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3,174,862

## PROCESS FOR IMPROVING THE COLOR RE- PRODUCTION IN COLOR PHOTOGRAPHIC MATERIAL

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A 32,837

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The present invention relates to a process for improving the color reproduction characteristics of color photographic material.

In the production of colored images by color development of exposed silver halide emulsion layers, a colored image is formed by reaction of the oxidation products of the developer with color couplers, in addition to the formation of the silver image. For the production of yellow and magenta images, the color couplers used are inter alia compounds having activated methylene groups, for example, acetoacetic acid ester derivatives or pyrazolone derivatives. For the production of cyan images, phenols and naphthols are inter alia employed. A large number of embodiments based on this principle are already known.

With these processes, however, a series of undesired effects due to uncontrolled reaction of the oxidation product or products of the color developer are always produced, in addition to the desired image-wise color development. Thus, each color development is accompanied by the formation of a more or less strong color fogging. The diffusion which occurs with multi-layer materials and which is known as the penetration effect (according to which the oxidation product or products of the color developer diffuses into adjoining layers and couples with the component incorporated therein), leads to a blackening of the colors. The color developer which is not completely rinsed out after development causes so-called bleaching fogs in oxidizing baths, for example, bleaching baths. Furthermore, a color component having otherwise favorable properties can produce too steep a gradation in the color development.

A number of processes have been proposed for overcoming these effects. For example, French Patent No. 1,112,594 recommends using ascorbic acid for reducing the color fogging. U.S. Patents No. 2,732,300 and 2,735,765 use diffusion-resistant hydroquinone derivatives for the same purpose.

In U.S. Patent No. 2,675,314 is described the use of gentistic acid derivatives for the same purpose.

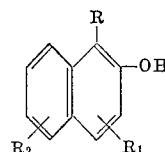
In United States Patent No. 2,998,314 and French patent specification No. 1,183,746 is disclosed the use in color photographic materials and bath of supplemental coupling compounds in which the hydrogen atom of an active methylene group coupling is replaced by an aliphatic, aromatic or mixed aromatic-aliphatic radical. Compounds of this type couple with the oxidation products of the color developer to give colorless coupled products instead of colored coupling products. Examples of such compounds are 1-phenyl-3,4-dimethyl pyrazolone,  $\alpha$ -methyl acetoacetic ester and  $\alpha$ -cyano-propiofenone.

Since it is a question with this process of a concurrent coupling of the colorless coupling compounds with the color couplers, great care is necessary in the selection of each of the two reactants, namely, the colorless coupling compound and the color coupler.

It has now been found that under the conditions of photographic development, stable colorless or practically colorless, coupled products are obtained by using as coupling components, alpha (or 1) -substituted derivatives of

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beta (or 2) -naphthol having the following general formula:



10 in which R is an alkyl, substituted alkyl (for example  $-\text{CH}_2\text{CH}_2\text{CN}$  allyl or  $-\text{CH}_2\text{CH}_2\text{COOH}$ ), or aralkyl radical,

15  $\text{R}_1$  and  $\text{R}_2$  each represent a hydrogen atom or any desired substituents, advantageously water-solubilizing groups and/or groups which give a diffusion-resisting effect.

Suitable supplemental coupling compounds are, for example, 1-methyl- $\beta$ -naphthol, 1-ethyl- $\beta$ -naphthol, 1-cyanoethyl- $\beta$ -naphthol, 1-methyl-2-naphthol-3-carboxylic acid.

20 Compounds of this type can be used in all cases where the interception of undesired oxidation products of the color developer appears to be advisable. For example, they can be incorporated in diffusion-resistant form in a separating layer between two photographic layers containing color developers in order to intercept the color developer diffusing from one layer to the other. The compounds can also be incorporated in diffusion-resistant form together with the color couplers in the silver halide emulsion layer or can be added to the color developer solution and/or to the bleaching bath or to preliminary or intermediate baths. The  $\beta$ -naphthols which have been described can also be dissolved in high-boiling solvents and be combined in the form of an emulsion into the photographic layers. The supplemental coupling compounds may also be used as an additive to the so-called mixed-grain emulsion for color photographic single-layer materials.

