

1

3,249,431 PRODUCTION OF COLOR PHOTO- GRAPHIC IMAGES

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11,036/60

16 Claims. (Cl. 96—9)

The present invention relates to the production of colored photographic images, more particularly to a process of color correction utilizing an integral masking procedure.

It is known that dyes formed by color development in subtractive multicolor photographic pictures do not transmit all of the light which practical considerations demand. The cyan dye which should absorb red light and transmit green and blue light usually absorbs a small amount of green and blue light, as well as a major proportion of red light. The magenta dye which should absorb green light and transmit blue and red light usually absorbs a considerable amount of blue light and a small amount of red light, as well as a major proportion of green light. The yellow dye which should absorb blue light and transmit green and red light is usually satisfactory.

Due to the above mentioned unwanted side-absorptions of the dyes formed by color development, it is practically impossible to obtain a true reproduction of the original colors on printing multicolor photographic transparencies containing such dyes.

Correction of the colors on printing is therefore desirable, and this is usually done by masking. Since separate masks are difficult to register with the color transparency, it is desirable that the mask be integral with the colored images.

A process for the production of a color photographic image wherein the mask is integral with the colored image is described in U.S. patent application Serial No. 705,508, filed December 27, 1957, now U.S.P. 3,012,884; No. 70,914, filed November 22, 1960, now U.S.P. 3,013,879; No. 72,298, filed November 29, 1960, by Maurice Antoine de Ramaix and Jan Jaeken, now U.S.P. 3,047,385; Serial No. 66,964, filed November 3, 1960, by Raphael Karel Van Poucke, Arthur Henri De Cat and Marcel Hendrik Verbrugghe for Process for the Manufacture of Photographic Color Images and Color Correction, now U.S.P. 3,079,256; and in the British patent specification No. 975,932.

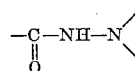
According to said pending applications a color corrected image is formed in a photographic element comprising a silver halide emulsion layer and a color coupler which is reactive with the oxidation product of an aromatic amino developing agent to form by color development a primary dye image which absorbs a major proportion of light in one region of the visible spectrum and undesirably absorbs a minor proportion of light in at least one other region of the visible spectrum, by treating the exposed and color-developed photographic element with an oxidizing solution, such as a photographic bleaching bath, in the presence of a compound, which after oxidation couples with the residual color coupler, whereby a secondary dye image having a gradation opposite to that of said primary dye image, and absorbing light in at least one of said unwanted minor absorption regions but transmitting substantially all the light in said major absorption region is formed.

It is an object of the present invention to provide a new method for correcting the colors of a photographic image used for printing. A further object is to provide a new method for the preparation of an integral mask in color film, more particularly to provide a mask image

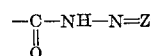
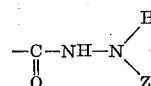
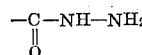
2

compensating the unwanted absorption of blue and/or green light by the cyan image dye, respectively the unwanted absorption of blue light by the magenta dye image. Other objects will appear from the following description and examples.

These objects are accomplished by treating after the color forming development an image-wise exposed photographic element comprising a silver halide emulsion layer and a color coupler which is reactive with the oxidation product of an aromatic amino developing agent to form by color development a primary dye image, with an oxidizing solution, such as a photographic bleaching bath, in the presence of a compound (called hereinafter mask forming compound) containing the following general structure:

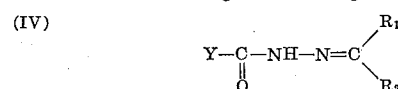
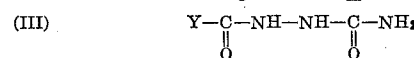
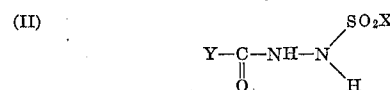


More particularly mask forming compounds are used containing the following general structures:



wherein Z and Z' are functional substituents which are sufficiently unstable for being split off during the oxidative coupling.

Mask forming compounds containing in their molecule groupings according to the foregoing general structures are e.g.:



wherein:

R₁ represents a member selected from the group consisting of a hydrogen atom, a lower alkyl radical and an aralkyl radical;

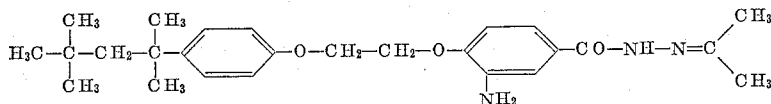
R₂ represents a member selected from the group consisting of a hydrogen atom, an alkyl radical, an aralkyl radical, and an aryl radical;

X represents a member selected from the group consisting of an alkyl radical, a substituted alkyl radical, an aralkyl radical, a substituted aralkyl radical, an aryl radical and a substituted aryl radical;

Y represents a member selected from the group consisting of an aryl radical such as a phenyl radical or a substituted phenyl radical such as a 4-methoxyphenyl radical, a 4-[β'-(β-n-butoxy-ethoxy)-ethoxy]-phenyl radical, a 4-n-hexadecyl sulfonamido-phenyl radical, a 3-amino-4-[β-(4'-isooctylphenoxy)-ethoxy]-phenyl radical, a 4-hexadecenyl succinoyl amino phenyl radical, a 4-decyloxyphenyl radical, a 3-(ω-carboxydecyl-sulfonamidophenyl) radical, a 3-(4'-carboxy-phenyl sulfonamido)-4-(n-hexadecyloxy)-phenyl radical, and a 4-(ω-carboxydecyloxy)-phenyl radical; a heterocyclic substituted aryl radical; a heterocyclic radical such as a thienyl radical; and a substituted heterocyclic radical.

