United States Patent Office

2,993,791

Patented July 25, 1961

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2,993,791
COLOR COUPLERS CONTAINING LONG CHAIN ALKYLAMINOISOPHTHALICESTER GROUPS

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No Drawing. Filed Oct. 31, 1957, Ser. No. 693,509
9 Claims. (Cl. 96—55)

This invention relates to color photography and particularly to color-forming compounds.

The use in color photography of color-forming compounds, which react with the oxidation or development product of primary aromatic amino developing agents to form colored images upon photographic development, is well-known. The colored compound thus formed is deposited next to the silver grains of the silver image during development. The coupler compounds as employed above may be added to the color developer solutions or they may be incorporated in the gelatino silver-halide emulsion.

When used in photographic emulsions, the couplers may be dissolved directly in the gelatin or other hydrophilic colloid. In such case, the couplers must have groups rendering them alkali soluble such as carboxylic acid or sulfonic acid groups.

Alternately, the couplers may be incorporated in a photographic emulsion by dissolving them in a water-immiscible or oily organic solvent and dispersing the resulting solutions in the photographic emulsion.

In the manufacture of emulsions containing couplers, considerable difficulty is encountered in obtaining couplers of high purity, particularly couplers containing carboxylic or sulfonic acid groups. In the case of couplers that are added to emulsions in the form of dispersions, problems are experienced in obtaining couplers of sufficient solubility in organic solvents. Similarly, many couplers have a tendency to diffuse in the medium in which they are incorporated. Finally, many of the couplers mentioned in the prior art give rise to colored photographic images of undesirable spectral characteristics.

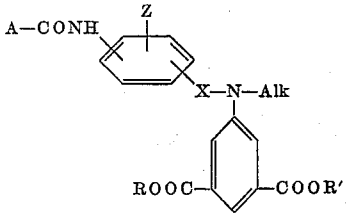
It is, therefore, an object of the present invention to provide color formers which can be readily purified by recrystallization.

A further object is to provide color formers which can be incorporated in gelatin emulsions either directly or by dispersing a solution of the coupler in organic solvents.

A still further object is to provide color couplers which are fast to diffusion in the emulsion.

Other objects will appear herein as the description proceeds.

These objects are realized by using a color coupler containing a 5-alkylaminoisophthalic acid radical. The alkyl group contains at least 10 carbon atoms. These couplers have a high solubility in solvents used for the preparation of dispersion of color formers, low melting points, and though they often have a low tendency toward crystallization, they can be easily prepared in high purity. The couplers of our invention have the following general formula:



wherein A represents that part of the coupler molecule

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containing the functional or reactive group which reacts with the oxidation products of the primary amino aromatic developing agents to yield color images, said reactive groups comprising a reactive methylene group, such as ketomethylene, i.e., —CO—CH_2—CO—;

—CO—CH_2—CN—

—CO—CH_2—C(=N)—

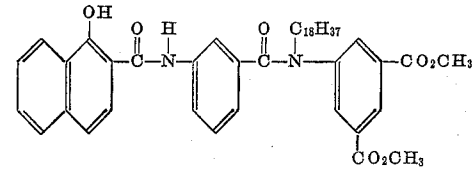
etc., or a reactive phenolic hydroxyl group, e.g.,

—C(OH)=C—

e.g., phenols and naphthols, which are reactive in the ortho or para position relative to the hydroxyl group; X represents a —CO— or —SO_2— group; Z represents hydrogen, halogen, e.g., chlorine, bromine and iodine, an alkyl group, e.g., methyl, ethyl, n-propyl, n-butyl, isobutyl, n-amyl, n-hexyl, etc., an aryl group, e.g., phenyl, halophenyl, e.g., chlorophenyl, bromophenyl, etc., naphthyl, etc., an alkoxyl group, e.g., methoxy, ethoxy, n-propoxy, n-butoxy, etc.; R and R' are short chain alkyl groups such as methyl or ethyl and Alk is an alkyl group of at least 10 carbon atom, i.e., decyl, dodecyl, tetradecyl, octadecyl, etc.

