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3,556,796

SILVER HALIDE EMULSION CONTAINING NAPHTHOL COLOUR COUPLERS FOR CYAN

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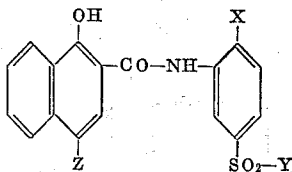
Int. Cl. G03c 1/40

U.S. Cl. 96—100

2 Claims

ABSTRACT OF THE DISCLOSURE

Cyan-forming color couplers suitable for use in negative silver halide color materials and the use of such color couplers in an integral mask process are described. The color couplers have the structure



wherein:

Z is a hydrogen atom or a halogen atom,

X is a halogen atom, an alkyloxy group, an alkylthio group, an alkylsulfonyl group, an aryloxy group, an arylthio group, an arylsulfonyl group, a monoalkylamino group, a dialkylamino group or an amino group, the nitrogen atom of which makes part of the ring atoms of a saturated heterocyclic nucleus,

Y is an alkyl radical, a monoalkylamino group, a dialkylamino group or an amino group, the nitrogen atom of which makes part of the ring atoms of a saturated heterocyclic nucleus, at least one of the alkyl radicals in the above groups being an aliphatic radical containing from 5 to 20 carbon atoms.

This invention relates to colour photography and the production of photographic colour images by colour development. It relates more particularly to novel cyan-forming colour couplers suitable for use in negative silver halide colour materials and to the use of said colour-forming couplers in an integral mask process.

It is known to produce photographic colour images wherein a colour former or coupling component reacts with the development product of a primary aromatic amino developing agent and forms a coloured compound in the same areas where the silver halide grains have been reduced.

The modern processes of colour photography are based on the subtractive colour principle according to which differently sensitized silver halide emulsions are superposed in the form of layers. Each of these layers contains a different colour-forming compound, which on development produces the corresponding subtractive yellow, cyan and magenta colour image.

For application in negative materials the cyan-forming colour couplers should yield on development a dye that absorbs light with a wavelength from 700 to 600 mμ (red light). In practice, however, there should be reckoned with more or less considerable side-absorptions in the colour regions of 600-500 mμ (green light) and 500-400 mμ (blue light).

Since the side absorptions are inherent to the dyes formed on development, correction systems have been proposed for masking the side-absorptions of said dyes, in order to obtain from the colour negative positive colour prints with more saturated dyes. This masking mainly relies on the formation of a mask image i.e. an image with opposite gradation in respect to the primary dye image formed on development and an absorption spectrum which corresponds as well as possible with the side-absorption of the primary dye image.

Several masking processes have been proposed hitherto for eliminating the deficiencies in colour tone of photographic dyes owing to their side-absorptions. The most interesting among them are those wherein the mask can be produced in the photographic material itself i.e. the so-called "integral masking processes."

According to such a process, very satisfactory correction results are obtained on printing the negative colour image, in the presence of a mask image which is formed in a photographic element comprising a silver halide emulsion layer containing a cyan-forming colour coupler of the naphthol type, which on colour development by reaction with the oxidation product of an aromatic amino developing agent forms a primary dye image that absorbs a major proportion of light in the red region of the visible spectrum and undesirably absorbs a minor proportion of light in at least one other region of the visible spectrum (the blue and/or green region), by treating the colour-developed photographic element with an oxidizing solution, such as an alkaline potassium hexacyanoferrate(III) bleaching bath, in the presence of a compound that oxidatively couples with the residual colour coupler thereby forming a secondary dye image having a gradation opposite to that of said primary dye image and absorbing light in at least one of said regions, wherein the primary dye image undesirably absorbs, but transmitting substantially all the light in said major absorption region.

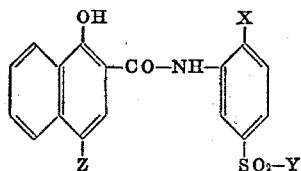
Masking processes for the correction of the unwanted side-absorptions of the primary dye image and working according to the above stated principles are described e.g. in Great Britain patent specifications 975,930, 975,932, 979,992, 993,749, 995,798 (corresponding with U.S. patent specifications 3,018,879, 3,245,787 and 3,245,788, 3,249,431, and with U.S. patent applications Ser. Nos. 296,942, 278,453 respectively).

From Great Britain patent specification 975,932 can be learned that 1-hydroxy-2-naphthoic acid anilide cyan-forming colour couplers having in the anilide part a sulphonic acid group are especially useful for obtaining a masking dye according to the integral masking technique described above. These colour couplers however possess the disadvantage of increasing the viscosity of the light-sensitive emulsion, and moreover give rise to changes in the viscosity of the emulsion with time, thus posing problems with regard to high speed and reproducible emulsion coating.

Cyan-forming colour couplers have now been found that possess the property of forming by coupling with an oxidized developing agent (in the areas of the exposed and reduced silver halide) a cyan dye image of intense colour density and high gradation, which image absorbs light in the green and blue region of the spectrum only to a very small extent, said couplers being at the same time able to form very easily a bright masking dye image by oxidative coupling according to the above described process, and being substantially indifferent towards gelatin, so that they do not at all influence the viscosity of a gelatin-colloid medium wherein they can be incorporated in a very high concentration without giving rise to flocculation.

The cyan-forming colour couplers according to the

present invention may be represented by the following general formula:



wherein:

Z represents a hydrogen atom, or a halogen atom, e.g. a chlorine atom,

X represents a halogen atom, e.g. a chlorine or fluorine atom, a $-OR_1$ group, a $-SR_1$ group, a $-SO_2R_1$ group, a $-O$ -aryl group, a $-S$ -aryl group, a $-SO_2$ -aryl group including the latter three groups wherein the aryl radical is substituted or a



group, wherein R_1 represents an alkyl group or an aralkyl group, e.g. a benzyl group or phenylethyl group, R_2 represents a hydrogen atom, an alkyl group, or an aralkyl group, e.g. a benzyl group or a phenylethyl group, or R_1 and R_2 together represent the atoms necessary to close a cycloaliphatic or saturated heterocyclic nucleus, such as a morpholine or piperidine nucleus, and

Y represents an alkyl radical, an aralkyl radical, a fluoro-substituted alkyl radical or a



radical, wherein R'_1 represents an alkyl group or an aralkyl group such as a benzyl group, and R'_2 represents a hydrogen atom, an alkyl group, an aralkyl group, e.g. a benzyl group, or R'_1 and R'_2 together represent the atoms necessary to close a saturated heterocyclic nucleus, such as a morpholine or piperidine nucleus at least one of the R_1 , R_2 , R'_1 and R'_2 radicals representing an aliphatic radical for making the molecule fast to diffusion, e.g. an alkyl radical containing from 5 to 20 carbon atoms, preferably containing 12 to 18 carbon atoms.

