1)



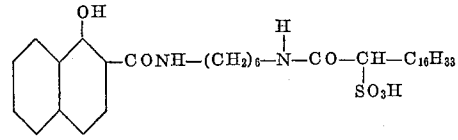
(2)



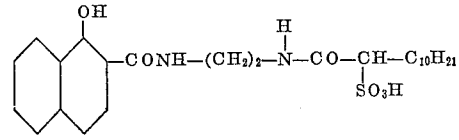
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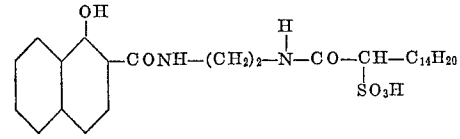
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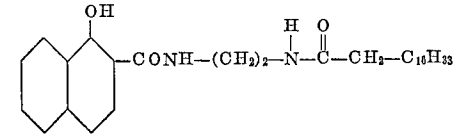
(5)



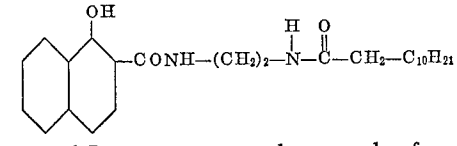
(6)



(7)



(8)



In general I prepare my novel cyan color formers by reacting 1-hydroxy-2-phenylnaphthoate with an alkylene diamine in a 1:1 mole ratio whereby is produced an N-aminoalkyl 1-hydroxy-2-naphthamide. This latter intermediate is then reacted with a higher alkanoic acid or acid halide thereof in order to acylate the amino group of the N-aminoalkyl 1-hydroxy-2-naphthamide with concomitant production of a naphthol-2-naphthamide coupler containing a non-diffusing chain attached to the terminal amino group.

In the event it is desired to produce a hydrophilic type coupler, then the intermediate N-aminoalkyl naphthamide is reacted with an α-sulfo higher alkanoic acid of from 10 to 20 carbon atoms employing, for instance, the well-known phosphazo reaction. If, on the other hand, it is desired to obtain a lipophilic color former, then the N-aminoalkyl 1-hydroxy-2-naphthamide is reacted with the unsubstituted higher chain alkanoic acid or the acid chloride thereof.

Suitable higher carboxylic acid derivatives which I have found suitable for practicing the invention include the following: caprylic acid, pelargonic acid, capric acid, undecylic acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, margaric acid, stearic acid and the like.

In the event that it is desired to use the α-sulfo alkanoic acid these entities are well-known in the chemical art and are, furthermore, commercially available. In general their preparation involves reacting the alkanoic acid with sulfur trioxide in a suitable solvent whereby introduction of the α-sulfo group is effected. α-Sulfocarboxylic acids are bi-functional acids and can react to give mono or dialkyl salts, ester amides or combinations of the reaction products. The α-sulfo alkanoic acids contain a strongly ionized sulfonic acid group in combination with a comparatively weakly ionized carboxylic group. Salt formation, for example, will occur first and completely at the stronger sulfonic acid group leaving a free carboxylic acid group if so desired. For further information on these chemical intermediates, reference is made to "Technical Bulletin G–7R1," March 20, 1957, and published by the Armour Industrial Chemical Company, Division of Armour & Company, 110 North Wacker Drive, Chicago 6, Illinois.

The alkylene diamines, which are reacted with 1-hydroxy-2-phenyl naphthoate to produce the requisite N-aminoalkyl 1-hydroxy-2-naphthamide intermediates, are also well-known chemical entities and are fully described in the technical literature. Alkylenediamines which we have found suitable for practicing the invention include ethylenediamine, tetramethylenediamine, hexamethylenediamine and the like.

The following are illustrative of the preparation of the couplers described herein, but such examples are not to be taken as limiting or in any way restricting the invention.

Example I

Compound 2 was prepared in the following manner.

(1) 115 g. (0.5 mole) ethylenediamine - 1 - hydroxy - 2-naphthamide (Intermediate I),
(2) 202.5 g. (0.5 mole) α-sulfostearic acid,
(3) 400 ml. dry pyridine,

and (4) 800 ml. benzene were charged into a round bottom 3-necked 5 liter flask. The flask was equipped with a dropping funnel, a stirrer and a water trap (Dean-Stark type) and a condenser with a drying tube. The mixture was refluxed (electric heating mantle) until all traces of moisture were removed. This required about 2 hours. Rapid stirring was used to prevent excessive foaming. The mixture was cooled to about 5° C. in an ice water bath and a solution of 55 ml. of PCl_3 in 100 ml. of dry benzene was added dropwise over a period of about 30 minutes. The mixture was stirred rapidly during the addition and stirring was continued for 2 hours at room temperature, followed by refluxing on a steam bath for 2½ hours.