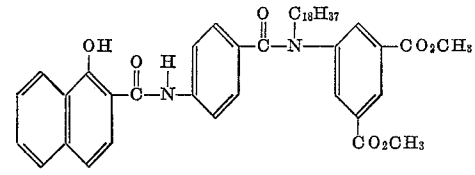
The following compounds illustrate the isophthalic esters which may be used according to our invention.

(1)



and the corresponding dicarboxylic acid and its water-soluble salts, i.e., sodium, potassium, ammonium, etc.

(2)



and the corresponding dicarboxylic acid and its water-soluble salts, i.e., sodium, potassium, ammonium, etc.

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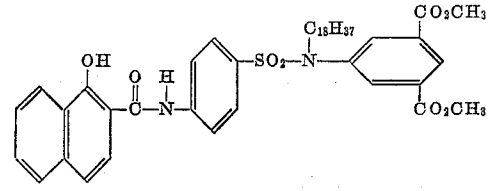

and the corresponding dicarboxylic acid and its water-soluble salts, i.e., sodium, potassium, ammonium, etc.

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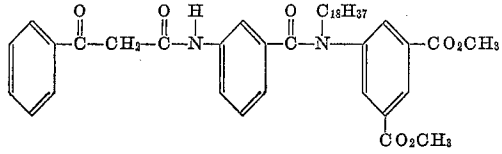

and the corresponding dicarboxylic acid and its water-soluble salts, i.e., sodium, potassium, ammonium, etc.

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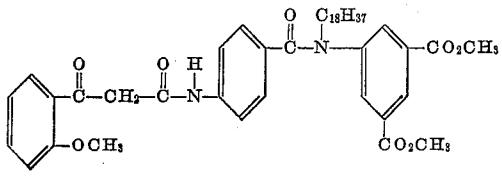

and the corresponding dicarboxylic acid and its water-soluble salts, i.e., sodium, potassium, ammonium, etc.

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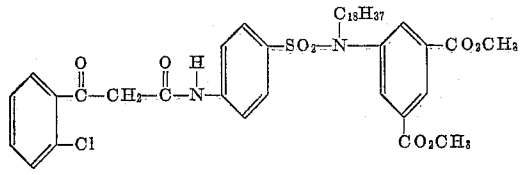
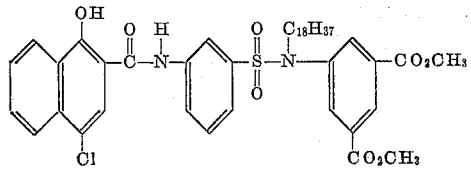


and the corresponding dicarboxylic acid and its water-soluble salts, i.e., sodium, potassium, ammonium, etc.

(7)



and the corresponding dicarboxylic acid and its water-soluble salts, i.e., sodium, potassium, ammonium, etc.

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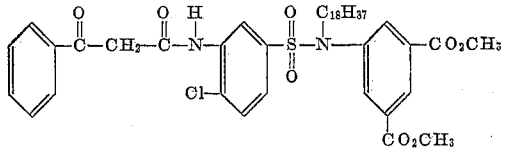

and the corresponding dicarboxylic acid and its water-soluble salts, i.e., sodium, potassium, ammonium, etc.

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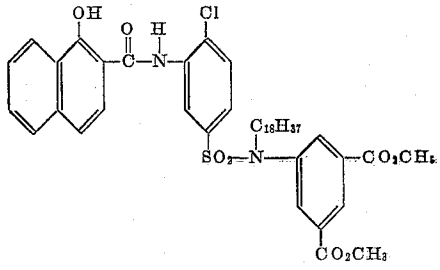

and the corresponding dicarboxylic acid and its water-soluble salts, i.e., sodium, potassium, ammonium, etc.

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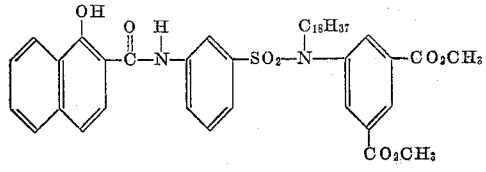
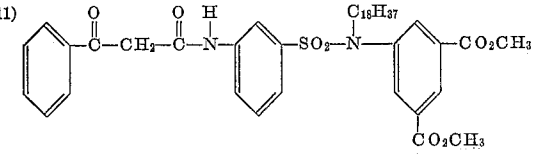


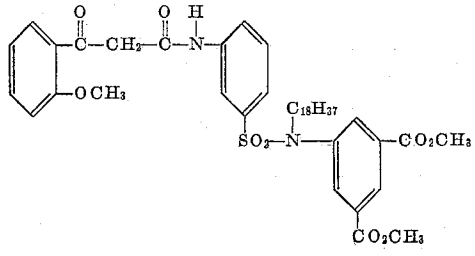
and the corresponding dicarboxylic acid and its water-soluble salts, i.e., sodium, potassium, ammonium, etc.