Preferred compounds are those wherein

X represents a chlorine atom, a methoxy group, or a



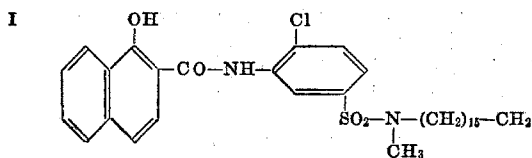
group wherein each of R_1 and R_2 represents an alkyl radical,

Y represents a

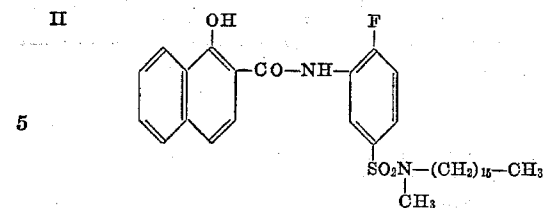


group, wherein R'_1 is a hydrogen atom or an alkyl radical, and R'_2 is an alkyl radical; at least one of the alkyl radicals in these compounds being an alkyl radical having from 5 to 20 carbon atoms in straight line.

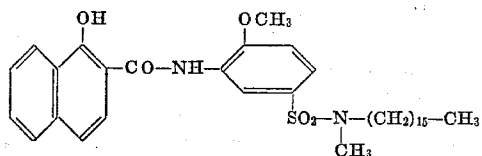
Specific compounds falling within the scope of the above formula have the following structure:



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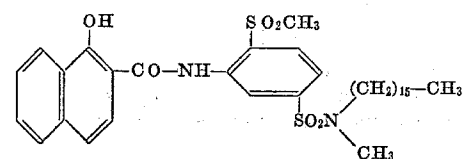


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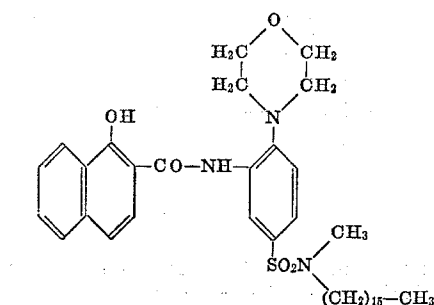


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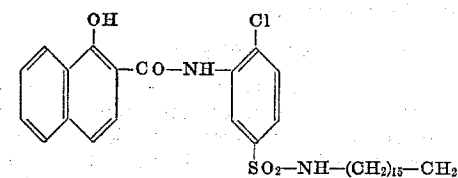
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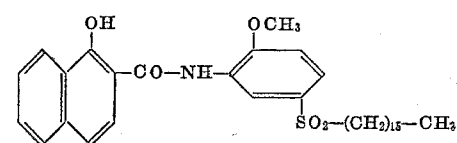
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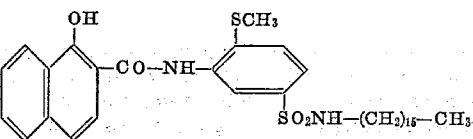


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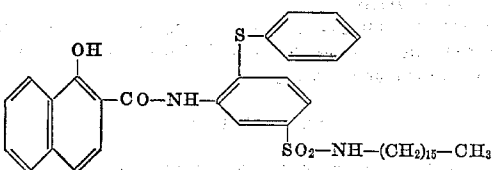
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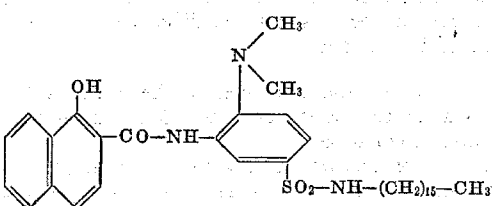


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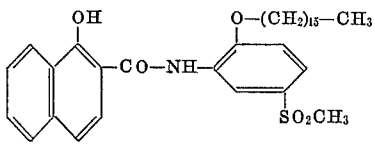
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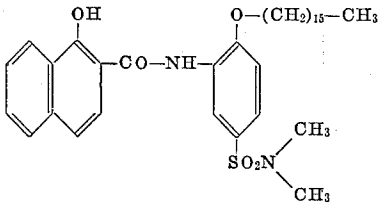
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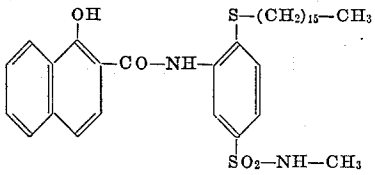
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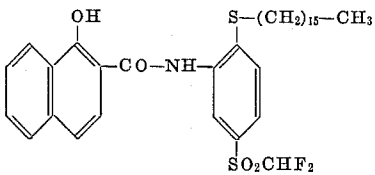
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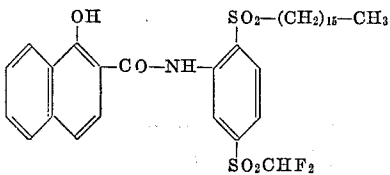
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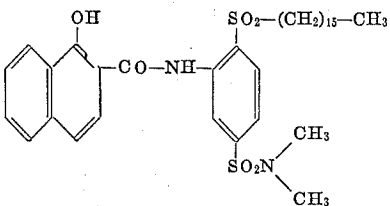
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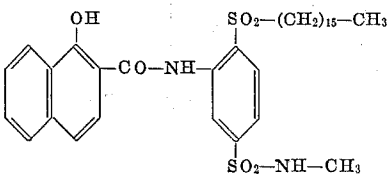
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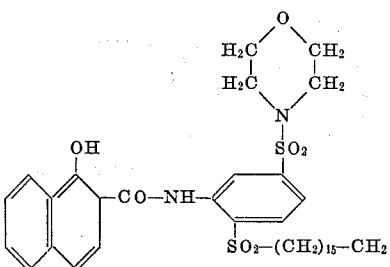
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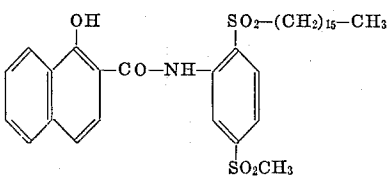
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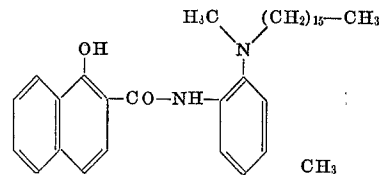


