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3,112,198

NON-DIFFUSING COLOR FORMERS IN WHICH THE LONG ALIPHATIC CHAIN THEREON IS PROVIDED WITH A TERMINAL SULFO GROUP

Gunther H. Klinger, Binghamton, N.Y., assignor to General Aniline & Film Corporation, New York, N.Y., a corporation of Delaware

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13 Claims. (Cl. 96—55)

The present invention relates to color formers in which the non-diffusing group comprises a long aliphatic chain substituted in the terminal position by a sulfo 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 wandering or diffusion of the couplers in the silver halide emulsion. It is, likewise, common practice to provide such couplers with certain acid radicals such as a carboxy or sulfo radical, the alkali metal or ammonium salts of which are soluble in water or aqueous solutions such as photographic emulsions. For a more detailed description of these color formers and to photographic emulsions containing them, reference is made to Wilmanns et al., U.S. Patent 2,186,849. It is, furthermore, customary to employ, as the yellow coupler, an open chain keto methylene compound, as the cyan coupler, a compound containing phenolic hydroxy groups and, as the magenta coupler, a pyrazolone nucleus particularly those bearing an aryl radical on the nitrogen atom in the 1-position pyrazolone ring.

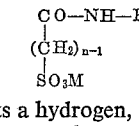
It is well recognized by artisans in the field that color couplers must possess certain key properties in order to render them valuable for use in color photography. In the case of the non-diffusing type of couplers, and the present application is directed to compounds of this type, the following properties are of prime importance. (1) The color formers and the dyes produced therefrom should be stable against light fading and high humidity fading. (2) The residual color former should remain inert and not produce extraneous colorations or stains. A common fault of many color formers in this connection is the production of the yellow coloration on aging with concomitant color degradation of the image. (3) Color couplers should produce a dye on color development having the correct spectral properties, that is, there should be no undesirable absorption peaks. Similarly, the residual color former should not exhibit any absorption of its own within the visible spectrum which might deleteriously affect the spectral properties of the dye image formed therefrom. (4) Color couplers must also posses certain non-photographic properties such as relative ease of preparation and purification as well as being compatible with the photographic emulsion in which they are incorporated.

As previously pointed out, it is a common practice to prepare color photographic emulsions in which the color coupler is incorporated therein in the form of its alkali metal or ammonium salt and to this end such couplers may contain a carboxyl or sulfo radical. Due to the extreme simplicity of incorporating color formers in a photographic emulsion by the aforesaid procedure, it is preferred by many artisans in the photographic field. However, for reasons not generally understood, photographic emulsions containing a color coupler incorporated therein in the form of its metal salt, as above described, may not yield dye images which possess the light stability and high humidity stability as similarly prepared emulsions in which the color former is employed in some form other than its metal salt. Thus, it is known to incorporate color formers in a photographic emulsion by a dispersion technique in which a lipophilic type of color former is dissolved in a water immiscible oily solvent and the resulting solution dispersed in a photographic emulsion with the result that minute oily droplets of the coupler solution are distributed throughout the hydrophilic photographic colloid matrix. Apparently, the presence of the oily solvent associated with the coupler exerts a stabilizing influence both on the residual coupler and the dyes produced therefrom. However, the process of incorporating lipophilic color formers in the photographic emulsion is both time consuming, cumbersome, and expensive since it requires an outlay of large, high energy, homogenizing equipment such as large colloid mills. Furthermore, the dispersion procedure requires couplers of extremely high solubility in the oily solvents in which they are dissolved. As a consequence, such compounds must generally posses very low melting points, a physical property which makes their isolation in a pure form rather difficult since they tend to be non-crystalline in nature. Another objection to the dispersion method can be attributed to the oily solvents, the presence of which may adversely affect the photographic emulsion by increasing fog or interfering with optical sensitization.

I have now discovered a class of color couplers of the salt-forming non-diffusing type in which the long aliphatic chain therein contains the salt-forming function as a terminal sulfo radical and which have extremely useful and valuable photographic properties. The color couplers of the type described herein give rise to highly stable colored images on color photographic development; that is to say, colored dye images which show high stability towards light fading and high humidity fading. Furthermore, these couplers are, in themselves, quite stable so that their presence in excess in the emulsion does not result in any deleterious side effects such as yellowing or other undesirable staining. In addition, my color couplers yield dye images of the desired spectral characteristics and properties. Of prime practical importance is the fact that my color formers are economical and easy to prepare and purify, using simple crystallization techniques.

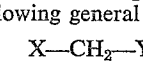
The preparation and use of such color formers accordingly constitute the purposes and objects of my invention.

My color formers, the preparation and use of which are described herein, can be depicted by the following structural formula:



wherein M represents a hydrogen, ammonium or an alkali metal, R represents a coupler molecule of the type containing a reactive methylene or phenolic hydroxy group capable of reacting, by color development, with the oxidation products of a primary aromatic amino developing agent to produce a color dye image and *n* represents a positive integer of 9 or more.

By reactive methylene group is meant the type commonly encountered in color couplers and which can be depicted by the following general formula:

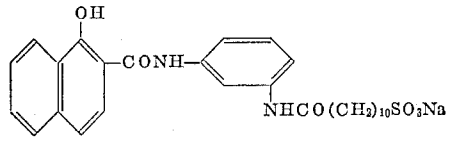


wherein X and Y stand for electron attracting groups such as carbonyl, cyano, nitro and the like. By phenolic hydroxy group is meant the phenolic phenyl groups commonly understood in the color coupler art and includes the phenolic or hydroxy naphthoic types having a reactive position para to the said hydroxy group, that is, a position which is unsubstituted or which is substituted with

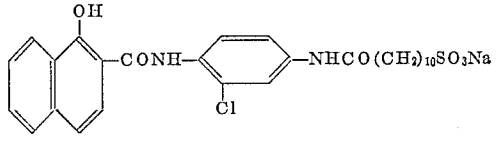
a replaceable group. The aforesaid groups are well recognized in the photographic field so that further discussion of such entities would be superfluous.