(11)



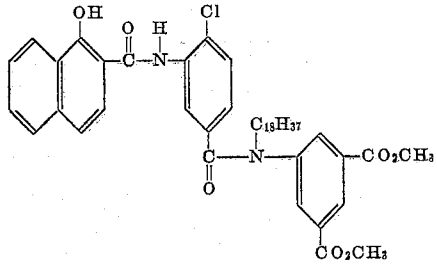
and the corresponding dicarboxylic acid and its water-soluble salts, i.e., sodium, potassium, ammonium, etc.

(12)



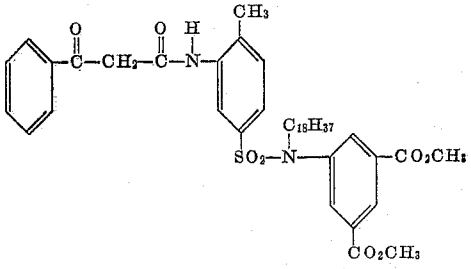
and the corresponding dicarboxylic acid and its water-soluble salts, i.e., sodium, potassium, ammonium, etc.

(13)



and the corresponding dicarboxylic acid and its water-soluble salts, i.e., sodium, potassium, ammonium, etc.

(14)



and the corresponding dicarboxylic acid and its water-soluble salts, i.e., sodium, potassium, ammonium, etc.

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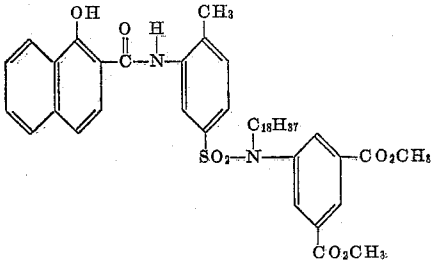
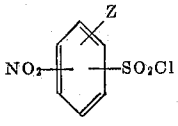
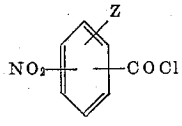


and the corresponding dicarboxylic acid and its water-soluble salts, i.e., sodium, potassium, ammonium, etc.

The compounds hereof are prepared by condensing a 5-alkylaminoisophthalate with an acid chloride or sulfonylchloride of the following general formulae:



or



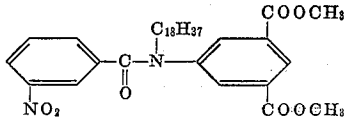
with Z representing the same groups as above. The condensations are advantageously carried out in an inert solvent like benzene or xylene at elevated temperatures so that the hydrogen chloride formed during the reaction is discharged immediately. After reduction of the nitro group, the resulting amine is condensed with a carboxylic acid derivative of the color-forming residue by known methods. Naturally, the esters can be hydrolyzed and their carboxylic acids used as color formers in the same way as used herein. The above compounds may be used in the form of their esters or their acids. If the esters are employed, they are dissolved in a suitable solvent such as a mixture of 50 parts phenethyl alcohol, 40 parts of tricresyl phosphate and 10 parts of n-butyl phthalate and the resulting solution incorporated in the emulsion as a fine dispersion. If the acids are employed, they are

introduced into the emulsion directly as an alkali metal salt such as the sodium salt.

Example I

Compound (1) is prepared as follows:

Dimethyl 5-(3-nitro-N-octadecylbenzamido)isophthalate

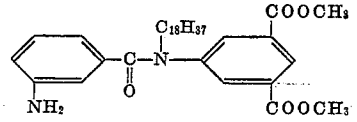


46.1 grams (0.1 mole) of 1,3-dimethyl-5-octadecylaminoisophthalate was dissolved in 200 ml. of toluene by warming. After addition of 19.5 g. (0.105 mole), of 3-nitrobenzoyl chloride and 1 drop of pyridine, the mixture was refluxed overnight. The development of hydrogen chloride was vigorous in the beginning and had ceased completely by the next morning.