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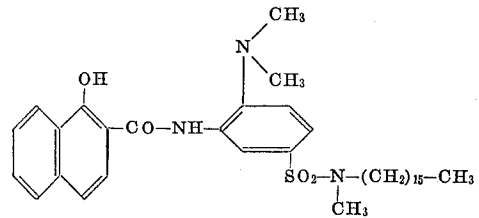
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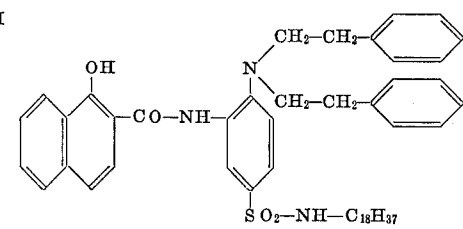
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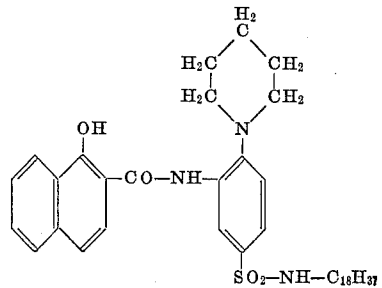
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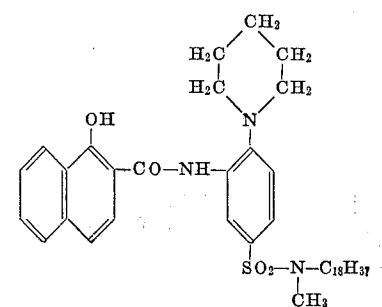
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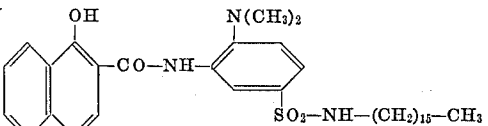
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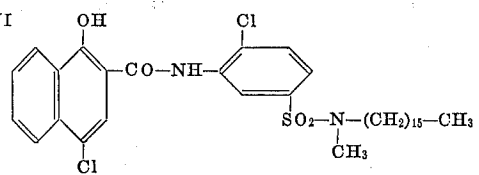
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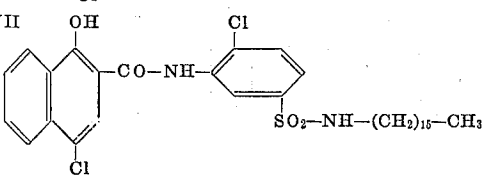
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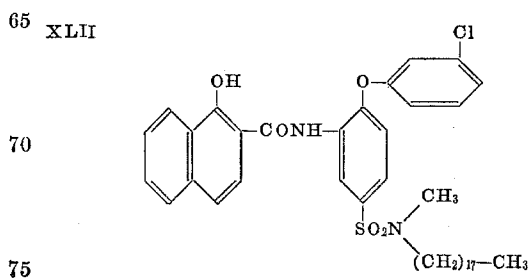
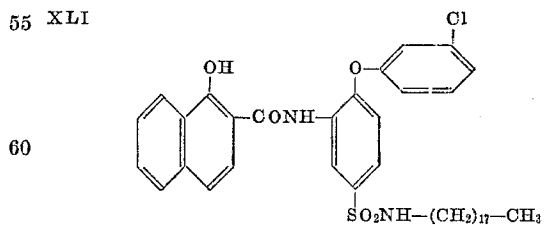
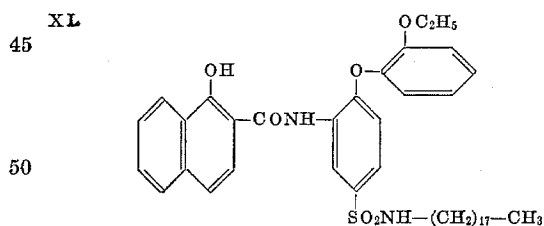
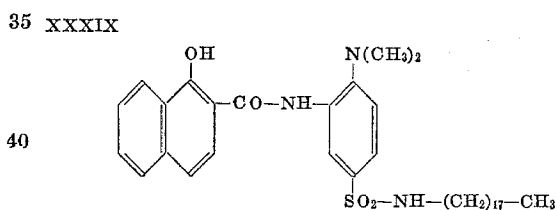
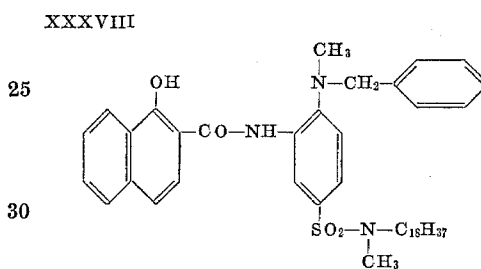
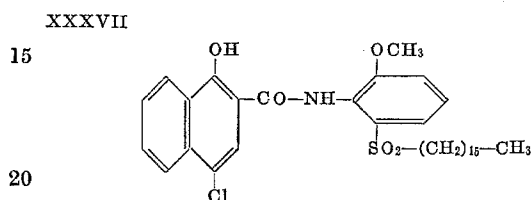
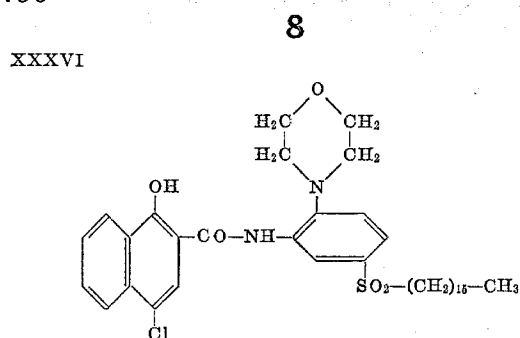
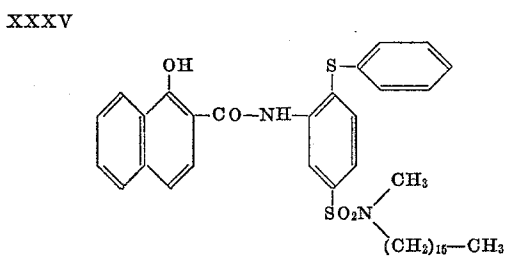
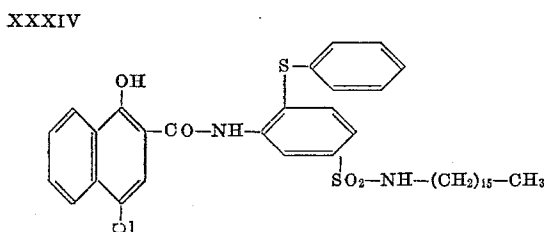
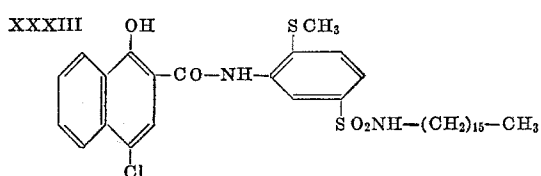
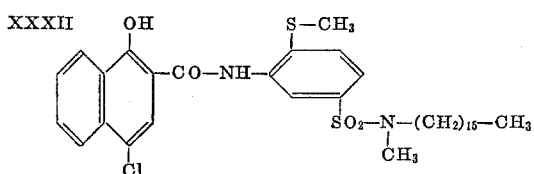
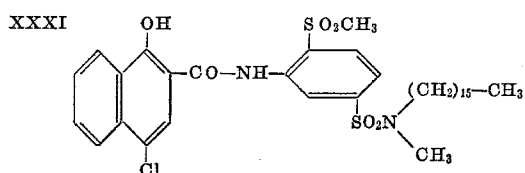
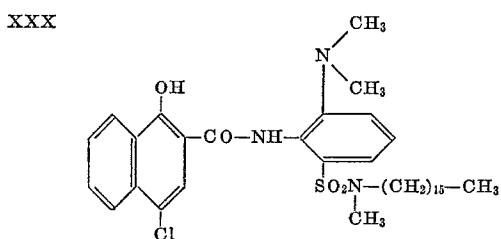
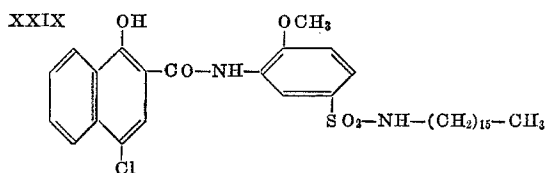
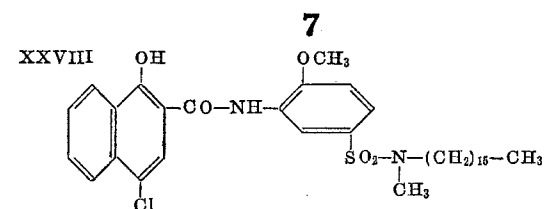


