

1

3,013,879

## PRODUCTION OF COLOR PHOTOGRAPHIC IMAGES

Maurice A. de Ramaix and Jan Jaeken, Hove-Antwerp, Belgium, assignors to Gevaert Photo-Producten N.V., Mortsel-Antwerp, Belgium, a Belgian company  
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5 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 therefor 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 applications Ser. No. 705,508, filed December 27, 1957, by Maurice Antoine de Ramaix and Jan Jaeken, and Ser. No. 66,964, filed November 3, 1960, by Raphael Karel Van Poucke, Arthur Henri De Cat and Marcel Hendrik Verbrugge for Process for the manufacture of photographic color images and color correction.

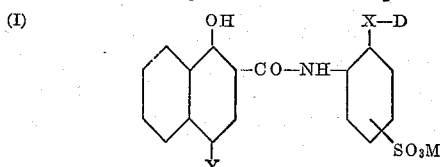
According to said pending applications a color corrected image is formed in a photographic element comprising a silver halide emulsion layer and a color coupler (more particularly a color coupler of the naphthol type) which is reactive with the oxidation product of an aromatic amino developing agent to form by color development a primary dye image which absorbs a major proportion of light in one region of the visible spectrum (more particularly the red light) and undesirably absorbs a minor proportion of light in at least one another region of the visible spectrum (more particularly the green light), by treating the exposed and color-developed photographic element with an oxidizing solution, more particularly a photographic bleaching bath, in the presence of a compound, more particularly a 4-amino-pyrazolone-3-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 (more particularly the green light) but transmitting substantially all the light in said major absorption region (more particularly the red light) is formed.

It is an object of the present invention to provide an improved 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

2

mask in color film, more particularly to provide a magenta colored mask image compensating the unwanted absorption of green light by the cyan image dye. Other objects will appear from the following description and examples.

These objects are accomplished by treating an image-wise exposed photographic element comprising a silver halide emulsion layer and a color coupler of the formula



wherein:

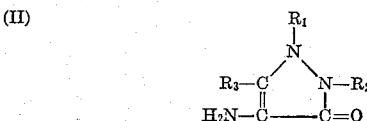
X represents a member selected from the group consisting of an oxygen atom, a sulfur atom, a  $-\text{NH}-\text{CO}-$  group, a  $-\text{CO}-\text{NH}-$  group, a  $-\text{SO}_2-\text{NH}-$  group, a  $-\text{NH}-\text{SO}_2-$  group and a  $-\text{N}-$ alkyl group;

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

D, an aliphatic radical comprising a linear chain of at least 5 and at most 20 carbon atoms, preferably 14, 16 or 18 carbon atoms.

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

which is reactive with the oxidation product of an aromatic amino developing agent to form by color development a cyan dye image, after the color forming development, with an oxidizing solution, such as a photographic bleaching bath, in the presence of a 4-aminopyrazolone-3-derivative (called hereinafter mask forming compound) with the following general formula



wherein:

R<sub>1</sub> represents a lower alkyl group e.g. a methyl group;

R<sub>2</sub> represents a member selected from the group consisting of a lower alkyl group, e.g. a methyl group, and an aryl group, e.g. a phenyl group and a substituted phenyl group;

R<sub>3</sub> represents an aliphatic radical making the molecule non-migratory with more than 5 and less than 20 carbon atoms e.g. consisting of a nonyl-, an undecyl-, a tridecyl- or a pentadecyl group.

Suitable compounds which give good results and which correspond to the above general Formula I are:

N - (2' - cetyloxy - 5' - sulfo) - phenyl - 1 - hydroxy-2-naphthoic acid amide sodium salt,  
N - (2' - cetyloxy - 5' - sulfo) - phenyl - 1 - hydroxy - 4-chloro-2-naphthoic acid amide sodium salt,  
N - (2' - cetyl mercapto - 5' - sulfo) - phenyl - 1 - hydroxy-2-naphthoic acid amide sodium salt,  
N - (2' - cetyl mercapto - 5' - sulfo) - phenyl - 1 - hydroxy-4-bromo-2-naphthoic acid amide sodium salt,  
N - (2' - cetyl mercapto - 5' - sulfo) - phenyl - 1 - hydroxy-4-chloro-2-naphthoic acid amide sodium salt,  
N - (2' - palmitoyl amino - 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.