Examples of compounds falling within the ambit of the above formula in which I have found to be suitable for practicing the invention are depicted by the following formulae:

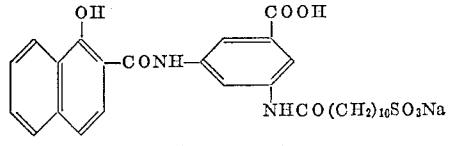
Compound 1



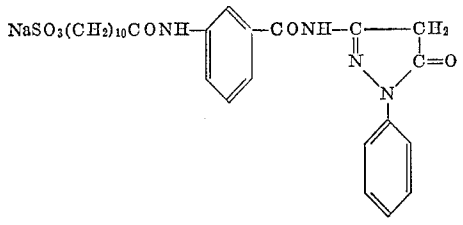
Compound 2



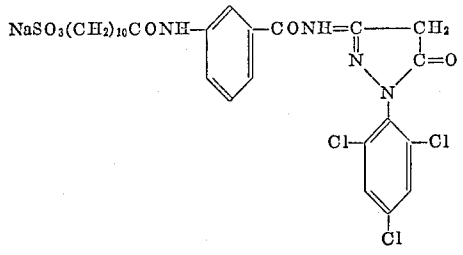
Compound 3



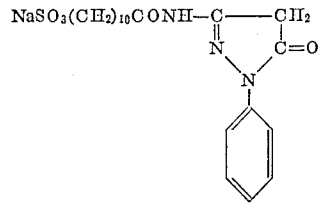
Compound 4



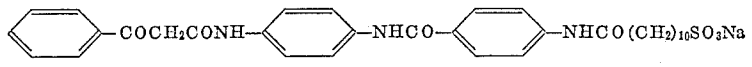
Compound 5



Compound 6



Compound 7



It is to be understood that the above compounds are preferably used in the form of their alkali metal or ammonium salts. The term ammonium salt as used herein is meant to include substituted ammonium salts such as alkyl ammonium salts or the ammonium salt may be part of a heterocyclic base such as pyridium or morpholium and the like.

The above coupler compounds are generally prepared by reacting a long chain aliphatic carboxylic acid having on the terminal carbon atom thereof a sulfo group with the amino group of a color-forming moiety. Preferably,

the long chain aliphatic carboxylic acid is used in the form of the alkali metal or ammonium salt of the terminal sulfo group. The aforesaid condensations are normally carried out in the presence of phosphorous trichloride, such a reaction being known in the art as the phosphazo reaction.

The long chain aliphatic carboxylic acid having a terminal sulfo group thereon may be prepared from the corresponding terminally unsaturated carboxylic acid and sodium sulfite heptahydrate according to a method disclosed in J.C.S., page 2560 (1956).

The amine coupling components referred to above have been previously described in the color photographic literature and my invention is to be considered in the light of this prior art. Thus, many of the amine coupling components used herein have been described in numerous U.S. patents to which reference is made for the particular and specific directions for the synthesis of such amine coupling components.

As previously noted above, color formers produced in accordance with the present invention are easily isolated in a pure form and yield dyes on color development which are highly transparent and very stable towards light and conditions of high humidity. Furthermore, they exhibit good stability and absorption characteristics and the dyes derived therefrom are not affected by the presence of residual or unreacted couplers.

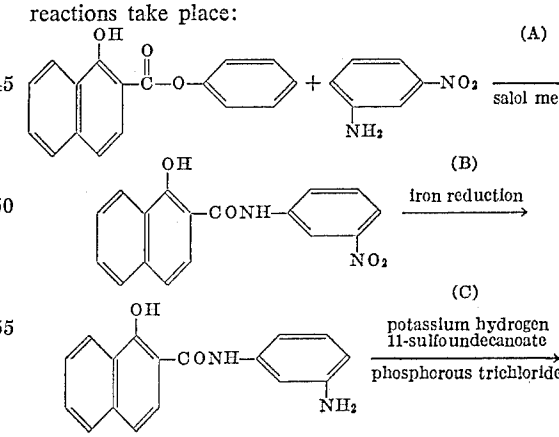
Apparently, the presence of the salt-forming group on the terminal position of the non-diffusing chain in this type of color coupler produces, in a manner as yet undetermined, a more stable structure of the dyes derived therefrom than similar couplers of the prior art in which the salt-forming radical is located at a more central site in the coupler molecule.

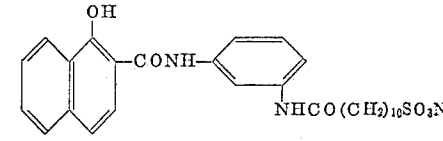
The following illustrate the present invention but it is to be understood that the invention is not restricted thereto.

PREPARATION OF COMPOUNDS

Compound 1

In the synthesis of Compound 1 above, the following reactions take place:





Reaction A was carried out in the following manner:

Apparatus—1-liter round bottom flask, metal-bath.

250 grams of phenyl-1-hydroxy-2-naphthoate (0.95 M) and 119 g. of m-nitroaniline (0.86 M) were heated for 2 hours at 150° C., 1 hour at 170° C. in a metal-bath (bath

temperature). During the last hour, the phenol was distilled off at 5–10 mm. Hg. The cooled melt was ground with methanol in a mechanical blender, filtered on a Buchner funnel and washed on the funnel with methanol until the washings were nearly colorless. It was recrystallized from dimethylformamide containing some methanol.