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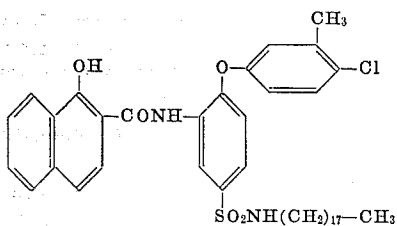


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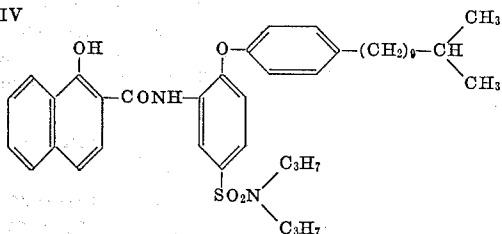


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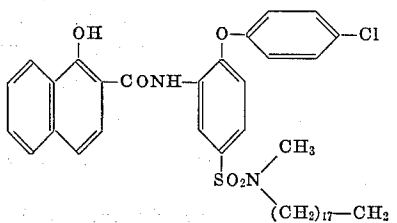
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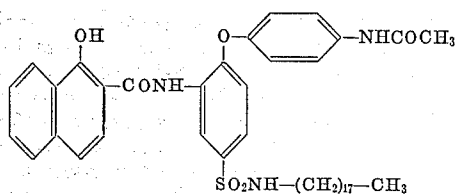
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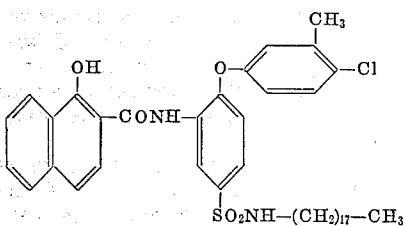
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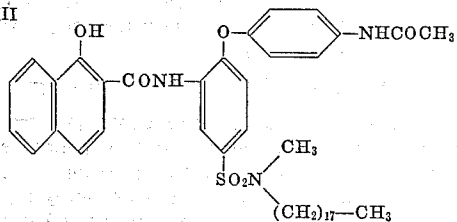
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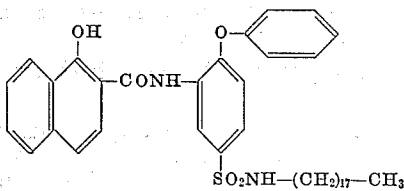
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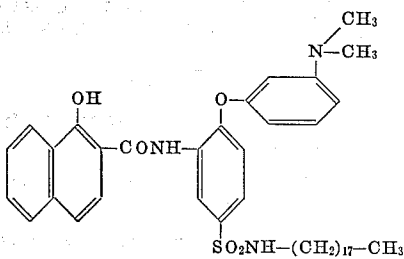
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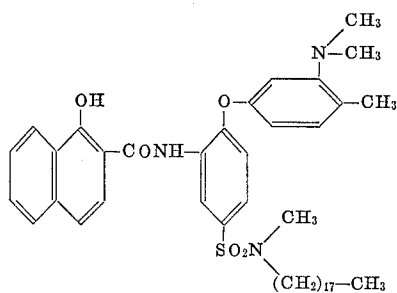
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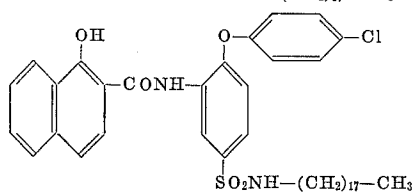
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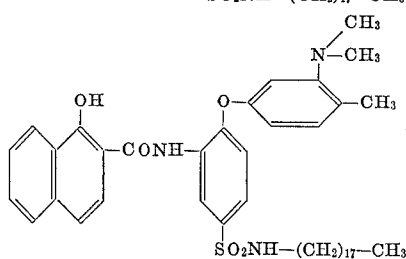
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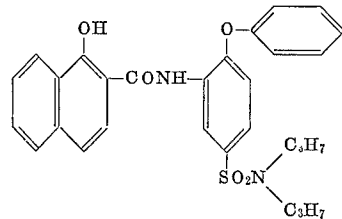
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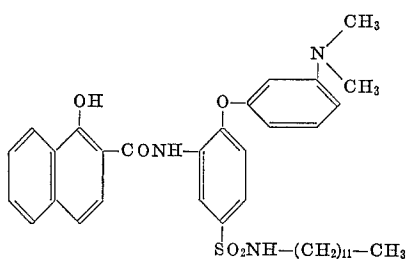
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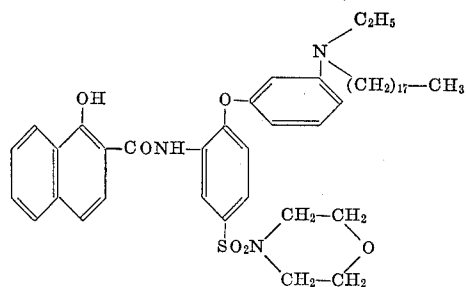
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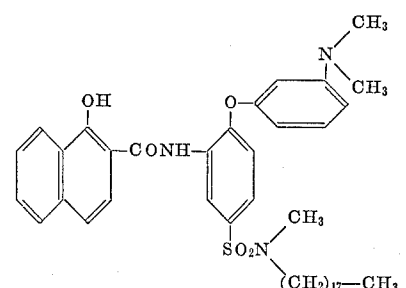
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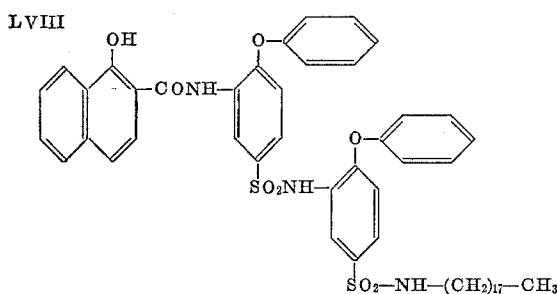
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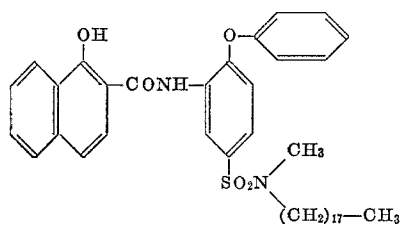
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LIX



The cyan-forming colour couplers of the present invention can be prepared analogously to the following detailed preparation methods by condensing a corresponding anilino compound with e.g. 1 - hydroxy - 2 - phenyl-naphthoate.