A solution of 80 g. of sodium carbonate monohydrate and 150 g. of sodium acetate (anhydrous) in 500 ml. of water was added and the mixture refluxed for 5 minutes. After cooling to 30–35° C., the mixture was transferred to a separatory funnel and the organic phase separated. Two hundred ml. of benzene were added and the layer was washed 3 times with saturated salt solution. The solvent was removed by distillation at normal pressure until the distillate was free of water, then by distillation at reduced pressure (1–2 mm.) until all the benzene and pyridine were removed. The residue was crystallized from propanol (6 ml. per 1 g. of residue) and treated with decolorizing charcoal (5% by weight). The yield after two recrystallizations=160–180 g. The material was dried at reduced pressure (1–5 mm. Hg). For further purification (to insure the removal of photo-active impurities) it was dissolved in 80% acetic acid, (2 ml. of 80% acetic acid per 1 g. of color former) cooled and precipitated with 6 N.HCl (4 ml. per 1 g. of color former). The aqueous layers were decanted and the syrup transferred to a round bottom flask. To the syrup were added a 10 fold amount of benzene, based on amount of color former, and all the water was removed by azeotropic distillation. The benzene was removed by distillation under reduced pressure. The dry residue was dissolved in the 6 fold amount of n-propanol, filtered and the filtrate distilled to dryness. The residue was finally dried on a steam bath at 0.1 mm. Hg and then powdered. Yield 120–135 g.

The N-aminoethyl-1-hydroxy-2-naphthoate used in the above described preparation was obtained as follows:

(*a*) 180 g. (3 mole) of ethylenediamine (98%)
(*b*) 264 g. (1 mole) of phenyl-1-hydroxy-2-naphthoate
(*c*) 2000 ml. benzene

(*a*) and 1000 ml. of benzene were charged into a 5 liter 3-necked flask equipped with a dropping funnel, stirrer, condenser and thermometer. The amine-benzene mixture was heated to 50° C. on a steam bath and a solution of (*b*) phenyl-1-hydroxy-2-naphthoate in (*c*) was added slowly (temperature maintained at 50° C.). After the addition was completed, the temperature was kept at 50° C.

for 1 hour and then refluxed for 1 hour. On cooling, the solid was filtered, washed and crystallized from propanol using ether as the final wash solvent. Yield=135 g.; M.P. 161–163° C.

Example II

Using the procedure as given above for Example I, compound 6 was prepared excepting that α-sulfopalmitic acid was substituted for α-sulfostearic acid.

As disclosed elsewhere the color-forming components described herein are of the non-diffusing variety, that is, they are designed to be incorporated directly in the silver halide emulsion. The methods employed for combining color couplers in a photographic emulsion are known and described in the prior art and such methods are applicable to the couplers of the present invention. In the event that color-forming components include a solubilizing group as represented by a sulfo substituent, such entities can be used in the form of their soluble salts as, for example, their alkali metal salts which are miscible with aqueous solutions of colloids of the type commonly employed as carriers for silver halide emulsions. As previously pointed out, the couplers described herein may be of the lipophilic or hydrophobic variety. In the latter instance, the couplers are advantageously dissolved in a high boiling organic water immiscible oily solvent and the resulting solution dispersed or homogenized in the silver halide emulsion. For instance, a solution of 1.5 g. of the coupler is dissolved in 6.0 g. of a mixture consisting of 50 parts of phenyl alcohol, 40 parts of tricresyl phosphate and 10 parts of n-butylphthalate, and the resulting solution dispersed in 20 milliliters of 6% gelatin solution containing 0.05 ml. of lauryl sulfate as a surfactant. Emulsification is effected by high speed agitation in a small Waring Blendor.

The coupler dispersion is then mixed with 50 g. of a melted silver halide gelatin emulsion and then coated on a suitable support, set and dried in the usual manner. On exposure and development of the coatings with a primary aromatic amino developing agent and subsequent removal of the silver image, a brilliant cyan dye image is obtained, the principal absorption being in the highly desired 660–670 mμ of the visible spectrum while simultaneously showing little or none of the undesirable absorption in the green portion of the spectrum.