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 amides according to Ger-

man patent application No. G 30,287, filed August 13, 1960.

Suitable mask forming compounds are e.g. the following 4-amino pyrazolone-3 derivatives:

- 1,2-dimethyl-4-amino-5-nonyl pyrazolone-3,
- 1,2-dimethyl-4-amino-5-undecyl pyrazolone-3,
- 1,2-dimethyl-4-amino-5-tridecyl pyrazolone-3,
- 1,2-dimethyl-4-amino-5-pentadecyl pyrazolone-3,
- 1 - methyl-2(p-carbethoxy phenyl)-4-amino-5-pentadecyl pyrazolone-3,
- Methylester of 1-methyl-2-(p-succinyl amido phenyl)-4-amino-5-pentadecyl pyrazolone-3,
- 1-methyl-2-(2'-chloro-5'-carbomethoxy phenyl)-4-amino-5-pentadecyl pyrazolone-3.

These compounds can be prepared as follows:

(1) 1,2-DIMETHYL-4-AMINO-5-TRIDECYLPYRAZOLONE-3

1180 g. (4.15 mols) of myristoyl acetic acid methyl-ester and 470 g. (3.53 mols) of symmetrical dimethyl-hydrazine dihydrochloride are dissolved in 20 l. of isopropanol and refluxed for 50 h. The reaction mixture is cooled at room temperature, and hydrogen chloride gas is led through the mixture until the amount of the precipitate formed does not increase any more.

The deposited dimethyl hydrazine dihydrochloride is sucked off and the filtrate is evaporated in vacuum. The thereby formed precipitates are recrystallized from about 11 l. of ethyl acetate together with the evaporating residue and 1,2-dimethyl-5-tridecylpyrazolone-3-hydrochloride is obtained.

496 g. (1.5 mols) of this compound are added, whilst stirring, to a mixture of 2450 cm.<sup>3</sup> of acetic acid and 240 cm.<sup>3</sup> of water. The whole is added, whilst stirring at 15° C., to 520 cm.<sup>3</sup> of a 20% aqueous sodium nitrite solution (1.5 mols).

The solution thus obtained is poured into 3 l. of methanol and to this mixture is slowly added, whilst stirring, 2 kg. of ice and stirring is continued for another hour until the crystal formation is completely finished. Next the crystals are centrifuged off acid free washed with water and dried in cold state in a desiccator, next, the dried precipitate, whilst stirring, is washed with ethyl acetate, first in 2 l. of ethyl acetate and for a second time in 1.5 l. The precipitate is sucked off and dried in cold state. 1,2-dimethyl-4-nitroso-5-tridecyl-pyrazolone-3 is obtained.

300 g. of this compound (0.93 mol) are reduced in 3 l. of anhydrous ethanol with 30 g. of Raney nickel as catalyst at 23° C. under about 70 kg./sq. cm. of hydrogen pressure in a shaking autoclave. After 7 h. 79% of hydrogen is absorbed. After sucking off the catalyst, the filtrate is heated, whilst stirring, and saturated with hydrogen chloride gas. After cooling in ice, sucking off and washing with acetonitrile, the product obtained is recrystallized from about 1.5 l. of ethanol and 1,2-dimethyl-4-amino-5-tridecyl pyrazolone-3-hydrochloride is obtained.

1,2 - dimethyl - 4 - amino-5-nonyl-pyrazolone-3, 1,2-dimethyl-4-amino-5-undecylpyrazolone-3 and 1,2-dimethyl-4-amino-5-pentadecylpyrazolone-3 are prepared in the same way.

(2) METHYLESTER OF 1 - METHYL - 2 - (p-SUC-CINYLAMIDOPHENYL) - 4 - AMINO-5-PENTA-DECYLPYRAZOLONE-3

The preparation of the methylester of 1-methyl-2-(p-succinyl-amidophenyl) - 4 - amino-5-pentadecylpyrazolone-3 is Preparation 10 in the pending U.S. patent application Serial No. 705,508, filed December 27, 1957.