The anilino compounds containing a long aliphatic chain can be prepared analogously to the preparation technique illustrated hereinafter. A detailed description of the preparation of all anilino compounds is not necessary since the preparation will not cause any difficulties to those skilled in the art of preparative organic chemistry.

PREPARATION 1

(a) 2-chloro-5-methyl-n-hexadecylaminosulphonyl-nitrobenzene

To a solution of 256 g. of 2-chloro-5-chlorosulphonyl-nitrobenzene in 400 ccs. of methylene chloride, a solution of 255 g. of N-methyl-N-n-hexadecylamine in 1 litre of methylene chloride and a solution of 44 g. of sodium hydroxide in 500 ccs. of water are subsequently added dropwise with thorough stirring. After stirring for another 30 minutes, the methylene chloride layer is separated, washed with water and evaporated. The residue obtained is recrystallised from isopropanol. Yield: 430 g. (90.5%). Melting point: 77° C.

(b) 2-chloro-5-methyl-n-hexadecylaminosulphonyl-aniline

411.75 g. of the 2-chloro-5-methyl-n-hexadecylaminosulphonyl-nitrobenzene are dissolved in 175 ccs. of isopropanol and reduced at 90° C. under a hydrogen pressure of 1500 p.s.i. and in the presence of Raney nickel as a catalyst. Thereupon the solution is diluted with 175 ccs. of n-hexane cooled, and the precipitate formed is sucked off and washed with n-hexane. Yield: 330 g. (85%). Melting point: 63-64° C.

(c) 1-hydroxy-2'-chloro-5'-methyl-n-hexadecylaminosulphonyl-2-naphthanilide

222.25 g. of 2-chloro-5-methyl-n-hexadecylaminosulphonylaniline and 132 g. of 1 - hydroxy - 2 - phenyl-naphthoate are heated together at 165° C. for 1 h. under reduced pressure. While still warm, the melt obtained is recrystallised from methyl acetate. Yield: 264 g. (86%). Melting point: 107-108° C.

PREPARATION 2

(a) 2 - methoxy - 5 - methyl-n-hexadecylaminosulphonylbenzene

A solution of 192 g. of 2-chloro-5-methyl-n-hexadecylaminosulphonyl-nitrobenzene, prepared as described above, and of 22.7 g. of sodium methylate in 1200 ccs. of methanol is refluxed for 30 minutes. The reaction mixture

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is freed from sodium chloride by filtration. The filtrate is allowed to cool and a yellow crystalline product precipitates, which is collected by filtration and dried. Yield: 181 g. (96%). Melting point: 68° C.

5 (b) 2-methoxy - 5 - methyl-n-hexadecylaminosulphonyl-aniline

179 g. of 2 - methoxy-5-methyl-n-hexadecylaminosulphonyl-nitrobenzene are dissolved in 600 ccs. of ethanol and reduced at 80° C. under a hydrogen pressure of 1500 p.s.i. and in the presence of Raney nickel as a catalyst. On cooling a product precipitates, which is collected by filtration and dried. Yield: 150 g. (90%). Melting point: 62-64° C.

15 (c) 1-hydroxy-2'-methoxy-5'-methyl-n-hexadecylaminosulphonyl-2-naphthanilide

A mixture of 112.4 g. of 2-methoxy-5-methyl-n-hexadecylaminosulphonyl-aniline and 66 g. of 1 - hydroxy-2-phenyl-naphthoate is heated for 90 minutes under reduced pressure at a temperature comprised between 160 and 170° C. While still warm, the melt is recrystallised from methyl acetate. Yield: 123 g. (80%). Melting point: 101° C.

PREPARATION 3

Preparation of 1 - hydroxy-5'-methylsulphonyl-2'-hexadecyloxy-2-naphthanilide.

(a) 2-hexadecyloxy-5-methylsulphonyl-nitrobenzene

46.15 g. of finely pulverised 2-hexadecyloxy-5-chlorosulphonyl-nitrobenzene (prepared as described in United Kingdom patent specification 983,648 filed May 8, 1961 by Gevaert Photo-Production N.V.) are added to a solution of 23.65 g. of anhydrous sodium sulphite in 100 ml. of water. At 40° C. and while vigorously stirring 20 ml. of 10 N sodium hydroxide are added dropwise at such a rate that the reaction mixture always remains slightly alkaline and the temperature does not rise above 50° C.

Then the mixture is stirred for 1 h. at 60° C. whereupon it is cooled and the solid separated by suction. The sodium salt of 4-hexadecyloxy-3-nitrobenzene-sulphonic acid thus obtained is dried at 40° C. after having been washed with water.

The crude product is added to 100 ml. of ethylene glycol monomethyl ether and treated at 70° C. for 15 h. with 42.6 g. of methyl iodide whereupon the warm solution is filtered. The precipitate formed in the filtrate is separated by suction and washed with methanol. Yield: 32.5 g. (73.5%). Melting point: 105° C.

(b) 2-hexadecyloxy-5-methylsulphonyl-aniline

31 g. of the compound prepared under (a) are dissolved in 120 ml. of ethylene glycol monomethyl ether and reduced at 80° C. under a hydrogen pressure of 1500 p.s.i. in the presence of Raney nickel as a catalyst. Then the solution is cooled and the precipitate formed is separated by suction and washed with methanol. Yield: 23.3 g. (80.5%). Melting point: 85° C.

(c) 1-hydroxy-5'-methylsulphonyl-2'-hexadecyloxy-2-naphthanilide

A mixture of 22.8 g. of 2-hexadecyloxy-5-methylsulphonyl-aniline and 14.65 g. of phenyl-1-hydroxy-2-naphthoate is heated for 1 h. at 150° C.-170° C. under reduced pressure. The warm melt is recrystallised from acetic acid and washed with n-hexane. Yield: 25.8 g. (80%). Melting point: 176° C.

PREPARATION 4

Preparation of 1 - hydroxy-5'-methylaminosulphonyl-2'-hexadecylthio-2-naphthanilide.

(a) Potassium salt of 4-hexadecylthio - 3 - nitrobenzenesulphonic acid

27.55 g. of the potassium salt of 4-chloro-3-nitrobenzenesulphonic acid and 25.8 g. of hexadecylmercap-

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tane are refluxed in 150 ml. of ethylene glycol mono-methyl ether while stirring. Within a period of 5 minutes 20 ml. of 5 N sodium hydroxide are added whereupon the mixture is refluxed for a further 30 minutes while stirring. The reaction mixture is cooled and after addition of 100 ml. of methanol the precipitate formed is separated by suction. The product is washed with water and dried. Yield: 39 g. (80%). The product does not melt under 260° C.