The solvent was evaporated in vacuum on a steam bath and the reesidue recrystallized from methanol. Yield 54 g., M.P. 70° C.

Analysis: Calc.—68.90% C, 8.20% H. Found—68.86% C, 8.26% H.

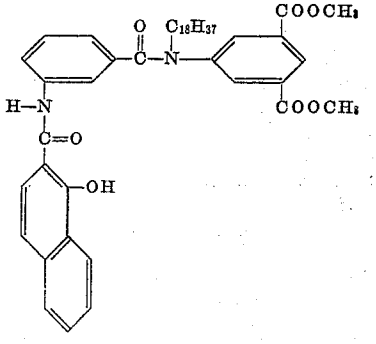
Dimethyl 5-(3-amino-N-octadecylbenzamido)isophthalate



80 grams of the foregoing product was hydrogenated with platinum oxide in 100 ml. of methanol at 50° C. More methanol was added and the solution filtered hot from the catalyst and a small quantity of an insoluble white residue. The solvent was evaporated on a steam bath in vacuum. Yield 66 g. of a slightly brownish viscous oil.

Analysis: Calc.—72.40% C, 8.96% H. Found—72.22% C, 9.17% H.

1-hydroxy-3′-[N-(3,5-dicarbomethoxyphenyl)-N-(octadecyl) carbamyl]-2-naphthanilide



18.3 grams (0.03 mole) of the foregoing product and 9 g. (0.033 mole) of phenyl 1-hydroxy-2-naphthoate were heated in vacuum to 160–170° C. for 2 hours. 2.3 grams of phenol was distilled off.

The residue was recrystallized from methanol with the addition of some Norite A. Yield 18.1 g., M.P. 107–108° C.

Analysis: Calc.—73.60% C, 7.73% H, 3.74% N. Found—73.56% C, 7.75% H, 3.54% N.

Example II

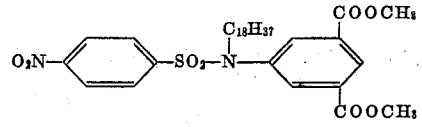
Compound (2) was prepared in the same way as Compound (1) while substituting the isomeric p-nitrobenzoyl chloride for the m-nitrobenzoyl chloride.

Compound (2) melted at 139–140° C.

Example III

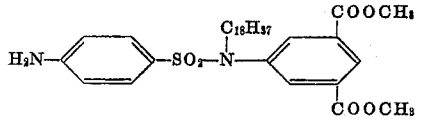
Compound (3) was prepared as follows:

Dimethyl 5-p-nitro-N-octadecylphenylsulfonamidoisophthalate



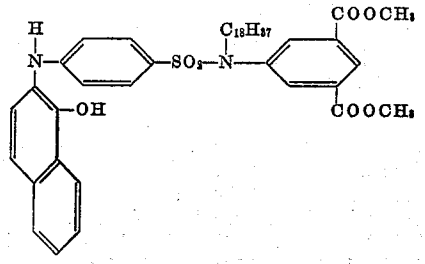
Dimethyl 5-octadecylaminoisophthalate was condensed with 4-nitrobenzenesulfonyl chloride in refluxing xylene according to Example I. The condensation product melted at 91–91.5° C.

Dimethyl 5-p-amino-N-octadecylphenylsulfonamidoisophthalate



The nitro compound was reduced to the corresponding amine using platinum oxide as catalyst; M.P. 91–91.5° C.

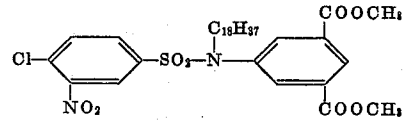
N′-(3,5-dicarbomethoxyphenyl)-N′-octadecyl-N⁴-(1-hydroxy-2-naphthyl)sulfanilamide



The final compound was prepared by condensing phenyl 1-hydroxy-2-naphthoate with dimethyl 5-p-amino-N-octadecylphenylsulfonamidoisophthalate employing the procedure of Example I. The condensation product melted at 136–137° C.