25 The use of the  $\beta$ -naphthols specified herein as supplemental coupling agents with color development oxidation products to form colorless compounds produces an improvement in the color fogging and a refining or improving of the color grain. Furthermore, the formation of bleaching fogs is prevented when these supplemental coupling agents are used in bleaching baths. It is possible by use of the supplemental coupling agents to control the color gradation.

30 As color developers, it is possible to use all known color developer substances having primary amino groups, for example, p-phenylene diamine and its derivatives, p-amino-phenol and derivatives, 4-amino-pyrazolones, etc.

The following examples further illustrate the invention:

### Example 1

35 An exposed silver halide layer containing incorporated therein as color coupler 10 g. of 1-(4'-phenoxy-3'-sulphophenyl)-3-heptadecyl-5-pyrazolone per kg. of emulsion, is developed in a developer having the following composition:

40 4-aminodiethyl aniline sulphate	2.5 g.
Anhydrous potassium carbonate	70 g.
Potassium bromide	2.0 g.
Sodium sulphite	2.0 g.
Water	1 liter.

45 With a development time of 5 minutes and a development temperature of 18° C., a color image with a gamma value of 1.8 is obtained after the image silver has been bleached and fixed in known manner. If 3 g. of 1-methyl-2-naphthol are added per liter of color developer, the gamma value of the color image is only 1.0.

1-methyl-2-naphthol may be prepared by the method

described by B. Linke in *Berichte der deut. chem. Ges.*, vol. 56, pages 846-848 (1923).

#### Example 2

An exposed silver halide layer containing 10 g. of 1-(3'-sulphophenyl)-3-heptadecyl-5-pyrazolone per kg. of emulsion as color coupler, is developed in a developer mixture exactly as described in Example 1. The color fogging is then 0.19. If 3 g. of 1-ethyl-2-naphthol (prepared according to *Annalen*, vol. 439, page 243) is added to the color developer, the fogging decreases to a value of 0.10.

#### Example 3

An exposed silver halide layer containing, as color coupler, 12 g. of N-octadecyl-1-hydroxy-4-sulfo-2-naphthamide per kg. of emulsion, is developed in a developer composition exactly as described in Example 1. A gamma value of 1.5 is produced. If 2 g. of 1-cyanoethyl-2-naphthol are added per liter of color developer, the gamma value is only 0.8. 1-Cyanoethyl-2-naphthol may be prepared as described in U.S. Patent No. 2,421,837.

#### Example 4

An exposed silver halide layer containing, as color developer, 12 g. of 1-hydroxy-4-sulpho-2-naphthoic acid stearylamine per kg. of emulsion, is developed in a developer having the composition according to Example 1. A gamma value of 1.5 is produced. If 4 g. per liter of 2-naphthol-1-propionic acid are added to the color developer, the gamma value is reduced to 1.0.

2-naphthol are added per liter of color developer, the gamma value falls to 0.8. 1-cyanoethyl-2-naphthol is prepared according to U.S. Patent No. 2,421,837.

#### Example 4a

An exposed silver halide layer containing, as color coupler, 12 g. of N-octadecyl-1-hydroxy-4-sulfo-2-naphthamide per kg. of emulsion, is developed in a developer composition exactly as described in Example 1. A gamma value of 1.5 is produced. If 4 g. per liter of 1-(2-carboxyethyl)-2-naphthol are added to the color developer, the gamma value is only 1.0.

1-(carboxyethyl)-2-naphthol may be prepared as follows:

10 g. of cyanoethyl- $\beta$ -naphthol are introduced at such a rate into 25 cc. of concentrated sulphuric acid while stirring that the temperature does not exceed 20° C. The combined solution is left standing for 6 hours at room temperature and is then poured onto 300 g. of ice. It is left until the viscous phase has settled and then the aqueous phase is decanted. The residue is taken up in 100 cc. of methanol, 100 cc. of water is added thereto and the product is allowed to crystallize out while cooling with ice. It is recrystallized from 50 percent methanol, M.P. 122-124° C.