(b) 4 - hexadecylthio-3-nitro-benzenesulphonyl chloride

150 g. of the compound prepared under (a) are dispersed in 150 ml. of thionyl chloride and to the dispersion 6.5 ml. of dimethyl formamide are added. The reaction mixture is refluxed for 3 h. while stirring whereby the compound dissolved and a precipitate of potassium chloride forms. The excess of thionyl chloride is distilled off, benzene is added to the residue and the mixture is filtered from potassium chloride. The filtrate is evaporated to dryness and the residue recrystallised from n-hexane. Yield: 100 g. (70%). Melting point: 60.5° C.

(c) 2-hexadecylthio-5-methylaminosulphonyl-nitrobenzene

119.4 g. of 4 - hexadecylthio-3-nitro-benzenesulphonyl chloride dissolved in 500 ml. of methylene chloride are treated while being stirred with 58 ml. of a 40% aqueous methylamine solution. After having been refluxed for 30 minutes, 200 ml. of water are added. The warm methylene chloride layer is separated and evaporated to dryness; the residue is recrystallised from methyl acetate. Yield: 96 g. (81%). Melting point: 116-7° C.

(d) 2-hexadecylthio-5-methylaminosulphonyl-aniline

47.2 g. of the compound prepared under (c) are dissolved while being stirred and heated in 150 ml. of methanol and 16.72 g. of iron powder are added. Then 116 ml. of 6.2 N alcoholic hydrochloric acid are gradually added at boiling temperature and the mixture is further refluxed for 30 minutes.

The mixture is filtered warm and the filtrate is poured into 2 N hydrochloric acid. The precipitate formed is separated by suction, washed with water and recrystallised from ethanol. Yield: 35 g. (80%). Melting point: 72° C.

(e) 1-hydroxy-5'-methylaminosulphonyl-2'-hexadecylthio-2-naphthanilide

A mixture of 22.1 g. of 2-hexadecylthio-5-methylaminosulphonyl aniline and 13.2 g. of phenyl-1-hydroxy-2-naphthoate are heated for 1 h. at 150° C. under reduced pressure. The warm melt is recrystallised from methyl acetate. Yield: 25 g. (81.5%). Melting point: 130-1° C.

PREPARATION 5

1-hydroxy-4-chloro-2'-chloro-5'-methyl - n - hexadecylaminosulphonyl-2-naphthanilide.

A mixture of 44.45 g. of 2-chloro-5-methyl-n-hexadecylaminosulphonylaniline, prepared as described in preparation 1, and 29.85 g. of 1-hydroxy-4-chloro-2-phenylnaphthoate is heated for 1 h. under reduced pressure at 165° C. While still warm, the melt obtained is recrystallised from isopropylether. Yield: 57.7 g. (89%). Melting point: 95° C.

PREPARATION 6

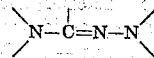
1-hydroxy-4-chloro-2'-methoxy-5'-methyl - n - hexadecylaminosulphonyl-2-naphthamide.

A mixture of 28.6 g. of 2-methoxy-5-methyl-n-hexadecylaminosulphonyl-aniline, prepared as described in preparation 2, and 19.4 g. of 1-hydroxy-4-chloro-2-phenylnaphthoate is heated for 1 h. under reduced pressure at 170° C. While still warm, the melt obtained is recrystallised from methylacetate. Yield: 37 g. (88%). Melting point: 109° C.

Mask-forming compounds preferably used in combination with the colour couplers according to the present

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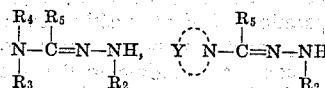
invention are amidrazone compounds, which are characterized by a grouping of the following structure:



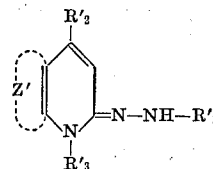
and vinylene homologues, phenylene homologues or azavinylene homologues which contain the vinylene grouping, the phenylene radical or the azomethine group in the above formula between the carbon atom and the amino group.

Representatives containing said structure and which are very suited for use in combination with a colour coupler according to the present invention are within the scope of the general formulae of the mask-forming compounds described in the United Kingdom patent specifications 975,932 filed Feb. 13, 1961 and 993,749 filed July 30, 1962 by Gevaert Photo-Producten N.V.

More particularly mask-forming compounds are preferably used which correspond to the following general formulae:



and



wherein:

R₂ represents a radical of the formula —CONH₂ or —SO₂X wherein X represents a hydroxyl radical an amino radical, a substituted amino radical such as a dialkylamino radical, a heterocyclic radical such as a N-morpholinyl radical or a N-piperidyl radical, an alkyl radical, e.g. a methyl radical or a hexadecyl radical, a substituted alkyl radical, an aryl radical or a substituted aryl radical, e.g. a methoxy-, or a hexadecyloxy-substituted phenyl radical, a carbethoxy-substituted phenyl radical, an alkyl-substituted phenyl radical such as a tolyl radical, a sulphonic acid-substituted phenyl radical, a sulphonic acid ester-substituted phenyl radical, a sulphamoyl-substituted phenyl radical, a halogen-substituted phenyl radical, e.g. a 2,5-dichlorophenyl radical or an acylamino-substituted phenyl radical,

R₃ represents a hydrogen atom, an alkyl radical such as a methyl or hexadecyl radical, an allyl radical, an aralkyl radical, e.g. a benzyl radical, an aryl radical e.g. phenyl or naphthyl, a substituted aryl radical e.g. a methoxy-substituted phenyl radical,

R₄ represents a hydrogen atom, an alkyl radical e.g. a methyl or a hexadecyl radical, a substituted alkyl radical, an aralkyl radical, e.g. a benzyl radical, an aryl radical, e.g. phenyl or naphthyl, and a substituted aryl radical, e.g. a methoxy-substituted phenyl radical,

R₅ represents a hydrogen atom, an amino radical or a substituted amino radical, e.g. a methylphenylamino radical, an alkyl radical, e.g. a methyl or ethyl radical, an aralkyl radical, e.g. a benzyl radical, a substituted benzyl radical such as a methoxy-substituted benzyl radical, an alkenyl radical e.g. an allyl radical, an aryl radical, a substituted aryl radical, e.g. a mono- or dihalogen-substituted phenyl radical, a hydroxy-substituted phenyl radical, an alkoxy-substituted phenyl radical, e.g. a mono- or dimethoxyphenyl radical or a hexadecyloxyphenyl radical, an alkylthiophenylphenyl radical, an acyloxyphenyl radical, e.g. a palmitoyloxyphenyl radical, an acylaminophenyl radical, a dialkylaminophenyl radical, an alkylsulphonylphenyl radical, a heterocyclic radical, e.g. a furyl radical, a thienyl radical, a pyridyl radical or a 5-1,3-benzodioxyl radical,

Y represents the non-metallic atoms necessary to form a 5- or 6-membered heterocyclic nucleus, e.g. a morpholine nucleus or a piperidine nucleus, and R₁ represents a —CONH₂ or —SO₂X radical, wherein X has the same value as described for R₂, each of R₂ and R₃ represents an alkyl, aralkyl or aryl radical, which may be substituted, Z' represents the non-metallic atoms necessary to complete a 6-membered aromatic ring, which may be substituted.