Various photographic developing agents can be employed with the couplers of my invention. The primary aromatic amino developing agents are generally suitable including the phenylenediamines and aminophenols. Suitable compounds are 4-aminoaniline, 4-ethylaminoaniline, 4-dialkylaminoaniline, e.g., 4-dimethyl-aminoaniline, 4-diethylaminoaniline, 4-[N-(β-hydroxyethyl)-N-ethyl] amino aniline, 4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-2-methylaniline sulfate, and the like. The above developing agents are preferably used in the form of their salts such as the hydrochloride or hydrosulfate as they are more soluble and stable than the three bases. All of these compounds have a primary amino group which enables the oxidation product of the developer to couple with the color compounds to form dye images. After removal of the silver image by bleaching and fixing in a manner well-known to the art, the color image remains in the emulsion.

A suitable developing solution can be prepared as follows:

	G.
2-amino-5-diethylaminotoluene	2
Sodium carbonate (anhydrous)	20
Sodium sulfite (anhydrous)	2
Potassium bromide	0.2
Water to make 1 liter.	

The exposed silver-halide emulsions containing the color formers are developed in the above solution in the usual manner.

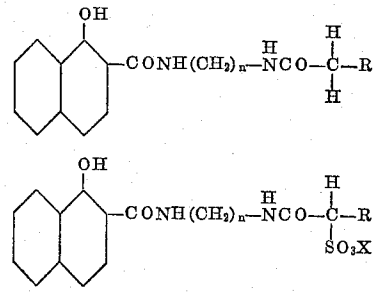
The photographic dye images produced from my couplers can be contained in the usual colloidal carriers such as layers of gelatin or similar water permeable carriers and in this connection mention is made of albumen, organic esters of cellulose, polyvinyl alcohol, carboxyl methyl cellulose, starch, casein and the like. The carrier may be supported by a transparent medium such as glass, a cellulose ester or synthetic resin, or a non-transparent reflecting medium as represented by paper or an opaque cellulose ester containing suspended pigment. The emulsion may be coated as a single layer on a support or as one of a number of superimposed layers, or one of both sides of the support. The various layers may be differently sensitized to specific portions of the electromagnetic spectrum by the use of optical sensitizing dyes such as the well known cyanine dyes. The sensitization of silver-halide emulsions is described in detail in the photographic literature.

As above pointed out, the coupler structures of the type described herein yield on color development cyan dye images having their principal absorption between 660–670 mμ while exhibiting very little absorption below 560 mμ. These spectral properties are extremely valuable and useful in color photography.

It will be understood that the examples and modifications set forth herein are illustrative only and my invention is to be taken as limited only by the scope of the appended claims.

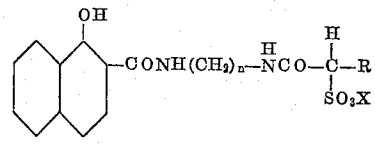
I claim:

1. A light sensitive silver halide photographic emulsion containing a coupler selected from the class represented by those of the following formulae:



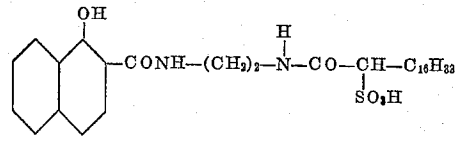
wherein R is an alkyl group of from 8 to 20 carbon atoms, *n* is an even integer ranging from 2 to 6, and X is selected from the class consisting of hydrogen, ammonium and alkali metal.

2. A light sensitive silver halide photographic emulsion containing a coupler represented by the following formula:

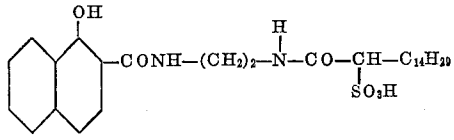


wherein R is an alkyl group of from 8 to 20 carbon atoms, *n* is an even integer ranging from 2 to 6, and X is selected from the class consisting of hydrogen, ammonium and alkali metal.

3. A light sensitive silver halide photographic emulsion containing a coupler represented by the following formula:



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



References Cited in the file of this patent

UNITED STATES PATENTS

2,694,718	Salminen et al.	Nov. 16, 1954
2,710,803	Salminen et al.	June 14, 1955
2,829,975	Popeck et al.	Apr. 8, 1958
2,848,326	Whitmore	Aug. 19, 1958
3,080,233	Roth et al.	Mar. 5, 1963

FOREIGN PATENTS

1,146,556	France	Nov. 13, 1957