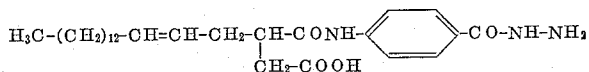
5

Preparation 4.—3-amino-4-[β -(p-iso-octyl phenoxy)-ethoxy]-benzoic acid hydrazide acetone hydrazone



0.8 g. (0.002 mol) of 3-amino-4-[β -(p-iso-octyl phenoxy)-ethoxy]-benzoic acid methyl ester, prepared as described in Example 5 of our British specification 774,421, is heated for 3 h. with an excess (1 cm.³) of anhydrous hydrazine. After cooling and pulverizing in ethanol, 0.68 g. of 3-amino-4-[β -(p-iso-octyl phenoxy)-ethoxy]-benzoic acid hydrazide melting at 173° C. is obtained. By recrystallization from ethanol this melting point remains unchanged. Calculated total amount of amino and hydrazide functions: 5.02 m. eq./g. Found by titration with perchloric acid in acetic acid: 5.02 m. eq./g. 1 g. (0.0025 mol) of the hydrazide thus obtained is heated for a few minutes with 20 cm.³ of acetone on a water-bath. For a short while the hydrazide is dissolved whereafter it precipitates immediately as hydrazone. Heating is continued for 5 minutes and then the precipitate obtained is sucked off. 0.6 g. of hydrazone melting at 173° C. is obtained. After recrystallization from ethanol, this melting point increases to 174° C. Because of the slight difference in melting point with the starting material, a mixed melting point of 154° C. is found which proves that conversion has indeed occurred.

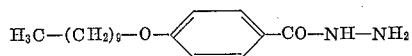
Preparation 5.—p-Hexadecenyl succinyl amino benzoic acid hydrazide



3.2 g. (0.01 mol) of hexadecenyl succinic anhydride and 1.65 g. (0.01 mol) of p-amino benzoic acid ethyl ester dissolved in 10 cm.³ of acetonitrile are heated for 3 h. on a water-bath. After cooling the reaction mixture, 4.2 g. of p-hexadecenyl succinoylamino benzoic acid ethyl ester are obtained melting non-sharply at about 90° C. taken on the Kofler hot stage. This melting point remains unchanged when recrystallized from acetonitrile. Calculated amount of carboxylic acid groups: 2.05 m. eq./g. Found by titration with sodium hydroxide in ethanol: 2.07 m. eq./g.

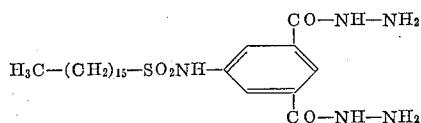
1.2 g. (0.0025 mol) of this synthesized ester is heated for 1 h. on a water-bath with an excess of 1 cm.³ of hydrazine hydrate. After solidifying, the reaction mass is pulverized in acetonitrile and sucked off. 1.15 g. of this product is obtained having a decreasing and non-sharp melting point at 154° C. taken on the Kofler hot stage. This melting point remains unchanged after repeated recrystallizations from ethanol.

Preparation 6.—p-Decyloxy benzoic acid hydrazide



14.6 g. (0.05 mol) of p-decyloxy benzoic acid methyl ester and 3.75 g. (mol 0.075) of hydrazine hydrate are refluxed for 12 h. Whilst cooling, the reaction mixture is completely solidified and it melts non-sharply at 85° C. After recrystallization from acetonitrile 9 g. of p-decyloxy-benzoic acid hydrazide melting at 93° C. are obtained.

Preparation 7.—5-(n-hexadecyl sulfonamido)isophthalic acid dihydrazide



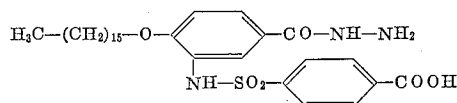
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10.5 g. (0.05 mol) of 5-amino-isophthalic acid dimethyl ester and 16.25 g. (0.05 mol) of n-hexadecyl sul-

fonyl chloride are reacted at room temperature for 48 h. in 50 cm.³ of pyridine. After pouring the reaction mixture in an aqueous solution of N hydrochloric acid the resulting product is recrystallized from ethanol. 20 g. of 5-(n-hexadecyl sulfonamido)-isophthalic acid dimethyl ester are obtained. Melting point: 126° C.

24 g. (0.05 mol) of the preceding ester and 16 g. (0.5 mol) of a 95% aqueous solution of hydrazine are reacted at reflux temperature in 250 cm.³ of ethanol. After cooling the formed reaction product is sucked off, washed with ether and recrystallized from n-butanol. 21 g. of 5-n-hexadecyl-sulfonamido-isophthalic acid dihydrazide are obtained. Melting point: 216° C.