Mixtures of mask-forming compounds can be used with good results where sometimes one mask-forming compound will not suffice to yield the desired compensating light absorption.

The mask-forming compounds are preferably incorporated in the photographic material in a form resisting to diffusion. Therefore they contain in their structure a long aliphatic carbon chain preferably a carbon chain having from 5 to 20 carbon atoms in a straight line.

In the preparation of light-sensitive colour material according to the present invention, a non-migratory cyan-forming colour coupler according to the above general formula and preferably also a masking compound that oxidatively couples with said colour coupler in an alkaline oxidizing bleaching bath are homogeneously mixed in dissolved state with a light-sensitive silver halide emulsion, preferably immediately before the coating of the emulsion. They may, however, also be added to the composition of a water-permeable non-light-sensitive layer, which is in direct contact with the light-sensitive silver halide emulsion layer, or they may be incorporated into a non-light-sensitive layer, which is separated from the light-sensitive layer by a water-permeable non-light-sensitive layer. The silver halide emulsion contains the usual colloids such as gelatin, poly(vinyl alcohol), collodion or other suitable natural or synthetic colloids. The photographic emulsion may further contain usual ingredients such as hardeners, chemical sensitizing agents, optical sensitizing agents, plasticizers, development accelerators, stabilizing agents and wetting agents.

The cyan-forming colour couplers described in the present invention are usually incorporated into a red-sensitized silver halide emulsion. According to a common procedure in the art, this silver halide emulsion is coated as the first colour coupler-containing layer of a photographic multilayer colour material. Such photographic multilayer colour material usually consists in the given sequence of a support, a red-sensitized silver halide emulsion layer with a cyan-forming colour coupler, a green-sensitized silver halide emulsion layer with a magenta-forming colour coupler and a blue-sensitive silver halide emulsion layer with a yellow-forming colour coupler. The support of this multilayer material preferably consists of a transparent material e.g. glass, cellulose nitrate, a cellulose ester such as cellulose triacetate, polyester, polystyrene or another synthetic or natural resin.

A yellow filter layer generally comprising colloidal silver dispersed in gelatin is usually provided between the silver halide emulsion layer containing the yellow-forming colour coupler and the green-sensitized silver halide emulsion layer.

The cyan-forming colour couplers according to the present invention may also be applied in so-called "mixed-grain" type and "mixed packet" type emulsions, as e.g. described in the United States patent specifications 2,592,243 by B. H. Carroll and W. T. Hanson, issued Apr. 8, 1952 and 2,698,794 by L. Godowsky, issued Jan. 4, 1955.

For the production of photographic colour images according to the present invention the exposed silver halide emulsion layer is developed with an aromatic primary amino developing substance in the presence of a cyan-forming colour coupler according to the present invention.

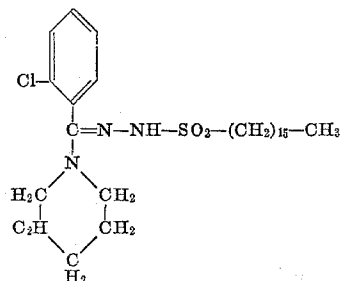
All colour developing agents capable of forming quinonimine dyes can be utilized as developers. Aromatic primary amino compounds such as p-phenylenediamine and derivatives such as N,N-diethyl-p-phenylenediamine, N,N-diethyl - N' - sulphomethyl - p - phenylenediamine and N,N-diethyl - N' - carboxymethyl - p - phenylenediamine are commonly used.

On colour development with aromatic primary amines such as N,N-diethyl-p-phenylenediamine, the cyan-forming colour couplers according to the present invention form cyan dyes having an absorption spectrum that makes these colour couplers, as already mentioned, apt to be used in negative material.

The following examples illustrate the present invention without however limiting it thereto.

EXAMPLE 1

To 250 g. of a red-sensitized silver bromo-iodide (5 mol percent iodide) emulsion containing 0.735 mole of silver halide and being acidified with 14.5 ccs. of 1 N acetic acid are added successively 4.5 g. of the colour coupler of the Formula I dissolved in a mixture of 22.5 ccs. of ethanol, 6.75 ccs. of aqueous 2 N sodium hydroxide and 16 ccs. of distilled water, 2.25 g. of the masking compound of the formula:



dissolved in 31 ccs. of ethanol, 2.25 ccs. of aqueous 2 N sodium hydroxide and 11 ccs. of distilled water.

After adding the necessary stabilizing, hardening and wetting agents the emulsion is coated onto 10 sq. m. and dried.

After exposure through a gray wedge with constant 0.15 the photographic material is developed for 9 minutes at 20° C. in a colour developing bath of the following composition:

	G.
Sodium hexametaphosphate	2
N,N-diethyl-p-phenylenediaminehydrochloride	3
Sodium sulphite	4
Sodium carbonate	57
Hydroxylamine hydrochloride	1.5
Potassium bromide	1
Water to 1000 ccs. (pH=10.6).	

This material is rinsed for 30 minutes at 18 to 20° C. and fixed for 5 minutes at 20° C. in a fixing bath of the following composition:

	G.
Sodium thiosulphate	200
Sodium bisulphite	25
Potassium alum	20
Equimolar mixture of acetic acid and sodium acetate	20
Boric acid	7.5
Water to 1000 ccs. (pH=4).	

Next, the material is rinsed again for 10 minutes at 18 to 20° C. and treated for 5 minutes in a bleaching bath of the following composition:

	G.
Potassium hexacyanoferrate (III)	100
Potassium bromide	15
Borax	20
Magnesium sulphate	20
Water to 1000 ccs. (pH=8.6).	

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Rinsing is continued for another 10 minutes at 18 to 20° C. and then the material is fixed again for 5 minutes at 20° C. in a bath of the following composition:

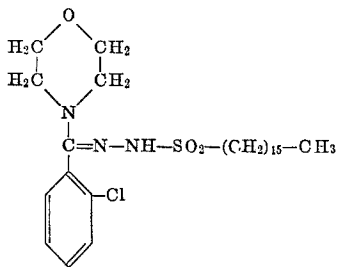
	G.	
Sodium thiosulphate	130	5
Sodium salt of ethylenediamine tetraacetic acid	1	
Sodium carbonate (anhydrous)	6	
Sodium bicarbonate	14	
Sodium sulphite (anhydrous)	10	
Water to 1000 ccs. (pH=8.8).		10

Finally, rinsing is continued for 10 minutes at 18 to 20° C. and the material is dried.

A primary cyan dye image together with a secondary orange-red mask image of opposite gradation to the said primary dye image is formed.