(3) 1 - METHYL-2 - (2' - CHLORO-5' - CARBOMETH-OXYPHENYL) - 4 - AMINO-5-PENTADECYLPYRAZOLONE-3

124 g. (2/3 mol) of 3-amino-4-chloro benzoic acid

methyl ester are suspended in 300 cm.<sup>3</sup> of water and 500 cm.<sup>3</sup> of concentrated hydrogen chloride solution. The amino compound is diazotized at 0° C. with 55 g. of sodium nitrite dissolved in 300 cm.<sup>3</sup> of water. After filtering the obtained diazonium salt solution, the latter is slowly added at 0 to 5° C. to 6 l. of a saturated aqueous sulfur dioxide solution. Sulfur dioxide is led through the reaction mixture for 1 h. and left overnight. Next, the mixture is freed in vacuum from the dissolved sulfur dioxide. The hydrazine hydrochloride crystallizes out by addition of 7.5 l. of concentrated hydrochloric acid. The hydrochloride is dissolved in about 4 l. of water and then the hydrazine is set free as base with about 300 g. of crystallized sodium acetate. After sucking off, washing and recrystallizing from petroleum ether, 2-chloro-5-carbomethoxyphenylhydrazine is obtained.

140 g. of palmitoyl acetic acid methyl ester and 90 g. of this hydrazine compound are refluxed for 6 h. in 1600 cm.<sup>3</sup> of acetic acid. After cooling and pouring into 5 kg. of ice and 5 l. of water, the solution is left overnight for coagulation. The precipitate is sucked off, washed acid free state, and crystallized from methanol. 2 - (2' - chloro-5' - carbomethoxy-phenyl) - 5-pentadecylpyrazolone-3 is obtained.

92 g. of this pyrazolone are melted together for 20 h. at 140° C. with 41 g. of methyltoluolsulfonate. After cooling, the melt is treated with about 750 cm.<sup>3</sup> of ether and 750 cm.<sup>3</sup> of a 10% aqueous sodium acetate solution. The supernatant ether layer is removed and is neutrally washed with water. The separated ether layer is dried and the ether evaporated. The obtained residue is recrystallized from n-hexane. 1-methyl-2-(2'-chloro-5'-carbomethoxyphenyl) - 5 - pentadecylpyrazolone - 3 is obtained.

19 g. of this pyrazolone are dissolved in 200 cm.<sup>3</sup> of ethylene chlorohydrine and 20 cm.<sup>3</sup> of concentrated hydrochloride solution are added. Next, the solution is nitrosified at 0 to 5° C. with 16 cm.<sup>3</sup> of a 20% aqueous sodium nitrite solution. After adding the nitrite, the solution is stirred for another 40 minutes and the reaction mixture is poured into water. The nitroso compound is sucked off, washed with water in acid free state, dried in cold state and recrystallized from methanol. 1-methyl-2 - (2'-chloro-5'-carbomethoxyphenyl) - 4-nitroso-5-pentadecyl pyrazolone-3 is obtained.

33.5 g. of the nitroso compound are reduced under an hydrogen pressure of 28 kg./sq. cm. in 240 cm.<sup>3</sup> of methanol with Raney-nickel as catalyst. After evaporation of the solvent and recrystallization from n-hexane, 1 - methyl - 2 - (2' - chloro-5'-carbomethoxyphenyl) - 4-amino-5-pentadecylpyrazolone-3 is obtained.

(4) 1-METHYL-2-(p-CARBETHOXYPHENYL)-4-AMINO-5-PENTADECYLPYRAZOLONE-3

21 g. of p-carbethoxyphenylhydrazine and 39 g. of palmitoyl acetic acid methyl ester are boiled for 3 hours in 400 cm.<sup>3</sup> of isopropanol. The flask is connected with a distilling device so that during this time the separated water, resp. the methanol is collected with a part of the isopropanol. After cooling, the formed crystals are sucked off and 2-(p-carbethoxyphenyl)-5-pentadecylpyrazolone-3 is obtained.

145 g. of this pyrazolone and 66 g. of methyl-p-tolu-sulphonate are melted for 72 hours at 140° C. The reaction mixture is dissolved in ether. This solution is washed several times with a 10% sodium acetate solution until the toluene sulphonic acid is completely removed and the washing solution remains alkaline. After drying, the ether layer is evaporated to dryness; the residue is washed with n-hexane and recrystallized from the same solvent. 1-methyl-2-(p-carbethoxyphenyl)-5-pentadecylpyrazolone-3 is obtained.