Preparation 8.—3-(4'-carboxyphenyl-sulfonamido)-4-(n-hexadecyloxy)-benzoylhydrazide

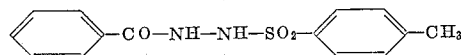


39 g. (0.1 mol) of 3-amino-4-n-hexadecyl-benzoic acid methyl ester, prepared according to Example 5b of our French patent specification 1,203,594, 22 g. (0.1 mol) of p-carboxyphenyl sulfonyl chloride and 30 g. (0.3 mol) of calcium carbonate are reacted at reflux temperature whilst stirring for 3 h. in 50 cm.³ of acetonitrile.

Then 600 cm.³ of a 5% aqueous solution of sodium carbonate are added in order to convert the carboxylic acid calcium salt in the corresponding sodium salt. The reaction mixture is filtered whilst hot and acidified with N hydrochloric acid. After sucking off, washing with N hydrochloric acid and recrystallizing from acetic acid, 47 g. of 3-(4'-carboxyphenylsulfonamido)-4-(n-hexadecyloxy)-benzoic acid methyl ester are obtained. Melting point: 150° C. (unsharp).

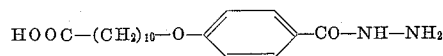
2.3 g. (0.004 mol) of the preceding compound and 1.3 cm.³ (0.04 mol) of hydrazine are heated on a water-bath for 3 h. After cooling, sucking off and grinding under N hydrochloric acid the resulting product is recrystallized from ethylacetate. 0.7 g. of 3-(4'-carboxyphenyl sulfonamido)-4-(n-hexadecyloxy)-benzoylhydrazide are obtained. Melting point: 120° C. (with decomposition).

Preparation 9.—N-benzoyl-N'-p-tolulsulfonyl-hydrazine



1.36 g. (0.01 mol) of benzoylhydrazide, 1.9 g. (0.01 mol) of p-tolulsulfochloride and 1.5 g. (0.01 mol) of calcium carbonate are stirred for 9 h. at room temperature in 50 cm.³ of ethylacetate. After filtering the reaction product is precipitated from the obtained filtrate by adding n-hexane. After recrystallizing from benzene and drying 0.6 g. of N-benzoyl-N'-p-tolulsulfonyl hydrazine are obtained. Melting point: 179° C.

Preparation 10.—4-(ω -carboxy-decyloxy)-benzoylhydrazide



0.5 g. (0.02 mol) of sodium are dissolved in 25 g. of anhydrous methanol, 3.04 g. (0.02 mol) of p-hydroxy benzoic acid methyl ester and 5.3 g. (0.02 mol) of ω -bromo-hendecanoic acid are reacted for 14 h. at reflux temperature. The solvent is distilled off and after dis-

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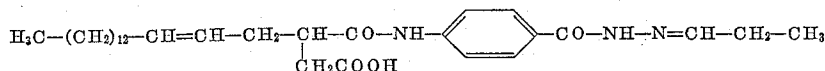
solving the solid residue in acetic acid and adding hot water the crude 4-(ω -carboxy-decyloxy)-benzoic acid methyl ester crystallizes out. After recrystallizing from acetonitrile, 2 g. of the purified compound are obtained. Melting point: 101° C.

1.71 g. (0.005 mol) of the preceding compound and 2 cm.³ of hydrazine are heated for 3 h. on a water-bath. After cooling, sucking off and washing with ether, the formed carboxylic acid hydrazinium salt is converted in the free carboxylic acid by storing the product for 2 days under 5 N hydrochloric acid. 1.4 g. of 4-(ω -carboxy-

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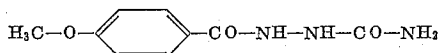
in cold water and treated with a concentrated solution of sodium acetate to precipitate it as free hydrazide. After sucking off, washing with water and recrystallized from ethylene glycol monomethyl ether, 5.5 g. of 5-(ω -carboxy-decyl sulfonamido)-isophthalic acid dihydrazide are obtained. Melting point: 232° C. By further recrystallization from ethylene glycol monomethyl ether, the melting point rises to 238° C.

10 Preparation 13.—p-(2-hexadecenylsuccinoylamino)-benzoic acid hydrazide propional hydrazone



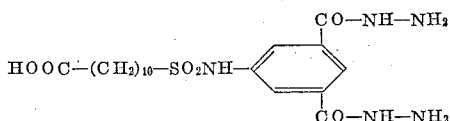
decyloxy)-benzoyl hydrazide are obtained. Melting point: 139° C. After recrystallization from acetonitrile the melting point does not change.

Preparation 11.—4-methoxy-benzoyl semicarbazide



3.32 g. (0.02 mol) of p-methoxybenzoic acid hydrazide, prepared according to Curtis, J. Prakt. Chem. [2], 81, 548 are dissolved in a hot solution of 10 cm.³ of water and 2 cm.³ of acetic acid. By cooling till 30° C. a suspension of fine crystals is formed. At the same temperature 1.86 g. (0.023 mol) of potassium cyanate dissolved in 5 cm.³ of water are added thereto. The precipitate formed is sucked off and washed with water. After recrystallization from water 3 g. of 4-methoxy-benzoyl semicarbazide is obtained. Melting point: 259° C.

Preparation 12.—5-(ω -carboxy-decylsulfonamido)-isophthalic acid dihydrazide



13.5 g. (0.05 mol) of 11-bromohendecanoic acid and 3.8 g. (0.05 mol) of thiourea are refluxed for 2 h. in 100 cm.³ of ethanol. After evaporating the solvent, the residue is washed with ether and recrystallized from dioxane. 10.2 g. of S-(ω -carboxydecyl)-isothiuronium bromide is obtained. Melting point: 148° C.