#### Example 5

An exposed Agfacolor negative film is developed in the developer mixture described in Example 1 at 18° C. and for 7 minutes. The gamma value after development is 0.9. If 15 g. per liter of 1-methyl-2-naphthol-3-carboxylic acid are added to the color developer, the average gamma value is then 0.6.

1-methyl-2-naphthol-3-carboxylic acid (3-hydroxy-4-methyl-2-naphthoic acid) may be prepared in three steps as follows:

(1) Preparation of 1-formyl-2-naphthol-3-carboxylic acid: 60 g. of 2-naphthol-3-carboxylic acid (3-hydroxy-2-naphthoic acid) are suspended in 150 cc. of methanol, then dissolved with 117 g. of sodium hydroxide in 210 cc. of water, and heated to boiling on a steam bath. 131 g. of chloroform are introduced dropwise from a dropping funnel into the boiling solution until the reaction is started. After the reaction is proceeding, the heat is removed and the rate of addition of the chloroform is so

regulated that the mixture remains just at its boiling point. After the reaction has subsided, boiling is continued for another 30 minutes, the solvent is distilled off, the residue is neutralized with concentrated hydrochloric acid until it is just acid to Congo red indicator, diluted with 100 cc. of water, suction-filtered and dried.

(2) Preparation of hydrazone of 1-formyl-2-naphthol-3-carboxylic acid: 100 g. of 1-formyl-2-naphthol-3-carboxylic acid as prepared in Step 1 is suspended in 1.5 liters of water and heated to boiling. 30 cc. of 90 percent hydrazine hydrate are added to the boiling solution and boiling is continued for an additional 5 minutes.

The solution is then adjusted with glacial acetic acid to a pH value of 6 to 7 and heated for another 30 minutes at its boiling point. After cooling, it is suction-filtered, the precipitate is boiled with 500 cc. of methanol and dried after being suction-filtered.

(3) Preparation of 1-methyl-2-naphthol-3-carboxylic acid: 60 g. of the hydrazone that was prepared in Step 2 is dissolved while heating in 500 cc. of diethyl glycol (ethylene glycol diethyl ether, 1,2-diethoxyethane), 50 cc. of 90 percent hydrazine hydrate and 40 g. of sodium hydroxide.

The temperature is raised cautiously in an oil bath to 250° C., since the mixture may suddenly foam strongly. 50 cc. of the solvent is distilled off at this temperature and stirring is continued for another 3 hours at 200° C. The mixture is then poured into 5 liters of iced water, neutralized with concentrated hydrochloric acid until it is just acid to Congo red indicator and the precipitate is filtered off with suction. It is recrystallized from 90 percent glacial acetic acid. M.P. 239-241° C.

#### Example 6

An exposed silver halide layer, into which are incorporated 7 g. of 1-(4'-phenoxy-3'-sulphophenyl)-3-heptadecyl-5-pyrazolone as color coupler per kg. of emulsion, is developed in the developer composition described in Example 1. After a development time of 5 minutes and with a development temperature of 18° C., a color image is obtained having a gamma value of 1.6. If such an emulsion layer also has added thereto, in addition to the color coupler, 14 g. of 5'-methyl-6'-hydroxy-2-(N-methyl-N-octadecylamino)-4-sulfo-2'-naphthoylanilide per kg. of emulsion and if the development is carried out in similar manner, the gamma value is only 1.3.

The 5'-methyl-6'-hydroxy-2-(N-methyl-N-octadecylamino)-4-sulfo-2'-naphthoylanilide may be prepared as follows:

1-methyl-2-naphthol-6-carboxylic acid is prepared in three steps in exactly the same manner as described in Example 5 hereinbefore for the production of 1-methyl-2-naphthol-3-carboxylic acid except that the 2-hydroxy-3-naphthoic acid used therein as the starting product is replaced by the same quantity of 2-hydroxy-6-naphthoic acid (6-hydroxy-2-naphthoic acid). The next two steps (4 and 5) follow.

(4) Preparation of the potassium salt of 1-methyl-2-naphthol-6-carboxylic acid: 100 g. of the 1-methyl-2-naphthol-6-carboxylic acid thus obtained is suspended in 250 cc. of water. The suspension is adjusted with 50 percent potassium hydroxide solution to a pH value of 8 and boiled.