EXAMPLE 2

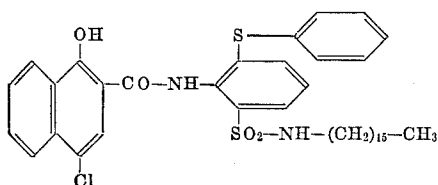
Example 1 is repeated but instead of 2.25 g. of the masking compound of the mentioned formula of same amount of the masking compound of the formula:



dissolved in a mixture of 2.25 ccs. of aqueous 1 N sodium hydroxide, 2.25 ccs. of ethanol and 6.75 ccs. of distilled water are used. In the processed material a mask image of orange colour is obtained.

EXAMPLE 3

To 250 g. of a red-sensitized silver bromo-iodide (5 mole percent iodide) emulsion containing 0.735 mole of silver halide and being slightly acidified with 21 ccs. of 1 N acetic acid 4.5 g. of the colour coupler of the formula



and 4.5 g. of the masking compound of Example 1 dissolved in 90 ccs. ethanol, 11.25 ccs. aqueous 2 N sodium hydroxide and 34 ccs. of distilled water are added.

After neutralizing and adding the necessary stabilizing, hardening and wetting agents the emulsion is coated onto 10 sq. m. and dried.

A primary cyan dye image together with a secondary orange-red mask image of opposite gradation to the said primary dye image is formed.

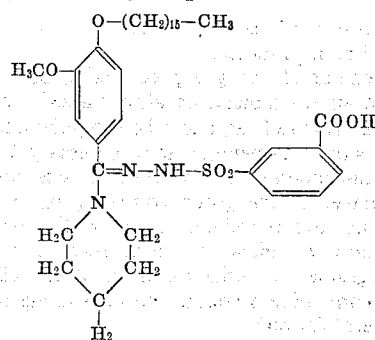
EXAMPLE 4

To 250 g. of a red-sensitized silver bromo-iodide (5 mole percent iodide) emulsion containing 0.735 mole of silver halide and being slightly acidified with 10 ccs. of 1 N acetic acid are added:

- (a) 4.5 g. of the colour coupler of the Formula X dissolved in 18 ccs. of ethanol and 4.5 ccs. of aqueous 2 N sodium hydroxide,
- (b) 1.12 g. of masking compound of Example 2 dissolved in 1.12 ccs. of aqueous 2 N sodium hydroxide and 3.36 ccs. of distilled water, and

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(c) 1.12 g. of masking compounds of the formula:



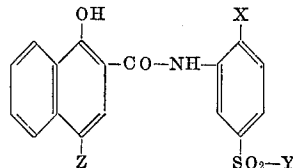
dissolved in 5.6 ccs. of ethanol, 2.24 ccs. of 2 N aqueous sodium hydroxide and 3.35 ccs. of water.

After neutralizing and adding the necessary stabilizing, hardening and wetting agents, the emulsion is coated onto 10 sq. m. of support and dried.

After processing as described in Example 1 a primary cyan dye image together with a secondary mask image of opposite gradation is obtained. The colour of said mask image lies between orange and magenta which are the colours obtained respectively when using the masking compounds separately.

We claim:

1. A light-sensitive silver halide photographic material containing in a light-sensitive silver halide emulsion a non-diffusing coupler of the general formula:



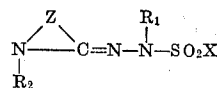
wherein:

Z is a hydrogen atom or a halogen atom,

X is a halogen atom, an alkyloxy group, an alkylthio group, an alkylsulfonyl group, an aryloxy group, an arylthio group, an arylsulfonyl group, a monoalkylamino group, a dialkylamino group, or an amino group the nitrogen atom of which makes part of the ring atoms of a saturated heterocyclic nucleus, and

Y is an alkyl radical, a monoalkylamino group, a dialkylamino group or an amino group, the nitrogen atom of which makes part of the ring atoms of a saturated heterocyclic nucleus, at least one of the alkyl radicals in the above groups being an aliphatic radical containing from 5 to 20 carbon atoms;

and a non-diffusing coupler a mask-forming compound corresponding to one of the following general formulae:



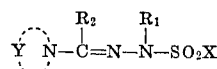
wherein:

R₁ is a member of the group consisting of a hydrogen atom and an acyl group,

R₂ is a member of the group consisting of an alkyl radical and an aryl radical,

Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing 5-6 members, at least one of which is a nitrogen atom, and

X is a member of the group consisting of an hydroxyl radical, an amino radical, an alkyl radical, an aryl radical, and a heterocyclic radical; and



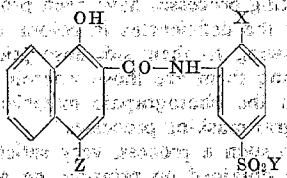
wherein:

R₁ is a member of the group consisting of a hydrogen atom and an acyl radical,

R₂ is a member of the group consisting of a hydrogen atom, an amino radical, an alkyl radical, an alkylene radical, an aryl radical, and a heterocyclic nucleus, and Y represents the non-metallic atoms necessary to complete a nitrogen-containing heterocyclic nucleus, and

X is a member of the group consisting of an hydroxyl radical, an amino radical, an aliphatic hydrocarbon radical, an aryl radical, and a heterocyclic radical.

2. Photographic material having a silver halide emulsion layer containing a coupler corresponding to the following general formula:



wherein Z is a hydrogen atom or a halogen atom, X is a methoxy group, or a dialkylamino group, Y is a monoalkylamino group, or a dialkylamino group, at least one of the alkyl radicals in the said formula being an alkyl radical having from 5 to 20 carbon atoms in straight line.

wherein: R₁ is a member of the group consisting of a hydrogen atom and an acyl radical, R₂ is a member of the group consisting of a hydrogen atom, an amino radical, an alkyl radical, an alkylene radical, an aryl radical, and a heterocyclic nucleus, and Y represents the non-metallic atoms necessary to complete a nitrogen-containing heterocyclic nucleus, and X is a member of the group consisting of an hydroxyl radical, an amino radical, an aliphatic hydrocarbon radical, an aryl radical, and a heterocyclic radical. 2. Photographic material having a silver halide emulsion layer containing a coupler corresponding to the following general formula: [Chemical structure] wherein Z is a hydrogen atom or a halogen atom, X is a methoxy group, or a dialkylamino group, Y is a monoalkylamino group, or a dialkylamino group, at least one of the alkyl radicals in the said formula being an alkyl radical having from 5 to 20 carbon atoms in straight line.

wherein:

Z is a hydrogen atom or a halogen atom, X is a methoxy group, or a dialkylamino group, Y is a monoalkylamino group, or a dialkylamino group, at least one of the alkyl radicals in the said formula being an alkyl radical having from 5 to 20 carbon atoms in straight line.

References Cited

UNITED STATES PATENTS

2,350,138	5/1944	Weissberger	96-100
2,993,791	7/1961	Coles et al.	96-100
3,244,520	4/1966	Schulte et al.	96-100
3,245,787	4/1966	Willems et al.	96-100
3,245,788	4/1966	Jaeken et al.	96-9

J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

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