57 g. of this methyl compound are added in small parts whilst stirring, to 100 cm.<sup>3</sup> of nitric acid (d.=1.5) but it is to be noted that by appropriate cooling the temperature is kept at 0° C. Subsequently, stirring is con-

5

tinued for 1 hour at this temperature and thereafter the reaction mixture is poured into ice and the precipitated product is sucked off, washed to neutral with water and recrystallized from ethanol. 1-methyl-2-(p-carbethoxyphenyl)-4-nitro-5-pentadecylpyrazolone-3 is obtained.

36 g. of this nitro compound are reduced with hydrogen as catalyst in 500 cm.<sup>3</sup> of ethylene glycol monomethyl ether at 50° C. and using Raney-nickel. After filtering off the catalyst and evaporation of the solvent, the residue is dissolved in ether. The amino hydrochloride is precipitated by leading through the etheric solution hydrochloric acid gas. After sucking off, washing with ether and recrystallizing from acetonitrile, 1-methyl-2-(p-carbethoxyphenyl)-4-amino-5-pentadecyl pyrazolone-3 is obtained.

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 red sensitive silver halide emulsion layer containing the cyan coupler and wherein the mask image is to be formed by oxidative coupling of the residual cyan color coupler present in that layer with the mask forming substance.

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 multi-layer 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. Usually there is a yellow filter, composed in most of the cases of colloidal silver, located between the blue-sensitive and the emulsion layer sensitized to green. 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 and the primary amine aromatic developing agent is at the same time oxidized. The oxidized developing agent reacts with the color coupler and forms a dye stuff, the mask forming compound according to the invention not being affected. After the color development, the material comes in the bleaching bath wherein the oxidation of the mask forming compound takes place. The remaining color coupler still available at the non-exposed areas of the material couples with the oxidizing product of the compound thus formed whereby the color mask 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-phenylenediamine, and derivatives thereof such as N,N-dialkyl-N'-sulphomethyl- or carboxymethyl-p-phenylenediamine. As useful mono-amino-developers should be cited: aminophenols and aminocresols or their halogen derivatives and also the aminonaphthols.

The bleaching bath contains generally potassium bromide, borax, magnesium sulphate and especially potassium ferricyanide. These elements are dissolved in pre-

6

cisely determined amounts of water so that a solution with a determined pH value is obtained.

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

#### Example 1

To ½ kg. of a red sensitized bromoiodide emulsion (2% iodide) containing ¼ mol of silver halide are added 40 cm.<sup>3</sup> of a slightly alkaline alcoholic 10% solution of N-(2'-cetyloxy-5'-sulfo)-phenyl-1-hydroxy-4-chloro-2-naphthoic acid amide sodium salt, and next 20 cm.<sup>3</sup> of a 10% solution of 1,2-dimethyl-4-amino-5-tridecylpyrazolone-3 in methyl-Cellosolve (reg. trademark for ethylene glycol monomethylether) with a little sodium hydroxide.

After acidification to pH 6 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 red filter (Gevafilter R 678 marketed by Gevaert Photo-Producten N.V., Mortsel-Belgium) and a grey wedge with a constant 0.15, the photographic material composed in this way is developed for 9 minutes at 20° C. in a color-developing bath with the following composition:

|    |                                                   |      |
|----|---------------------------------------------------|------|
| 25 | Sodium hexametaphosphate.....                     | G. 2 |
|    | N,N-diethyl-p-phenylenediamine hydrochloride..... | 3    |
|    | Sodium sulphite.....                              | 4    |
|    | Sodium carbonate.....                             | 57   |
| 30 | Hydroxylamine hydrochloride.....                  | 1.5  |
|    | Potassium bromide.....                            | 1    |
|    | Water to 1000 cm. <sup>3</sup> (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:

|    |                                          |     |
|----|------------------------------------------|-----|
| 35 |                                          | G.  |
|    | Sodium thiosulphate.....                 | 200 |
|    | Sodium bisulphite.....                   | 25  |
|    | Potassium alum.....                      | 20  |
| 40 | Sodium biacetate.....                    | 20  |
|    | Boric acid.....                          | 7.5 |
|    | Water to 1000 cm. <sup>3</sup> (pH=4.0). |     |