At 10 to 20° C., through a suspension of 117 g. (0.344 mol) of the preceding thiuronium compound in 500 cm.³ of water and 500 cm.³ of ethanol a stream of chlorine gas is led. The resulting compound is precipitated by adding 250 cm.³ of water. The product is sucked off and washed with water. After purifying by dissolving in benzene and carefully precipitating with n-hexane 70 g. of ω -carboxydecyl sulfonyl chloride are obtained. Melting point: 66° C.

To a solution of 10.5 g. (0.05 mol) of 5-amino-isophthalic acid dimethyl ester in 100 cm.³ of pyridine are gradually added at 10–15° C. 14.2 g. (0.05 mol) of the preceding sulfonyl chloride. The reaction mixture is left for 2 h. at this temperature. After pouring the reaction mixture in a mixture of 5 N hydrochloric acid and ice, the precipitate formed is sucked off and washed with water. After recrystallizing from acetonitrile, 12.5 g. of 5-(ω -carboxy-decyl sulfonamido)-isophthalic acid dimethyl ester are obtained. Melting point: 135° C.

11.5 g. (0.025 mol) of the preceding ester are heated on a water-bath with 8 g. (0.25 mol) of a 95% aqueous solution of hydrazine. After cooling, the obtained product is ground under 5 N hydrochloric acid. The dihydrazide dihydrochloride formed is sucked off, dissolved

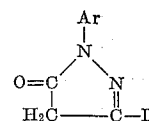
A solution consisting of 2.4 g. (0.005 mol) of the hydrazide prepared according to Preparation 5, and 0.7 g. (0.006 mol) of propionaldehyde in 20 cm.³ of ethanol is refluxed for ½ h. on a water-bath. After cooling, sucking off and washing with ethanol, 2.3 g. of p-(2-hexadecenylsuccinoylamino)-benzoic acid hydrazide propional hydrazone are obtained. Melting point: 182° C. (with decomposition). Recrystallization from dioxane does not raise the melting point.

According to a preferred embodiment of the present invention, the mask forming compound is incorporated in one of the layers present in the light-sensitive photographic material, preferably in the silver halide emulsion layer wherein the mask image is to be formed by oxidative coupling of the residual color coupler, present in that layer, with the mask forming substance; in order to prevent the diffusion of the mask forming compound out of the silver halide emulsion layer wherein this compound originally was incorporated, preferably mask forming compounds are used containing a radical comprising a linear chain of 5 to 20 carbon atoms.

The process of color correction of the present invention may be practised, i.e., by using a color photographic material containing a coupler for magenta belonging to the class of the pyrazolone color couplers and/or a coupler for cyan belonging to the class of the phenol- or naphthol color couplers. Depending upon the structure of the color coupler used in combination with the mask-forming compound according to the present invention, from yellow to red colored mask images are obtained on treating the photographic material with an oxidizing substance such as present in a potassium ferricyanide bleaching bath.

It has been found that by oxidative coupling of the mask-forming compounds of the present invention with a pyrazolone color coupler for magenta, a yellow colored mask image is obtained which compensates the undesirable side-absorption in the blue part of the spectrum of the magenta dye image obtained by color development of the exposed areas of the layer containing said coupler for magenta.

Pyrazolone color couplers which are especially useful for obtaining a mask image for magenta by reaction with the mask forming substances according to the present invention are e.g. those represented by the general formula:



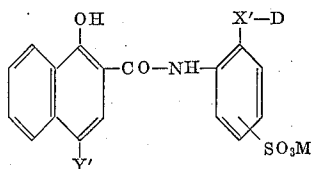
70 where in

Ar represents a member selected from the group consisting of a phenyl radical and a phenyl radical containing a solubilizing group such as a sulfonic acid group, and D represents an aliphatic radical making the molecule fast

to diffusion and comprising a linear chain of at least 5 and at most 20 carbon atoms, preferably 14, 16 or 18 carbon atoms.

It has further been found that by oxidative coupling of some of the mask-forming compounds of the present invention with naphthol color couplers for cyan, a yellow to magenta colored mask image is obtained which compensates the undesirable side-adsorption in the blue and/or green part of the spectrum of the cyan image obtained by color development of the exposed areas of the layer containing said cyan color coupler.

Naphthol color couplers which are especially useful for obtaining a mask image for cyan by reaction with the mask forming substances according to the present invention are, e.g., these represented by the general formula:



wherein:

X' represents a member selected from the group consisting of an oxygen atom, a sulfur atom, a —NH—CO— group, a —CO—NH— group, a $\text{—SO}_2\text{—NH—}$ group, a $\text{—NH—SO}_2\text{—}$ group, a



group and a sulfonyl group;

Y' represents a member selected from the group consisting of an hydrogen atom and a halogen atom;

M represents a member selected from the group consisting of an hydrogen atom, an alkali metal atom and an ammonium group; and

D has the same value as set forth above.