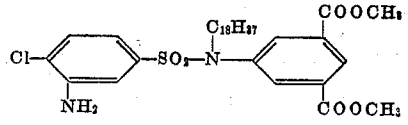
Example IV

Dimethyl 5-(4-chloro-3-nitrophenyl-N-octadecylsulfonamido) isophthalate



In a 1 liter 3-necked flask, equipped with a reflux condenser and stirrer was placed a solution of 92.4 g. (0.2 mole) of octadecylaminoisophthalic acid dimethyl ester in 500 ml. of dry toluene. 5 drops of pyridine was added followed by 51.2 g. (0.2 mole) of 4-chloro-3-nitrobenzenesulfonyl chloride. The solution was refluxed for 18 hours and the solvent then removed at reduced pressure. The 4-chloro-3-nitrobenzenesulfonyl chloride used above was prepared from the potassium salt of the corresponding acid using phosphorous pentachloride as the chlorinating agent and phosphorous oxychloride as a solvent. The residual oil was crystallized from about 1200 ml. of petroleum ether; B.P. 90–100° C. The resulting product was digested with 1 liter of boiling methanol, cooled and filtered. Yield 95 g., M.P. 93–94° C.

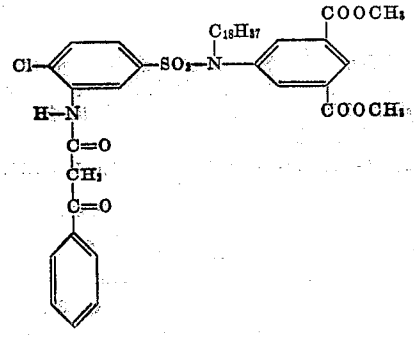
Dimethyl 5-(3-amino-4-chlorophenyl-N-octadecylsulfonamido) isophthalate



A mixture of 30 g. (0.044 mole) of the above nitro compound and 200 ml. of methanol were reduced in a low pressure heated hydrogenator with Raney nickel

catalyst. The solution was filtered and the fitrate cooled. The product was collected and twice crystallized with charcoal from methanol. Yield 25.5 g., M.P. 82–83° C.

Dimethyl 5-(3-α-benzoylacetamido-4-chlorophenyl-N-octadecylsulfonamido)isophthalate



In a 1 liter 3-necked flask, equipped with a stirrer, vertical steam jacketed condenser and dropping funnel, was placed a solution of the above amine (48 g., 0.074 mole) in 500 ml. of dry xylene. The solution was treated dropwise at reflux with etyl benzoylacetate (17.3 g., 0.09 mole) and the resulting solution was refluxed for 8 hours. After removal of the solvent on a steam bath at reduced pressure, the residual oil was dissolved in 800 ml. of methanol, treated with charcoal and filtered. The filtrate was decanted from a small amount of dark oil, treated again with charcoal and filtered. The filtrate was cooled, the product collected and washed with cold methanol. Yield 25 g., M.P. 107–108° C.

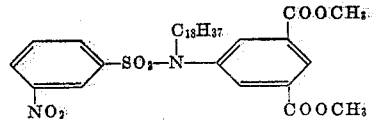
Example V

Compound (9) was prepared by condensing dimethyl 5-(3-amino-4-chlorophenyl - N - octadecylsulfonamido)-isophthalate (8.0 g., 0.012 mole) with phenyl 1-hydroxy-2-naphthoate (3.5 g., 0.01 mole) by heating in a metal bath at 150–170° C. under reduced pressure (5–10 mm.) until the phenol ceased to distill (1½ hours). 100 milliliters of petroleum ether (B.P. 90–100° C.) were then added and the solution cooled. The solid which crystallized was collected by filtration and dried. The yield of the final compound was 6.0 g., and melted at 105–106° C.