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:

|    |                                          |       |
|----|------------------------------------------|-------|
|    |                                          | Grams |
|    | Potassium ferricyanide.....              | 100   |
|    | Potassium bromide.....                   | 15    |
| 50 | Borax.....                               | 20    |
|    | Magnesium sulfate.....                   | 50    |
|    | Water to 1000 cm. <sup>3</sup> (pH=8.6). |       |

Then the material is rinsed again for 10 min. at 18 to 20° C. and fixed for 5 min. at 20° C. in a bath of the following composition:

|    |                                          |       |
|----|------------------------------------------|-------|
|    |                                          | Grams |
|    | Sodium thiosulphate.....                 | 130   |
|    | Borax.....                               | 20    |
| 60 | Magnesium sulfate.....                   | 50    |
|    | Water to 1000 cm. <sup>3</sup> (pH=8.9). |       |

Rinsing is continued for another 10 min. at 18 to 20° C. and finally the material is dried.

#### Example 2

To ½ kg. of a red sensitized bromoiodide emulsion (2% iodide) containing ¼ mol of silver halide are added 40 cm.<sup>3</sup> of a slightly alkaline alcoholic 10% solution of N-(2'-cetylmercapto-5'-sulfo)-phenyl-1-hydroxy-2-naphthoic acid amide sodium salt, and next 20 cm.<sup>3</sup> of a 10% solution of 1,2-dimethyl-4-amino-5-tridecylpyrazolone-3 in methyl-Cellosolve (reg. trademark for ethylene glycol monomethylether) with a little sodium hydroxide.

After acidification to pH 6 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 a further treatment according to Example 1, a cyan image is obtained wherein the disturbing influence of the side-absorptions is reduced by the formed magenta masking image with opposite gradation to the cyan image.

#### Example 3

To ½ kg. of a red sensitized bromiodide emulsion (2% iodide) containing ⅓ mol of silver halide are added 40 cm.<sup>3</sup> of a slightly alkaline alcoholic 10% solution of N-(2'-cetylmercapto - 5'-sulfo)-phenyl-1-hydroxy-4-bromo-2-naphthoic acid amide sodium salt, and next 20 cm.<sup>3</sup> of a 10% solution of 1,2-dimethyl-4-amino-5-tridecylpyrazolone-3 in methyl-Cellosolve with a little sodium hydroxide.

After acidifying to a pH 6 and after adding the usual additives such as hardeners, wetting agents and stabilizers, the emulsion obtained 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-absorptions is reduced by the formed magenta masking image with opposite gradation to the cyan image.

#### Example 4

To ½ kg. of a red sensitized bromiodide emulsion (2% iodide) containing ⅓ mol of silver halide are added 40 cm.<sup>3</sup> of a slightly alkaline alcoholic 10% solution of N-(2'-palmitoylamino - 4'-sulfo) - phenyl - 1-hydroxy-2-naphthoic acid amide sodium salt, and next 20 cm.<sup>3</sup> of a 10% solution of 1,2-dimethyl-4-amino-5-tridecylpyrazolone-3 in methyl-Cellosolve with a little sodium hydroxide.

After acidifying to a pH 6 and after adding the usual additives such as hardeners, wetting agents and stabilizers, the emulsion obtained 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-absorptions is reduced by the formed magenta masking image with opposite gradation to the cyan image.

#### Example 5

To ½ kg. of a red sensitized bromiodide emulsion (2% iodide) containing ⅓ mol of silver halide are added 40 cm.<sup>3</sup> of a slightly alkaline alcoholic 10% solution of N-(2'-cetylmercapto-5'-sulfo)-phenyl-1-hydroxy - 4-chloro-2-naphthoic acid amide sodium salt, and next 20 cm.<sup>3</sup> of a 10% solution of the methylester of 1-methyl-2-(p-succinylamidophenyl)-4-amino-5-pentadecyl - pyrazolone-3 in methyl-Cellosolve with a little sodium hydroxide.