Yield: 204 g. yellow needles=74%; M.P. 253° C. $C_{17}H_{13}N_2O_4$: Calc.—C, 66.04; H, 4.17. Found—C, 66.14; H, 4.32.

Reaction B was then carried out as follows:

Apparatus—3-neck round bottom flask, stirrer, condenser and electric heating mantle.

200 grams of iron powder (40 mesh), 30 ml. of hydrochloric acid, 70 ml. of water and 430 ml. of ethanol were combined in that order and then 30 g. (0.1 M) of the amide produced in reaction A was slowly added to the refluxing mixture. The addition of the amide required 2–4 hours; an excess of Fe^{++} has to be maintained during the addition.

The mixture was refluxed overnight and then rendered alkaline against phenolphthalein with 40% aqueous sodium hydroxide. The solution was filtered through a Buchner funnel and the filtrate acidified with glacial acetic acid. The resulting precipitate was filtered off after cooling.

Yield: 20 g. light red needles=74%; M.P. 196–197° C. An analytical sample was prepared by recrystallization from acetone/water. $C_{17}H_{14}N_2O_2$: Calc.—C, 73.36; H, 5.07; M.W., 278.29. Found—C, 73.28; H, 5.57.

The final Compound 1 was produced by reaction C as follows:

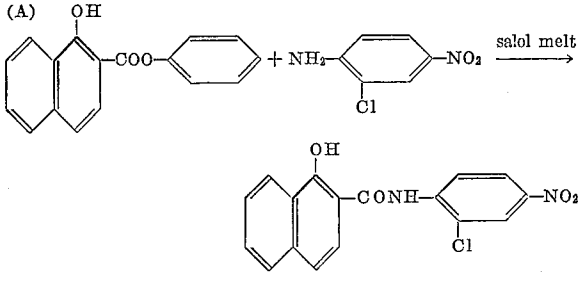
Apparatus—500 ml. 3-neck round bottom flask, stirrer, Dean-Stark moisture trap, condenser, calcium chloride-drying tube, dropping funnel. 19 grams amine produced in reaction B (0.066 M).

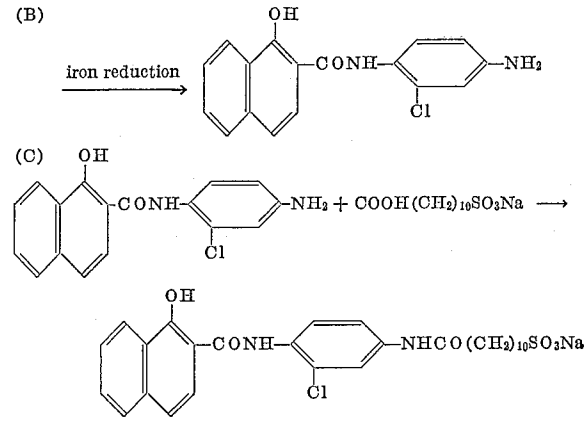
22 grams of potassium hydrogen 11-sulfoundecanoate (1.1 x 0.066 M), 66 ml. of dry pyridine and 260 ml. of dry benzene were combined in the flask and refluxed by means of an electric heating mantle until all traces of water were removed (req. about 2 hours). The Dean-Stark moisture trap was then removed and the condenser exchanged for a dry one. The mixture was cooled in an ice water bath and, with rapid stirring, a solution of 6.6 ml. of phosphorous trichloride in 50 ml. of dry benzene was added. The addition was made dropwise and required about 1 hour. The mixture was then refluxed on a steam bath for 2 hours. A solution of 9 g. of sodium hydroxide and 20 g. of anhydrous sodium acetate in 60 ml. of water was added slowly and the mixture cooled in ice. The precipitate was filtered on a Buchner funnel and the last traces of pyridine removed in vacuo. The so obtained 52 g. of yellow powderous material was recrystallized from 80% acetic acid. It was then recrystallized 2 times more from the same solvent.

Yield: 16.4 g.=45%; M.P. 284–285° C. $\frac{1}{2}H_2O \cdot C_{28}H_{33}N_2SO_6N$: 538.54. Calc.—C, 60.31; H, 6.14; S, 5.75; N, 5.02. Found—C, 60.41; H, 6.33; S, 5.74; N, 5.01.

Compound 2

The series of reactions for the preparation of Compound 2 may be represented as follows:





REACTION A

1 mole (172.58 g.) of 2-chloro-4-nitro aniline and 1.1 mole (264.28 g.) of phenyl-1-hydroxy-2-naphthoate were combined together in an open 1-liter, 1-neck round bottom flask and the mixture was heated without stirring for 3 hours in a metal bath at 155–160° C. The flask was then connected to an oil pump vacuum and the phenol distilled off at a bath temperature of 160° C. The cold melt was then crushed and transferred to a speed mixer (Waring Blendor, kitchen type). After the addition of 500 ml. of cold methanol, the mixer was run at full speed (120 volts) for about 5 minutes. The fine suspension was then filtered by means of a Buchner funnel and the product was washed on the funnel with methanol until the filtrate was colorless (1500 ml. of methanol). After crystallizing the solid once from chlorobenzene, it was filtered, sucked dry by means of an aspirator, washed again in small portions with a total of 1500 ml. of methanol, and used directly for the next reaction after letting it dry overnight at room temperature.