Example VI

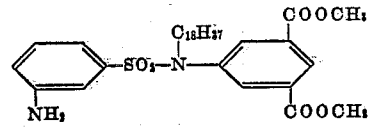
Compound (10) was prepared as follows:

Dimethyl 5-(3-nitrophenyl-N-octadecylsulfonamido)isophthalate



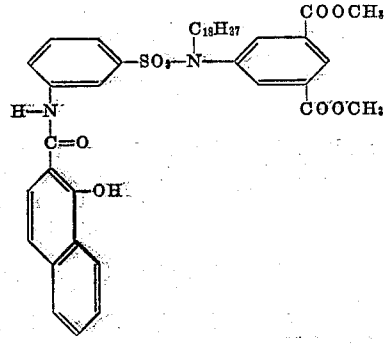
In a 500 ml. 3-necked flask, equipped with a stirrer and a reflux condenser, were placed 200 ml. of dry xylene and 46.2 g. (0.01 mole) of 3-octadecylamino-isophthalic acid dimethyl ester. 3-nitrobenzenesulfonyl chloride (22.2 g., 0.1+ mole) was added and the solution heated at gentle reflux for 18 hours. The solvent was removed from the dark solution at reduced pressure and the residue triturated with methanol (150 ml.). After cooling the solution, the solid was collected by filtration and washed with methanol. The product was dissolved in 200 ml. of petroleum ether; B.P. 90–100° C. The solution was treated with charcoal and filtered. The filtrate was diluted with an equal volume of petroleum ether; B.P. 30–60° C. After cooling, the white crystalline solid was collected by filtration and was washed with petroleum ether. The product was recrystallized from 400 ml. methanol; M.P. 74–75° C.

Dimethyl 5-(3-aminophenyl-N-octadecylsulfonamido)isophthalate



A mixture of 27.7 g., (0.043 mole) of the above nitro-compound in 200 ml. of methanol were reduced in a low pressure hydrogenator with platinum oxide catalyst. The white crystalline solid obtained was dissolved in 50 ml. of hot petroleum ether; B.P. 30–60° C. The solution was cooled in ice and the crystalline solid which separated was collected by filtration and dried. Yield 21 g., M.P. 76–78° C.

1-hydroxy-8′-[N-(3,5-dicarbomethoxyphenyl)-N-(octadecyl) sulfamyl]-2-naphthanilide



A mixture of the amine prepared as above (4.5 g., 0.017 mole) was heated at reduced pressure (5–10 mm.) on a metal bath first at 140–150° C. for ¾ hour and then at 160–170° C. for ¼ hour. Methanol (100 ml.) was added to the hot melt. After triturating for a short time, the oil crystallized. The warm mixture was filtered and the solid was crystallized from petroleum ether; B.P. 90–100° C. Yield 7.8 g., M.P. 114–115° C.

Analysis: Calc.—68.70% C, 7.38% H. Found—68.74% C, 7.39% H.

Example VII

Compound (11) was prepared by condensing dimethyl 5-(3 - aminophenyl-N-octadecylsulfonamido)isophthalate (10 g., 0.016 mole) with ethyl benzoylacetate (3.8 g., 0.02 mole) in 100 ml. of dry xylene, following the procedure used to prepare Compound (8).

The amine was the same used for the preparation of Compound (10).

A solution of 1.5 g. of Compound (5) was dissolved in 6.0 g. of a mixture consisting of 50 parts phenethyl alcohol, 40 parts of tricresyl phosphate and 10 parts of n-butyl phthalate and the resulting solution dispersed in 20 ml. of a 6% gelatin solution containing 0.05 ml. of lauryl sulfate. Emulsification was effected by high-speed agitation in a small Waring Blendor. The above dispersion of coupler was 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 this emulsion with a developing solution employing 2-amino-5-diethylaminotoluene as the developing agent and subsequent removal of silver, a yellow image was obtained.

Compound (5) was treated with alcoholic KOH to convert the di-ester into the corresponding potassium salt. The salt was dissolved in alkali and methanol and added to a silver-halide emulsion according to the procedure of U.S. Patent 2,186,849.

Various photographic developing agents can be employed with the couplers of our 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-dimethylaminoaniline, 4-diethylaminoaniline, 4-[N-(β-hydroxyethyl)-N-ethyl]aminoaniline, 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 free 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:

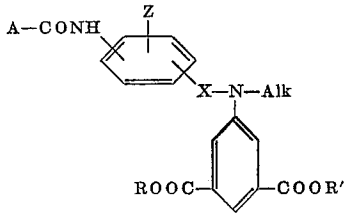
	G.
2-amino-5-diethylaminotoluene	2
Sodium carbonate (anhydrous)	20
Sodium sulfite (anhydrous)	2
Potassium bromide	0.2
Water to make 1 liter.	