After acidification to pH 6 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 a further treatment according to Example 1, a cyan image is obtained wherein the disturbing influence of the side-absorptions is reduced by the formed magenta masking image with opposite gradation to the cyan image.

#### Example 6

To ½ kg. of a red sensitized bromiodide emulsion (2% iodide) containing ⅓ mol of silver halide are added 40 cm.<sup>3</sup> of a slightly alkaline alcoholic 10% solution of N-(2'-cetylmercapto-5'-sulfo)-phenyl-1-hydroxy - 2-naphthoic acid amide sodium salt, and next 20 cm.<sup>3</sup> of a 10% solution of 1,2-dimethyl-4-amino-5-nonylpyrazolone-3 in methyl-Cellosolve with a little sodium hydroxide.

After acidifying to a pH 6 and after adding the usual additives such as hardeners, wetting agents and stabilizers, the emulsion obtained 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-absorptions is reduced by the formed magenta masking image with opposite gradation to the cyan image.

#### Example 7

To ½ kg. of a red sensitized bromiodide emulsion (2% iodide) containing ⅓ mol of silver halide are added 40 cm.<sup>3</sup> of a slightly alkaline alcoholic 10% solution of N-(2'-palmitoylamino-4'-sulfo)-phenyl-1-hydroxy-2-naphthoic acid amide sodium salt, and next 20 cm.<sup>3</sup> of a 10% solution of 1,2-dimethyl-4-amino-5-nonylpyrazolone-3 in methyl-Cellosolve with a little sodium hydroxide.

After acidification to pH 6 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 a further treatment according to Example 1, a cyan image is obtained wherein the disturbing influence of the side-absorptions is reduced by the formed magenta masking image with opposite gradation to the cyan image.

#### Example 8

To ½ kg. of a red sensitized silver bromo-iodide emulsion (2% iodide) containing ⅓ mol of silver halide are added 40 cm.<sup>3</sup> of a 10% slightly alkaline alcoholic solution of N-(2'-cetyloxy-5'-sulfo)-phenyl-1-hydroxy-4-chloro-2-naphthoic acid amide sodium salt, and next 20 cm.<sup>3</sup> of a 10% solution of 1,2-dimethyl-4-amino-5-tridecylpyrazolone-3 in methyl-Cellosolve with a little sodium hydroxide.

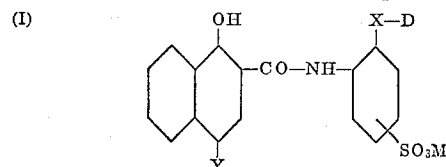
After acidification with acetic acid to pH 6 and after addition of the usual additives such as hardeners, wetting agents and stabilizers, the emulsion obtained is ready to be coated. After coating this emulsion forms part of a multilayer photographic material consisting of the following superposed layers in the indicated sequence: a support, an antihalation layer, a gelatin insulating layer, the above mentioned red-sensitized emulsion layer with color coupler for cyan, a gelatin interlayer, a green-sensitized emulsion layer, a yellow filter layer, a blue-sensitive emulsion layer with color coupler for yellow and at least 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 magenta dye image in the red-sensitized layer, said magenta image being of opposite gradation in respect of the cyan dye image and reducing the disturbing influence of the side-absorptions in the formed cyan image.

We claim:

1. Method of forming a color corrected image in a photographic element having at least one silver halide emulsion layer containing a color coupler of the formula:



wherein:

X represents a member selected from the group consisting of oxygen atom, a sulfur atom, a —NH—CO— group, a —CO—NH— group, a —SO<sub>2</sub>—NH— group, a —NH—SO<sub>2</sub>— group and a

—N—alkyl group

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

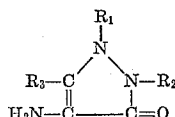
D, an aliphatic radical comprising a linear chain of at least 5 and at most 20 carbon atoms;

9

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

and which is reactive with the oxidation product of an aromatic amino developing agent to form by color development a cyan dye image which 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, which method comprises treating said photographic element, after image-wise exposure and color development, with an oxidizing solution in the presence of a mask forming compound of the formula:

(II)



wherein:

R<sub>1</sub> represents a lower alkyl group;

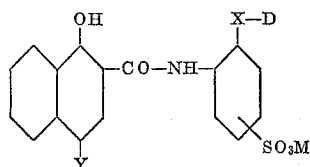
R<sub>2</sub> represents a member selected from the group consisting of a lower alkyl group and an aryl group of the benzene series and a substituted aryl group of the benzene series;

R<sub>3</sub> represents an aliphatic radical comprising a linear chain of at least 5 and at most 20 carbon atoms.