REACTION B

45 grams of iron powder (40 mesh) and 15 ml. of concentrated hydrochloric acid were mixed into a 3-neck, 1-liter round bottom flask provided with a stirrer and a reflux condenser. After 5 minutes, 100 ml. of water and 400 ml. of ethanol were added and the mixture heated to reflux temperature with vigorous mechanical stirring. 32 grams (about 0.1 mole) of the previously prepared air-dried and powdered nitro compound was then slowly added to the stirred, boiling reducing mixture over a period of 1 hour. The suspension was then refluxed, with efficient stirring, for 18 hours. The aqueous phase was made alkaline with aqueous, 6 N sodium hydroxide solution. After filtering from the iron-mud by means of a Buchner funnel and Filter-Cel (manufactured by Johns-Manville), the filtrate was acidified with glacial acetic acid. After cooling, the crystalline product was filtered and then recrystallized once from acetone. The product was air-dried and melted at 210° C.

REACTION C

21 grams (0.066 mole) of the above amine, 22 g. of 11-potassium sulfoundecanoic acid, 66 ml. of anhydrous pyridine and 260 ml. of dry benzene were refluxed for 2 hours under a Dean-Stark moisture trap. The flask was then cooled to 0° C. and to the cold, stirred solution was slowly and carefully added dropwise a solution of 6.6 ml. of phosphorous trichloride (PCl_3) in 50 ml. of dry benzene over a period of 1 hour. The temperature during this addition was carefully kept below 5° C. After the addition was complete, the mixture was heated to reflux temperature and then refluxed for 2 hours with stirring. To the hot solution was then slowly added a solution containing 9 g. of sodium hydroxide and 20 g. of anhydrous sodium acetate in 50 ml. of water. The rate of addition depended on the speed of refluxing caused by this exothermic reaction. After the addition was complete, which

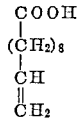
took about 5 minutes, the mixture was cooled to room temperature and the solid filtered through a Buchner funnel. The yellowish raw-product was freed from traces of pyridine and water by placing it into a desiccator over concentrated sulfuric acid. The product was finely powdered and then recrystallized from 80% aqueous acetic acid. After two recrystallizations, the product was white and exhibited a decomposition point at 287° C. Further recrystallizations did not raise the decomposition point. The yield was 27 g.

The 11-potassium sulfoundecanoic acid or potassium hydrogen 11-sulfoundecanoate (J. Chem. Soc., 1956, p. 2560),



used in this and the other examples was prepared as follows:

Into a 5-liter, 3-neck round bottom flask provided with stirrer and reflux condenser was charged 91 g. (0.5 mole) of undecenoic acid,

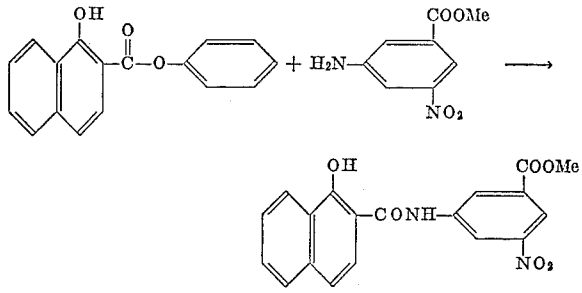


315 g. of sodium sulfite heptahydrate ($Na_2SO_3.7H_2O$), 600 ml. of ethanol and 300 ml. of water. The mixture was refluxed for 1 hour with stirring, at which time a clear solution was obtained. To the hot, stirred solution was then added, in one portion, 500 g. of anhydrous potassium chloride. The slurry was then cooled to 25° C. and allowed to stand for 1 hour and then filtered through a Buchner funnel. The solid was washed, on the funnel, with 200 ml. of an aqueous, 5% potassium chloride solution, then with 200 ml. of methanol and 200 ml. of ether. The washed product was recrystallized once with a solution containing 400 ml. of concentrated hydrochloric acid, 400 ml. of water and 40 g. of potassium chloride. The crystalline material was filtered again by means of a Buchner funnel and washed on the funnel with the following solvents: twice with 100 ml. each of ice water, twice with 100 ml. each of methanol and twice with 100 ml. each of ether. Yields of various batches: 117 g., 119 g., and 128 g.; melting point 193–197° C. The melting point range of the analytical sample was 195–197° C.

Compound 3

The preparation of Compound 3 may be represented as follows:

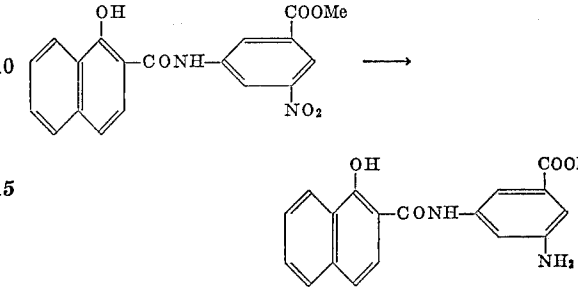
REACTION A



76 grams of 3-amino-5-nitromethylbenzoate (0.39 mole) and 114 g. of 1-hydroxy-2-phenyl naphthoate (1.1 x 0.39 mole) were charged into a 500 ml. round bottom flask. The mixture was heated over a period of 2 hours to 155–160° C. and then kept for 2 hours at 160° C. During the last 2 hours, vacuum was applied to the flask (5–10 mm./Hg) to remove the phenol. The material was then cooled, ground with 200 ml. of methanol in a mechanical blender, filtered through a Buchner funnel and washed on the funnel until the washings were nearly

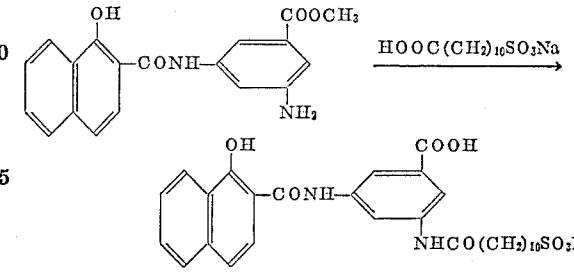
colorless. The crude product was recrystallized from dimethylformamide and methanol. Yield: 125 g., 87% (calculated on ester); M.P. 255–256° C. Anal. sample, M.P. 256–257° C. $C_{19}H_{14}N_2O_6$=366.32. Calc.—C, 62.29; H, 3.85; N, 7.65. Found—C, 62.27; H, 3.92; N, 7.58.