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

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

We claim:

1. A silver-halide emulsion containing a coupler compound of the following general formula:



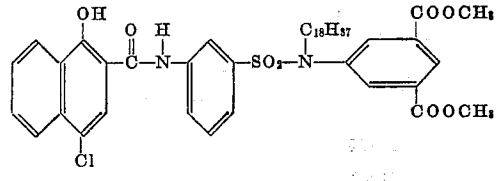
wherein A is an organic color forming residue of the type capable of color coupling with the oxidation products of a primary aromatic amino silver halide developing agent, said color forming residue having a grouping selected from the class consisting of a 1-hydroxy-2-phenyl group, 1-hydroxy-2-naphthyl group and a benzoylmethylene group; X is selected from the class consisting of —CO— and —SO_2—; Z is selected from the class consisting of hydrogen, halogen, lower alkyl, lower alkoxyl and an aromatic hydrocarbon radical of the benzene and naphthalene series; R and R' are selected from the class consisting of hydrogen, lower alkyl, an alkali metal, ammonium and Alk is an alkyl group of from 10 to 18 carbon atoms.

2. The article as defined in claim 1 wherein the organic color forming residue A is a 1-hydroxy-2-phenyl group.

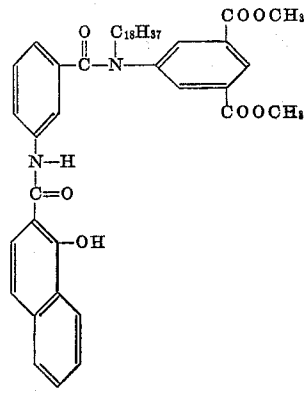
3. The article as defined in claim 1 wherein the organic color forming residue A is a benzoylmethylene group.

4. The article as defined in claim 1 wherein the organic color forming residue is a 1-hydroxy-2-naphthyl group.

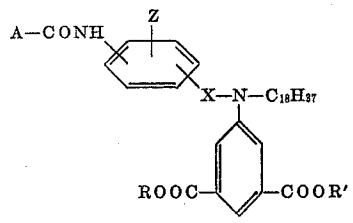
5. A silver-halide emulsion containing a coupling compound of the following formula:



6. A silver-halide emulsion containing a coupling compound of the following formula.

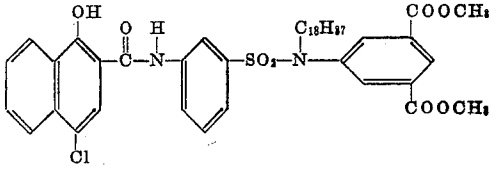


7. The method of producing a colored photographic image in a silver-halide emulsion layer which comprises exposing the layer and developing said layer with a primary aromatic amino developing agent in the presence of a coupler compound of the following formula:



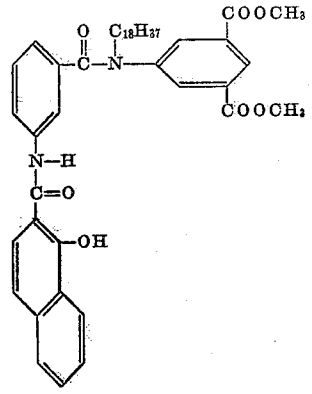
wherein A is an organic color forming residue of the type capable of color coupling with the oxidation products of a primary aromatic amino silver halide developing agent, said color forming residue having a grouping selected from the class consisting of a 1-hydroxy-2-phenyl group, 1-hydroxy-2-naphthyl group and a benzoylmethylene group; X is selected from the class consisting of —CO— and —SO_2—; Z is selected from the class consisting of hydrogen, halogen, lower alkyl, lower alkoxyl and an aromatic hydrocarbon radical of the benzene and naphthalene series; R and R' are selected from the class consisting of hydrogen, lower alkyl, an alkali metal, ammonium and Alk is an alkyl group of from 10 to 18 carbon atoms.

8. A photographic emulsion for forming colored images comprising a gelatino silver-halide emulsion having incorporated therein a coupling compound of the following formula:



9. A photographic emulsion for forming colored images comprising a gelatino silver-halide emulsion hav-

ing incorporated therein a coupling compound of the following formula:



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