2. Method of forming a color corrected image according to claim 1 wherein the mask forming compound is incorporated in the photographic element, and the oxidizing solution is a photographic bleaching bath.

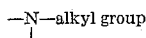
3. Method of forming a color corrected image in a photographic element having superposed silver halide emulsion layers sensitive to different regions of the visible spectrum, at least one of said layers containing a color coupler of the formula:

(I)



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 —SO<sub>2</sub>—NH— group, a —NH—SO<sub>2</sub>— group and a



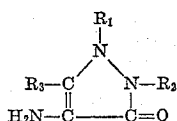
Y represents a member selected from the group consisting of an hydrogen atom and a halogen atom;

D, an aliphatic radical comprising a linear chain of at least 5 and at most 20 carbon atoms;

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

and which is reactive with the oxidation product of an aromatic amino developing agent to form by color development a cyan dye image which absorbs a major proportion of light in the red region of the visible spectrum and undesirably absorbs a minor proportion of light in the green region of the spectrum, said photographic element containing a mask-forming compound of the formula:

(II)



wherein:

R<sub>1</sub> represents a lower alkyl group;

10

R<sub>2</sub> represents a member selected from the group consisting of a lower alkyl group and an aryl group of the benzene series, and a substituted aryl group of the benzene series;

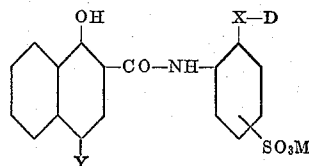
5 R<sub>3</sub> represents an aliphatic radical comprising a linear chain of at least 5 and at most 20 carbon atoms;

said color coupler being also reactive with the oxidation product of said mask forming compound to form a magenta dye image having a gradation opposite to that of said cyan dye image, and absorbing light in the green region of the spectrum, but transmitting substantially all the light in the red region, which method comprises exposing said layers to light, developing at least said layer containing said color coupler, by color development with an aromatic amino developing agent, whereby said cyan dye image is formed in the developed areas by coupling, leaving in the undeveloped areas of said one layer residual color coupler, and treating at least said layer containing said residual color coupler, and said mask forming compound, with a bleaching bath, said treatment resulting in the oxidation of said mask-forming compound, whereby said magenta dye image is formed by coupling said oxidized mask-forming compound with said residual color coupler.

4. Method of forming a color corrected image according to claim 3, wherein said mask-forming compound is contained in at least said one layer containing said color coupler.

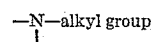
5. Photographic element having superposed silver halide emulsion layers sensitive to different regions of the visible spectrum, at least one of said layers containing a color coupler of the formula:

(I)



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 —SO<sub>2</sub>—NH— group, a —NH—SO<sub>2</sub>— group and a



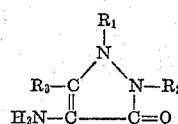
Y represents a member selected from the group consisting of an hydrogen atom and a halogen atom;

D, an aliphatic radical comprising a linear chain of at least 5 and at most 20 carbon atoms;

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

and which is reactive with the oxidation product of an aromatic amino developing agent to form by color development a cyan image which 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, and a mask forming compound of the formula:

(II)



wherein:

R<sub>1</sub> represents a lower alkyl group;

R<sub>2</sub> represents a member selected from the group consisting of a lower alkyl group, and an aryl group of the benzene series and a substituted aryl group of the benzene series;

11

$R_3$  represents an aliphatic radical comprising a linear chain of at least 5 and at most 20 carbon atoms, said color coupler being also reactive with the oxidation product of said mask-forming compound to form a secondary dye image having a gradation opposite to that of

5

12

said cyan dye image, and absorbing light in at least one of said unwanted minor absorption regions but transmitting substantially all the light in the red absorption region of the spectrum.

No references cited.