REACTION B



125 grams of the above nitro compound (0.34 M), 135 g. of iron-filings (40 mesh), 45 ml. of hydrochloric acid, 1400 ml. of ethanol and 250 ml. of water were charged into a 3-liter round bottom flask equipped with a stirrer and a reflux condenser. The nitro compound produced by reaction A was added in small portions to the refluxing mixture so that an excess of Fe^{++} was maintained. After the addition was complete (requires about 3 hours), the mixture was kept refluxing for another 15 hours. The mixture was then filtered, the filter cake extracted with boiling dimethylformamide and this extract combined with the filtrate which was diluted with water until the compound precipitated. Further precipitation was completed by cooling in ice. The solid was filtered off by means of a Buchner funnel, washed on the funnel with methanol until washings were nearly colorless and recrystallized from acetone. Yield: 65 g.; M.P. 240–241° C.

REACTION C



50 grams of the above amine (0.165 mole), 55 g. of 11-potassium sulfoundecanoic acid, 165 ml. of dry pyridine and 650 ml. of dry benzene were charged in a 2-liter, 3-neck round bottom flask equipped with stirrer, Dean-Stark moisture trap, reflux condenser, calcium chloride tube and a dropping funnel. The mixture was refluxed until all traces of water had been removed (requires about 2 hours). The mixture was cooled with ice water and a solution of 16.5 ml. of phosphorus trichloride in 50 ml. of dry benzene was added dropwise under rapid stirring (requires about 1 hour), followed by refluxing for 2 hours on a steam bath. To the hot solution was added a solution of 30 g. of sodium hydroxide and 35 g. of anhydrous sodium acetate in 200 ml. of water and the reaction cooled to 0° C. in a refrigerator for 15 hours. The solid was filtered and dried over sulfuric acid in a vacuum desiccator and recrystallized from 80% acetic acid and then 3 times from 70% methanol.

Yield 50 g. $C_{29}H_{33}SO_8N_2Na.\frac{1}{2}H_2O$=692.64. Calc.—C, 57.03; H, 5.61; S, 5.25; N, 4.59. Found—C, 57.12; H, 6.16; S, 5.14; N, 4.54.

Compound 4

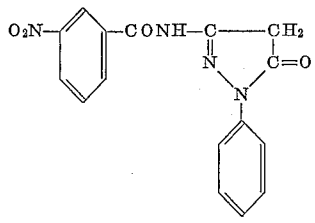
The preparation of Compound 4 may be represented as follows:

REACTION A

176 grams of 3-amino-1-phenylpyrazolone-5 (1-mole)

were slurried in a 2-liter round bottom flask with 600 ml. dry pyridine. To this was added a slurry of 186 g. of m-nitrobenzoylchloride (1 mole) in 200 ml. of dry benzene. After the main reaction has subsided, the mixture was heated on a steam bath for 5 hours and then poured in 2-liters of ice water, filtered and recrystallized from dimethylformamide and methanol.

The product obtained was:

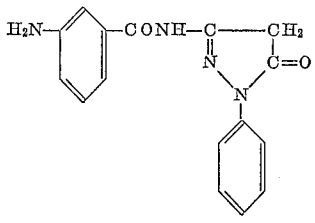


53% yield, 174 g.; M.P. 226–227° C.; Anal. sample, M.P. 227–228° C. $C_{16}H_{13}N_4O_4$=325.29. Calc.—C, 59.08; H, 4.027; N, 17.22. Found—C, 59.74; H, 4.30; N, 17.22.

REACTION B

400 grams of iron powder (40 mesh), 135 ml. of hydrochloric acid, 800 ml. of water and 3200 ml. of ethanol were combined in this order in a 5-liter, 3-neck flask equipped with stirrer and reflux condenser. After the mixture started refluxing, 174 g. of the compound (0.535 mole) (from reaction A) were added in small portions, always maintaining an excess of Fe^{++}. This required about 3–4 hours. The mixture was kept refluxing for 15 hours, then made basic with 50% sodium hydroxide (phenolphthalein as indicator). It was filtered by means of a Buchner funnel, the filtrate acidified with glacial acetic acid and cooled. The crystalline precipitate was filtered off and washed once with methanol. 73% yield, 117 g.; M.P. 225–226° C. Anal. sample, M.P. 227–228° C.

The product obtained was:

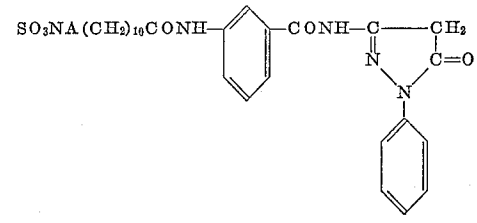


$C_{16}H_{15}N_4O_2$=295.31. Calc.—C, 65.08; H, 5.12; N, 18.97. Found—C, 65.33; H, 6.77; N, 18.81.

REACTION C

117 grams of the above amine (0.395 mole), 130 g. of potassium hydrogen 11 - sulfoundecanoate (1.1 x 0.395 mole), 395 ml. of dry pyridine and 1500 ml. of dry benzene were charged in a 3-neck, 3-liter round bottom flask equipped with stirrer, Dean-Stark moisture trap, dropping funnel, condenser, and a calcium chloride drying tube. The mixture was refluxed until all traces of water were removed (about 2 hours). After cooling the flask in ice water with rapid stirring, a solution of 18 ml. of phosphorous trichloride (PCl_3) in 200 ml. of dry benzene was added dropwise over a period of 1 hour and then kept at reflux temperature on a steam bath for 2 hours. To the hot mixture was added a solution of 31 g. of sodium hydroxide and 80 g. of anhydrous sodium acetate in 200 ml. of water. The flask was then cooled to 0° C. and kept in a refrigerator for 15 hours. The resulting solid was filtered by means of a Buchner funnel and dried in a vacuum desiccator over sulfuric acid. It was once recrystallized from 90% acetic acid and then twice from 70% methanol. Yield 95 g.