Suitable color couplers of the above general formula are for instance:

N-(2'-n-hexadecyloxy-5'-sulfo)-phenyl-1-hydroxy-2-naphthoic acid amide sodium salt,
N-(2'-n-hexadecyloxy-5'-sulfo)-phenyl-1-hydroxy-4-chloro-2-naphthoic acid amide sodium salt,
N-(2'-n-hexadecylmercapto-5'-sulfo)-phenyl-1-hydroxy-2-naphthoic acid amide sodium salt,
N-(2'-n-hexadecylmercapto-5'-sulfo)-phenyl-1-hydroxy-4-bromo-2-naphthoic acid amide sodium salt,
N-(2'-n-hexadecylmercapto-5'-sulfo)-phenyl-1-hydroxy-4-chloro-2-naphthoic acid amide sodium salt,
N-(2'-palmitoylamino-4'-sulfo)-phenyl-1-hydroxy-2-naphthoic acid amide sodium salt,
N-(2'-methyl cetyl-amino-5'-sulfo)-phenyl-1-hydroxy-4-chloro-2-naphthoic acid amide sodium salt,
N-(6'-n-hexadecylsulfonylphenyl)-1-hydroxy-2-naphthoic acid amide-3'-sodium sulfonate,
N-(6'-n-hexadecylsulfonylphenyl)-1-hydroxy-4-chloro-2-naphthoic acid amide-3'-sodium sulfonate,
N-(4'-n-hexadecylsulfonyl)-1-hydroxy-2-naphthoic acid amide-3'-sodium sulfonate.

These color couplers for cyan can be prepared, e.g., by condensation of 1-hydroxy-2-naphthoic acid or its derivatives with the suitable aromatic amines according to German patent application No. G 30,287, filed August 13, 1960, now German Patent No. 1,121,061.

It is to be noted that by oxidative coupling of some of the mask forming compounds of the present invention with color couplers for cyan of the formula given above, a yellow to orange colored mask image is obtained which compensates the undesirable side-adsorption in the blue as well as in the green part of the spectrum. In this way, if the mask forming compound is present in the emulsion layer containing the cyan color coupler as well as in the emulsion layer containing the magenta color

coupler, the cyan dye is masked in the green as well as in the blue range of the visible spectrum and at the same time the side absorption of the magenta dye can be corrected in the blue range of the visible spectrum, so that practically all the unwanted absorptions are compensated by a mask image.

For carrying out the process according to the present invention, the color couplers and mask compounds can be incorporated into a photographic silver halide emulsion prepared by means of the colloids usually employed therefor, such as for instance gelatin, polyvinyl alcohol, collodion or other natural or synthetic colloids. The silver halide emulsion can be coated on a support consisting of paper, glass, nitrocellulose, cellulose esters such as cellulose triacetate, polyester, polystyrene or another natural or synthetic resin, and forms part of a photographic material with one or more emulsion layers. The multilayer material usually comprises the following elements: a support, a red-sensitive emulsion layer having a color coupler for cyan, a green-sensitive emulsion layer having a color coupler for magenta and a blue-sensitive emulsion layer having a color coupler for yellow. There is a yellow filter composed in most of the cases of a gelatin layer containing dispersed colloidal silver, located between the blue-sensitive emulsion layer and the green-sensitive emulsion layer. It is not only possible to incorporate the color couplers into the light-sensitive silver halide emulsion layer itself but they can also be incorporated into an adjacent non-light-sensitive colloid layer or into a non-light-sensitive layer which is separated from the light-sensitive emulsion layer by a water-permeable colloid layer.

The process according to the invention proceeds as follows: silver halide is reduced to silver at the exposed areas in a color developing bath containing a primary amine aromatic developing agent which is at the same time oxidized. The oxidized developing agent reacts with the color coupler and forms a dyestuff on the exposed areas, the mask forming compound according to the invention not being affected. After the color development, the material comes into the bleaching bath wherein the oxidation of the mask forming compound takes place, and the remaining color coupler still available at the non-exposed areas of the material oxidatively couples with the oxidation product of the mask compound thus forming the mask dyestuff. In this way the colored mask image is formed. Subsequently, the photographic color material is washed with water, fixed and dried.

The following aromatic amino-compounds can be used as developers for such material: mono-, di- and triamino-aryl compounds, more especially N,N-dialkyl-p-phenylenediamines, such as N,N-diethyl-p-phenylenediamine and N,N-diethyl-2-methyl-p-phenylene diamine, and derivatives thereof such as N,N-dialkyl-N'-sulfomethyl- or carboxymethyl-p-phenylenediamine. As useful mono-amino-developers should be cited: aminophenols and aminocresols or their halogen derivatives and also the amino-naphthols.

The bleaching bath generally contains potassium bromide, borax, magnesium sulfate and especially potassium ferricyanide. These elements are dissolved in precisely determined amounts of water so that a solution with a determined pH value is obtained.

The following examples illustrate the invention without limiting, however, the scope thereof.