The product obtained was:



(Compound 4)

Compound 5

The preparation of Compound 5 may be represented as follows:

22.5 grams of 3-(m-aminobenzamido)-1-(2,4,6-trichlorophenyl)pyrazolone-5 (0.057 mole), 19 g. of potassium hydrogen 11-sulfoundecanoate (1.1 x 0.057 mole), 57 ml. of dry pyridine and 250 ml. of dry benzene were charged into a 500 ml. 3-neck round bottom flask equipped with stirrer, dropping funnel, Dean-Stark moisture trap, reflux condenser and a calcium chloride tube, and refluxed until all traces of water were removed (about 2 hours), then cooled in an ice water bath and a solution of 2.6 ml. of phosphorous trichloride (PCl_3) in 40 ml. of dry benzene added dropwise with rapid stirring. This required about 1 hour. The mixture was refluxed for 2 hours on a steam bath and to the still hot mixture was added a solution of 4.5 g. of sodium hydroxide and 11 g. of sodium acetate (anhydrous) in 40 ml. of water. The mixture was then cooled, filtered and dried in a vacuum desiccator over concentrated sulfuric acid. The product was purified by dissolving it in 250 ml. of hot 70% methanol which had previously been adjusted to a pH of 9 with 2 N sodium hydroxide and precipitating it with 5 N hydrochloric acid after filtration.

The above 3-(m-aminobenzamido)-1-(2,4,6-trichlorophenyl)pyrazolone-5 was obtained by the acylation of 3-amino-1-(2,4,6-trichlorophenyl)pyrazolone-5 with m-nitrobenzoyl halide in pyridine solvent. The resulting 3-(m-nitrobenzamido)pyrazolone-5 was then reduced to the corresponding amino compound by catalytic hydrogenation using Raney nickel as a catalyst.

Compound 6

The preparation of Compound 6 may be represented as follows:

18 grams of 3-amino-1-phenylpyrazolone-5, 31 g. of potassium hydrogen 11-sulfoundecanoate, 60 ml. of dry pyridine and 260 ml. of dry benzene were charged in a 1-liter, 3 -neck round bottom flask equipped with stirrer, Dean-Stark moisture trap, dropping funnel, condenser and calcium chloride tubing. The mixture was refluxed until all traces of water were removed, then cooled in an ice water bath and a solution of 4.5 ml. of phosphorous trichloride in 50 ml. of dry benzene was slowly added. This addition was made dropwise and required about 1 hour. The mixture was refluxed for 2 hours on a steam bath and a solution of 8 g. of sodium hydroxide and 21 g. of anhydrous sodium acetate in 50 ml. of water was added to the hot mixture. The flask was stored in a refrigerator for 15 hours and the contents then filtered on a Buchner funnel and dried in a vacuum desiccator over sulfuric acid. Recrystallization from three times 80% acetic acid.

Yield 23 g. of purified product. $C_{20}H_{28}N_3SO_5Na$: Calc.—C, 53.92; H, 6.34; N, 9.43; S, 7.19. Found—C, 54.75; H, 8.04; N, 9.59; S, 6.74.

Compound 7

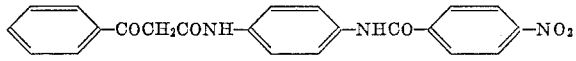
The preparation of Compound 7 may be represented as follows:

REACTION A

96 grams of 1-amino-α-benzoylacetanilide were slurried in 200 ml. of dry benzene and a slurry of 71. g. of p-nitro-

benzoylchloride in 400 ml. of pyridine was added. The mixture was heated for 5 hours on a steam bath, then the pyridine removed by vacuum distillation. The residue was recrystallized from a mixture of dimethylformamide and methanol.

The compound produced was:

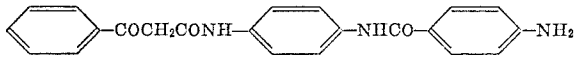


Yield 170 g.; M.P. 258–259° C. $C_{22}H_{17}N_3O_5$: Calc.—C, 65.34; H, 4.23; N, 10.39. Found—C, 65.73; H, 4.26; N, 10.63.

REACTION B

300 grams of iron powder (40 mesh), 100 ml. of hydrochloric acid, 400 ml. of water and 2000 ml. of ethanol were charged in a 3-liter, 3-neck round bottom flask equipped with stirrer and reflux condenser. To the refluxing mixture, 170 g. of the above nitro compound from reaction A were added in small portions, always maintaining an excess of Fe^{++}. The mixture was refluxed overnight, rendered alkaline against phenolphthalein with 50% sodium hydroxide, filtered and acidified with dry acetic acid. The nearly white precipitate was filtered off.

The compound produced was:

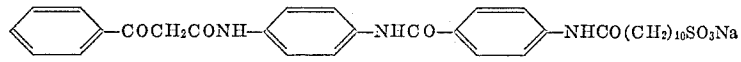


Yield 50 g.; M.P. 238–241° C. Calc.—C, 70.77; H, 5.13; N, 11.26. Found—C, 70.3; H, 5.14; N, 11.98.

REACTION C

56.5 grams of the above amine from reaction B, 49.5 g. of potassium hydrogen 11-sulfoundecanoate, 151 ml. of dry pyridine and 570 ml. of dry benzene were charged into a 1-liter, 3-neck flask equipped with stirrer, Dean-Stark moisture trap, reflux condenser, calcium chloride tube and a dropping funnel. The mixture was refluxed until all traces of water were removed (requires about 2 hours). The mixture was then cooled in an ice water bath and a solution of 7 ml. of phosphorous trichloride in 50 ml. of dry benzene was added dropwise under rapid stirring. The addition required about 1 hour. The mixture was refluxed on a steam bath for 2 hour. Then, a solution of 12 g. of sodium hydroxide and 30 g. of sodium acetate in 50 ml. of water was added. The reaction product was stored for 15 hours in a refrigerator, filtered on a Buchner funnel and recrystallized from 80% acetic acid.

The compound produced was:



(Compound 7)

The following example illustrates the manner by which my color formers may be incorporated in a color photographic light sensitive silver halide emulsion.

2.00 grams of the cyan color coupler, designated as Compound 2 above, were dissolved in 20 ml. of dimethylformamide. This solution was filtered and the filtrate then mixed into 50 ml. of a 6% aqueous gelatin solution with good stirring. A speed mixer (Waring Blendor, kitchen type) is desirable, although not necessary. The resulting emulsion was chilled and washed free of dimethylformamide by washing noodles of this emulsion for 6 hours in cold water. The washed noodles were then mixed into an equal weight of a color photographic emulsion and the coating obtained therefrom was photographically very satisfactory. An exposed strip showed, after reversal color development, a high cyan density. Microscopic examination of the unprocessed and processed coatings revealed an unusually fine distribution of color former and resulting dye in the gelatin which is indicative of greater sharpness, acutance and resolution.

The aforesaid procedure may be used with a magenta or yellow color coupler.

A typical color developing formulation suitable for color developing the coatings prepared in accordance with my invention has the following composition:

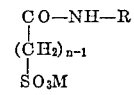
	G.
2-amino-5-diethylamino toluene HCl	2
Sodium sulfite, anhydrous	2
Sodium carbonate, monohydrate	20
Potassium bromide	2

Sodium hydroxide to give pH 10.8.
Water to 1-liter.

Modification of the invention will occur to persons skilled in the art. Thus, in lieu of the specific color formers of the examples, other color formers meeting the prerequisites of the above general formula may be employed. Similarly, the color formers may be incorporated in other photographic colloids and in this connection mention is made of synthetic resins such as polyvinyl alcohol, the properties of which are similar to those of gelatin. Photographic supports which may be utilized for coatings containing my color formers include a base such as cellulose ester, polystyrene, polyamide, polyester or a non-transparent reflecting material such as paper or cloth. I, therefore, do not intend to be limited in the patent granted except as necessitated by the appended claims.

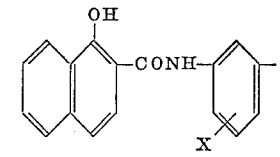
I claim:

1. A process of producing a colored dyestuff image in a silver halide emulsion layer which comprises exposing the layer to light and developing it with a solution of an aromatic primary amino developing agent, said emulsion layer containing a color former of the following structural formula:

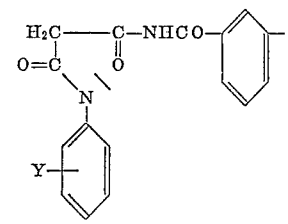


wherein M represents radicals of the group consisting of hydrogen, ammonium and alkali metal; *n* represents a positive integer of at least 9; and R represents radicals selected from the group consisting of—

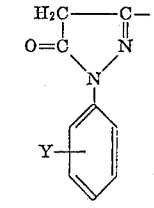
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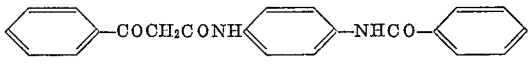
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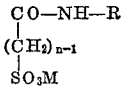


(4)



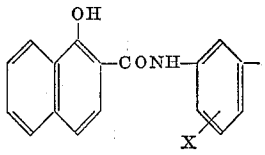
wherein X represents radicals of the group consisting of hydrogen, chloro and carboxy radicals and Y represents radicals of the group consisting of hydrogen and chloro.

2. A light sensitive silver halide emulsion containing a color former of the general formula:

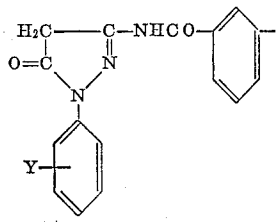


wherein M represents radicals of the group consisting of hydrogen, ammonium and alkali metal; *n* represents a positive integer of at least 9; and R represents radicals selected from the group consisting of—

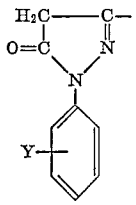
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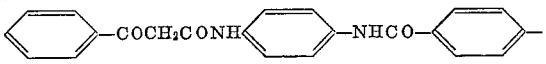
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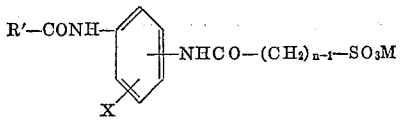


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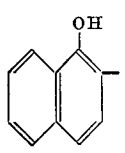
wherein X represents radicals of the group consisting of hydrogen, chloro and carboxy radicals and Y represents radicals of the group consisting of hydrogen and chloro.