Example 1

To $\frac{1}{2}$ kg. of a green-sensitized silver bromo-iodide emulsion containing $\frac{1}{8}$ mol. of silver halide are added a slightly alkaline alcoholic solution containing 9 g. of 1-p-sulfo-phenyl-3-heptadecyl-5-pyrazolone, and a solution in 40 cm.³ of ethanol of 4 g. of p-decyloxy benzoic acid hydrazide obtained according to Preparation 6. After acidification with acetic acid to pH 5.8 and after addition of the usual additives such as hardeners, wetting agents

and stabilizers, the emulsion obtained is coated on a suitable support and dried. After exposure through a grey-wedge with a constant 0.15, the photographic material is developed for 9 min. at 20° C. in a color developing bath of the following composition:

Sodium hexametaphosphate -----	G.	2
N,N-diethyl-p-phenylenediamine hydrochloride ----		3
Sodium sulfite -----		4
Sodium carbonate -----		57
Hydroxylamine hydrochloride -----		1.5
Potassium bromide -----		1
Water to 1000 cm. ³ .		
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:

Sodium thiosulfate -----	G.	200
Sodium bisulfite -----		25
Potassium alum -----		20
Sodium biacetate -----		20
Boric acid -----		7.5
Water to 1000 cm. ³ .		
pH=4.00.		

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:

Potassium ferricyanide -----	G.	100
Potassium bromide -----		15
Borax -----		20
Magnesium sulfate -----		50
Water to 1000 cm. ³ .		
pH=8.8.		

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:

Trisodium salt of ethylene diamine tetraacetic acid -----	G.	1
Sodium thiosulfate -----		130
Sodium carbonate -----		6
Sodium bicarbonate -----		14
Sodium sulfite -----		10
Water to 1000 cm. ³ .		
pH=8.8.		

A mainly magenta colored image is obtained together with a yellow dye image, said yellow image being of opposite gradation in respect of the magenta dye image and reducing the disturbing influence of the unwanted absorption in the blue region of the spectrum of the magenta image.

Example 2

To ½ kg. of a green-sensitized silver bromo-iodide emulsion containing ¼ mol. of silver halide are added a slightly alkaline alcoholic solution containing 9 g. of 1-p-sulfo-phenyl-3-heptadecyl-5-pyrazolone and a solution in 40 cm.³ of ethanol of 4 g. of p-decyloxybenzoic acid hydrazide obtained according to Preparation 6. After acidification with acetic acid to pH 6 and after addition of the usual additives such as hardeners, wetting agents and stabilizers, the emulsion obtained is ready to be coated. After coating, this emulsion forms part of a multilayer photographic material consisting of the following superposed layers in the indicated sequence: a support, an antihalation layer, a gelatin insulating layer, a red-sensitized emulsion layer containing a color coupler for cyan, a gelatin interlayer, the above-mentioned green-sensitized emulsion layer, a yellow filter layer, a blue-sensitive emulsion layer containing a color coupler for yellow and at last a gelatin overcoat as antistress layer.

After exposure through a grey wedge with a constant

0.15 the photographic material is developed and further treated as in Example 1.

A mainly magenta colored image is obtained together with a yellow dye image in the green-sensitized layer, said yellow image being of opposite gradation in respect of the magenta dye image and reducing the disturbing influence of the unwanted absorption in the blue region of the spectrum of the formed magenta image.

Example 3

To ½ kg. of a red-sensitive bromo-iodide emulsion (2% iodide) containing ¼ mol. of silver halide are added a solution of 10 g. of N-(6'-cetylsulfonylphenyl)-1-hydroxy-2-naphthoic acid amide-3'-sodium sulfonate in 193 cm.³ of water, 7 cm.³ of an aqueous solution of 2 N sodium hydroxide and a solution in 40 cm.³ of ethanol of 4 g. of p-decyloxybenzoic acid hydrazide prepared according to Preparation 6. After acidification to pH 5.8 and after addition of the usual additives such as hardeners, wetting agents and stabilizers, the necessary quantity of distilled water is added as to obtain 1 kg. of emulsion. This emulsion is coated on a suitable support and dried. After a further treatment according to Example 1, a cyan image is obtained wherein the disturbing influence of the side-absorption in the blue and in the green is reduced by the formed red masking image with opposite gradation to the cyan image.

Example 4

To ½ kg. of a red-sensitive silver bromo-iodide emulsion (2% iodide) containing ¼ mol. of silver halide are added a solution of 10 g. of N-(6'-n-hexadecylsulfonylphenyl)-1-hydroxy-2-naphthoic acid amide-3'-sodium sulfonate in 193 cm.³ of water, 7 cm.³ of aqueous 2 N sodium hydroxide and 4 g. of 5-(n-hexadecylsulfonamido)-isophthalic acid dihydrazide prepared according to Preparation 7 dissolved in a mixture of 12 cm.³ of aqueous 2 N sodium hydroxide and 4 cm.³ of distilled water. After acidification to pH 6, the usual additives such as hardeners, wetting agents and stabilizers and the necessary quantity of distilled water are added to the emulsion in order to obtain 1 kg. of flowable emulsion. After coating, this emulsion forms part of a multilayer photographic material consisting of the following superposed layers in the indicated sequence: a supporting antihalation layer, a gelatin insulating layer, the above-mentioned red-sensitive emulsion layer containing a color coupler for cyan, a gelatin interlayer, a green-sensitive emulsion layer, a yellow filter layer, a blue-sensitive emulsion layer containing a color coupler for yellow and at last a gelatin overcoat as antistress layer. After exposure through a grey wedge with a constant 0.15 the photographic material is developed and further treated as in Example 1. A mainly cyan-colored image is obtained together with a red dye image in the red-sensitive layer, said red image being of opposite gradation in respect of the cyan dye image and reducing the disturbing influence of the side-absorption in the blue and in the green in the formed cyan image.