3. A process of producing a colored dyestuff image in a silver halide emulsion layer which comprises exposing said layer to light and developing the same with a solution of an aromatic primary amino developing agent, said emulsion layer containing a color former characterized by the formula:

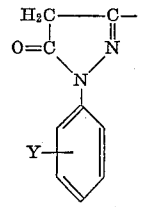


wherein X represents radicals of the group consisting of hydrogen, chloro and carboxy radicals; *n* represents a positive integer of at least 9; M represents radicals of the group consisting of hydrogen, alkali metals and ammonium radicals; and R′ represents radicals selected from the group consisting of—

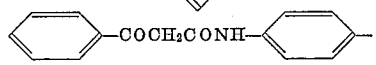
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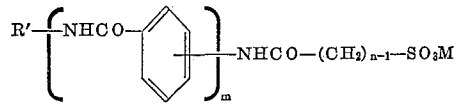


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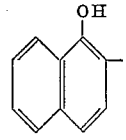
wherein Y represents radicals of the group consisting of hydrogen and chloro.

4. A process of producing a colored dyestuff image in a silver halide emulsion layer which comprises exposing said layer to light and developing the same with a solution of an aromatic primary amino developing agent, said emulsion layer containing a color former characterized by the formula:

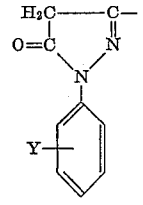


wherein *m* represents an integer of the group consisting of 0 and 1; *n* represents a positive integer of at least 9; M represents radicals of the group consisting of hydrogen, alkali metals and ammonium radicals; and R′ represents radicals selected from the group consisting of:

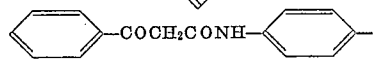
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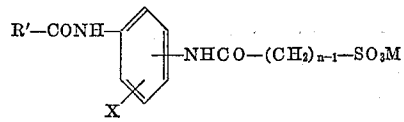


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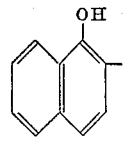
wherein Y represents radicals of the group consisting of hydrogen and chloro.

5. A light sensitive silver halide emulsion containing a color former of the formula:

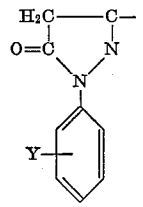


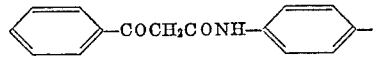
wherein X represents radicals of the group consisting of hydrogen, chloro and carboxy radicals; *n* represents a positive integer of at least 9; M represents radicals of the group consisting of hydrogen, alkali metals and ammonium radicals; and R′ represents radicals selected from the group consisting of—

(1)



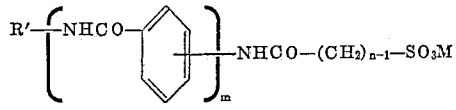
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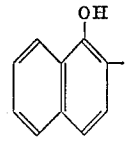
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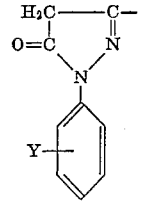
wherein Y represents radicals of the group consisting of hydrogen and chloro.

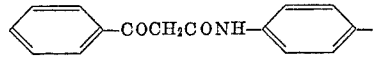
6. A light sensitive silver halide emulsion containing a color former of the formula:



wherein *m* represents an integer of the group consisting of 0 and 1; *n* represents a positive integer of at least 9; M represents radicals of the group consisting of hydrogen, alkali metals and ammonium radicals; and R′ represents radicals selected from the group consisting of:

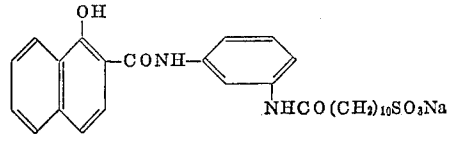
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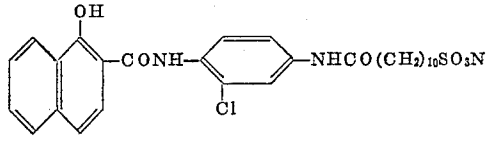
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wherein Y represents radicals of the group consisting of hydrogen and chloro.

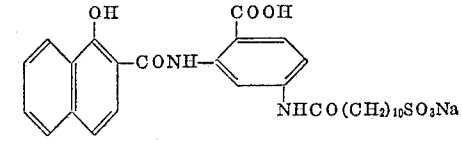
7. A light sensitive silver halide emulsion containing a color former of the formula:



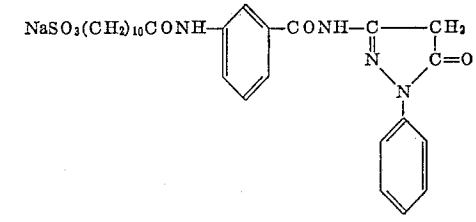
8. A light sensitive silver halide emulsion containing a color former of the formula:



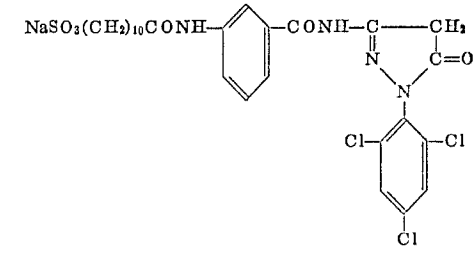
9. A light sensitive silver halide emulsion containing a color former of the formula:



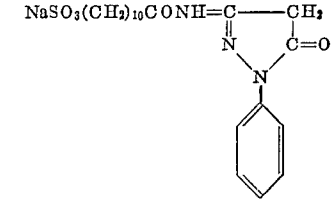
10. A light sensitive silver halide emulsion containing a color former of the formula:



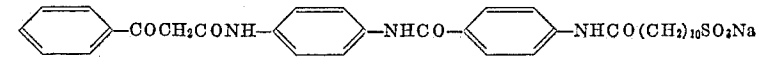
11. A light sensitive silver halide emulsion containing a color former of the formula:



12. A light sensitive silver halide emulsion containing a color former of the formula:



13. A light sensitive silver halide emulsion containing a color former of the formula:



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