Example 5

To ½ kg. of a green-sensitive silver bromo-iodide emulsion containing ¼ mol. of silver halide are added a slightly alkaline alcoholic solution containing 9 g. of 1-p-sulfo-phenyl-3-heptadecyl-5-pyrazolone and a solution of 5-(n-hexadecylsulfonamido)-isophthalic acid dihydrazide prepared according to Preparation 7 in a mixture of 12 cm.³ aqueous 2 N sodium hydroxide and 4 cm.³ of distilled water. After acidification with acetic acid to pH 6 and after addition of the usual additives such as hardeners, wetting agents and stabilizers, the emulsion obtained is coated onto a support. This emulsion forms part of a multilayer photographic material consisting of the following superposed layers in the indicated sequence: a support, an antihalation layer, a gelatin insulating layer, a red-sensitized emulsion layer containing a color coupler for cyan, a gelatin interlayer, the above-mentioned green-

sensitized emulsion layer, a yellow filter layer, a blue-sensitive emulsion layer containing a color coupler for yellow and at last a gelatin overcoat as antistress layer.

After exposure through a grey-wedge with a constant 0.15 the photographic material is developed and further treated as in Example 1.

A mainly magenta colored image is obtained together with a yellow dye image in the green-sensitized layer, said yellow image being of opposite gradation in respect of the magenta dye image and reducing the disturbing influence of the unwanted absorption in the blue region of the spectrum of the formed magenta image.

Example 6

A photographic multilayer material is manufactured as in the foregoing example, the red-sensitive and the green-sensitive emulsion layers being prepared as follows: the red-sensitive emulsion layer is prepared by adding to ½ kg. of a gelatino silver bromo-iodide emulsion (2% of iodide) containing ⅓ mol of silver halide a solution of 9 g. of N-(6'-cetylsulfonyl-phenyl)-1-hydroxy-2-naphthoic acid amide-3'-sodium sulfonate in a mixture of 175 cm.³ of water and 6.3 cm.³ of aqueous 2 N sodium hydroxide and a solution of 4 g. of 5-(n-hexadecylsulfonamido)-isophthalic acid dihydrazide prepared according to Preparation 7 in a mixture of 12 cm.³ of aqueous 2 N sodium hydroxide and 4 cm.³ of distilled water. Next, this emulsion is acidified with acetic acid to pH 6, and after adding the usual additives such as hardeners, wetting agents, stabilizers and the necessary quantity of distilled water, 1 kg. of flowable emulsion is obtained.

The green-sensitive emulsion layer is prepared by adding to ½ kg. of gelatino silver bromo-iodide emulsion (2% of iodide) containing ⅓ mol of silver halide 9 g. of a slightly alkaline alcoholic solution of 1-p-sulfophenyl-3-heptadecyl-5-pyrazolone and a solution of 4 g. of the mask compound 5-(n-hexadecylsulfonamido)-isophthalic acid dihydrazide prepared according to Preparation 7, in a mixture of 12 cm.³ of aqueous 2 N sodium hydroxide and 4 cm.³ of distilled water. Next, this emulsion is acidified with acetic acid to pH 5.8 and after adding the usual additives such as hardeners, wetting agents, stabilizers and the necessary quantity of distilled water, 1 kg. of flowable emulsion is obtained.

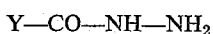
The light-sensitive multilayer photographic material is exposed through a grey-wedge, developed and further treated as described in Example 1.

In the red-sensitive emulsion layer a red dye mask image is formed in addition to the cyan image with a gradation opposed to that of the cyan image, and which compensates the side-absorptions of the cyan image in the blue as well as in the green region of the spectrum.

In the green-sensitive emulsion layer a yellow dye mask image is formed in addition to the magenta dye image with a gradation opposed to that of the magenta image, and which reduces the disturbing influence of the unwanted absorption in the blue region of the spectrum of the formed magenta image.

I claim:

1. In a method of forming a color corrected image in a photographic element having at least one silver halide emulsion layer containing a color coupler for magenta which is reactive with the oxidation product of an aromatic amino developing agent to form by color development a magenta primary dye image which absorbs a major proportion of light in one region of the visible spectrum, and undesirably absorbs a minor proportion of light in at least one other region of the visible spectrum, in which method said element is exposed to said image to be photographed, developed with said developing agent and thereafter treated with an oxidizing solution, the improvement wherein said element has present therein a mask forming compound having the formula:



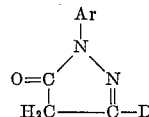
wherein:

Y is a member of the group consisting of an aryl radical and a heterocyclic radical;

whereby the residual color coupler oxidatively couples with said mask-forming compound to form a secondary dye image having a gradation opposite to that of said magenta primary dye image, said secondary image absorbing light in at least one of said undesirable minor absorption regions but transmitting substantially all the light in said major absorption region.

2. The method of claim 1 wherein said color coupler for magenta is a pyrazolone compound.

3. The method of claim 2 wherein said pyrazolone compound has the formula:



wherein:

Ar is a member of the group consisting of a phenyl radical and a phenyl radical containing a solubilizing group, and

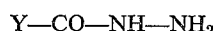
D is an aliphatic radical comprising a linear chain of 5-20 carbon atoms.

4. The method of claim 1 wherein said oxidizing solution is a photographic bleaching bath.

5. The method of claim 1 wherein said mask-forming compound is incorporated in the same emulsion layer containing said magenta color coupler.

6. The method of claim 3 wherein said color coupler forms a yellow secondary dye image.

7. A color photographic element useful in the method of claim 1, said element having superposed silver halide emulsion layers sensitive to different regions of the visible spectrum, at least one of said layers containing a color coupler for magenta which is reactive with the oxidation product of an aromatic amino developing agent to form by color development a magenta primary dye image which absorbs a major proportion of light in one region of the spectrum, and undesirably absorbs a minor proportion of light in at least one other region of the visible spectrum, such layer also containing a mask-forming compound of the formula:

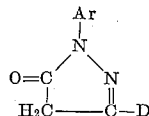


wherein:

Y is a member of the group consisting of an aryl radical and a heterocyclic radical;

said color coupler for magenta also being reactive with the oxidation product of said mask-forming compound to form a secondary dye image having a gradation opposite to that of said magenta primary dye image, and absorbing light in at least one of said unwanted minor absorption regions but transmitting substantially all the light in said major absorption region.

8. The element of claim 7 wherein said color coupler is a compound having the formula:



wherein:

Ar is a member of the group consisting of a phenyl radical and a phenyl radical containing a solubilizing group, and

D is an aliphatic radical comprising a linear chain of 5-20 carbon atoms.

9. In a method of forming a color corrected image in a photographic element having at least one silver halide emulsion layer containing a color coupler for cyan which is reactive with the oxidation product of an aromatic amino developing agent to form by color development a cyan primary dye image which absorbs a major propor-

15

tion of light in one region of the visible spectrum, and undesirably absorbs a minor proportion of light in at least one other region of the visible spectrum, in which method said element is exposed to said image to be photographed, developed with said developing agent and thereafter treated with an oxidizing solution, the improvement wherein said element has present therein a mask-forming compound having the formula:



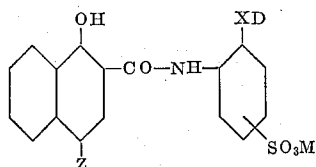
wherein:

Y is a member of the group consisting of an aryl radical and a heterocyclic radical;

whereby the residual color coupler oxidatively couples with said mask-forming compound to form a secondary dye image having a gradation opposite to that of said cyan primary dye image, said secondary image absorbing light in at least one of said undesirable minor absorption regions but transmitting substantially all the light in said major absorption region.

10. The method of claim 9 wherein said color coupler for cyan is a naphthol compound.

11. The method of claim 10 wherein said naphthol compound has the formula:



wherein:

X is a member of the group consisting of $-O-$, $-S-$, $-NHCO-$, $-CONH-$, $-SO_2NH-$, $-NHSO_2-$, $-N-alkyl$

and $-SO_2-$,

Z is a member of the group consisting of hydrogen and halogen,

D is an aliphatic radical comprising a linear chain of 5-20 carbon atoms, and

M is a member of the group consisting of hydrogen, alkali metal, and ammonium.

12. The method of claim 9 wherein said oxidizing solution is a photographic bleaching bath.

13. The method of claim 9 wherein said mask-forming compound is incorporated in the same emulsion layer containing said cyan color coupler.

14. The method of claim 11 wherein said mask-forming compound forms a yellow-to-magenta secondary dye image.

15. A color photographic element useful in the method of claim 9, said element having superposed silver halide emulsion layers sensitive to different regions of the visible spectrum, at least one of said layers containing a color coupler for cyan which is reactive with the oxidation

16

product of an aromatic amino developing agent to form by color development a cyan primary dye image which absorbs a major proportion of light in one region of the spectrum, and undesirably absorbs a minor proportion of light in at least one other region of the visible spectrum, such layer also containing a mask-forming compound of the formula:

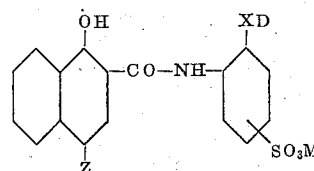


wherein:

10 Y is a member of the group consisting of an aryl radical and a heterocyclic radical;

said color coupler for cyan also being reactive with the oxidation product of said mask-forming compound to form a secondary dye image having a gradation opposite to that of said cyan primary dye image, and absorbing light in at least one of said unwanted minor absorption regions but transmitting substantially all the light in said major absorption region.

20 16. The element of claim 15 wherein said cyan color coupler has the formula:



wherein:

30 X is a member of the group consisting of $-O-$, $-S-$, $-NHCO-$, $-CONH-$, $-SO_2NH-$, $-NHSO_2-$, $-N-alkyl$

and $-SO_2-$,

Z is a member of the group consisting of hydrogen and halogen,

D is an aliphatic radical comprising a linear chain of 5-20 carbon atoms, and

40 M is a member of the group consisting of hydrogen, alkali metal, and ammonium.

References Cited by the Examiner

UNITED STATES PATENTS

2,276,254	3/1942	Schinzel	96-55
2,419,975	5/1947	Trivelli et al.	96-66
2,498,418	2/1950	Hanford	96-55
2,518,739	8/1950	Young	96-55
2,823,998	2/1958	Jennen	96-100
3,012,884	12/1961	De Ramaix et al.	96-9
3,013,879	12/1961	De Ramaix et al.	96-55 X
3,028,237	4/1962	Loffler	96-9

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