The solution is filtered and then 150 cc. of water are distilled off in vacuo. 100 cc. of potassium chloride solution are added to the distillation residue, the precipitate is filtered off with suction and dried quickly.

(5) Preparation of 5'-methyl-6'-hydroxy-2-(N-methyl-N-octadecylamino)-4-sulfo-2'-naphthoylanilide: 24 g. of the potassium salt of 1-methyl-2-naphthol-6-carboxylic acid and 35 g. of 2-amino-N-methyl-N-octadecylaniline-4-sulfonic acid are suspended in 400 cc. of pyridine and 500 cc. of benzene and then boiled. The precipitate is dissolved. Boiling is continued with a water separator under reflux until all water is thus removed and then 500

cc. of benzene are distilled off. The mixture is then cooled to 20° C. and 10 cc. of phosphorus trichloride mixed with 100 cc. of benzene is added. The mixture is left standing overnight and then boiled for 3 hours under reflux. The solution obtained is mixed while still hot with a solution of 8 g. of sodium hydroxide and 13 g. of sodium acetate in 5 cc. of water, the solution obtained is then evaporated to dryness in vacuo on a steam bath. The residue is dissolved in 1 liter of water with addition of such a quantity of sodium hydroxide solution that the solution is definitely alkaline. The solution is filtered and the filtered solution is introduced into 600 g. of ice and 300 cc. of concentrated hydrochloric acid. The precipitate obtained is filtered off with suction and again reprecipitated in the same manner and then dried.

#### Example 7

An exposed silver halide layer as described in Example 1 is developed in the color developer composition and in the manner described in Example 1. A color image is obtained having a gamma value of 1.8. When 1 g. per liter of 1-benzyl-2-naphthol is added to the color developer, the gradation only reaches a gamma value of 1.4.

The 1-benzyl-2-naphthol, may be prepared by the method described by M. Gomberg and C. C. Buckler in the Jour. of the American Chem. Soc., vol. 42, pages 2059-2072 (1920).

#### Example 8

An exposed silver halide layer as described in Example 1 is developed in the color developer composition and in the manner described in Example 1. A color image is obtained having a gamma value of 1.8. When 2 g. per liter of 1-allyl-2-naphthol is added to the color developer, the gradation only reaches a gamma value of 1.3.

The 1-allyl-2-naphthol may be prepared by the method described by L. Clausen in Berichte der deutschen Chem. Ges., vol. 45, page 3159.

#### Example 9

An exposed silver halide layer as described in Example 1 is developed in the color developer composition and in the manner described in Example 1 and a color image is obtained having a gamma value of 1.8. When 3 g. per liter of sodium 1-methyl-2-naphthol-5-sulfonate are added to the color developer, the gradation only reaches a gamma value of 1.2.

Sodium 1-methyl-2-naphthol-5-sulfonate may be produced by dissolving 10 g. of 1-methyl-2-naphthol in 50 cc. of concentrated sulphuric acid in such manner that the temperature does not exceed room temperature. Stirring is continued for 30 minutes and the mixture is discharged on to 300 g. of ice. The pH value is adjusted with concentrated potassium carbonate solution to approximately 5. The precipitate is suction-filtered, triturated with a little water, again suction-filtered and dried in vacuo.

#### Example 10

Arranged on a layer support, for example, a paper suitable for photographic purposes, and in the sequence indicated below, are the following:

(1) A red-sensitive layer containing, as cyan coupler, 10 g. of 1-naphthol-2-carboxylic acid stearyl anilide-4-sulphonic acid per kg. of emulsion.

(2) A separation layer which has been prepared by emulsifying in 100 c. of a 7.5 percent gelatin solution: a solution of 3 g. of 1-methyl-2-naphthol-6-carboxylic acid stearylamine in 25 cc. of methanol and 5 cc. of a 10 percent solution of isopropyl naphthalene sulphonic acid.

(3) A green-sensitive layer containing, as magenta-coupling component, 10 g. of 7-octadecenyl succinamino-indazolone per kg. of emulsion.

If this material is developed in a developer of the following composition:

4-amino-N-ethyl-N-(hydroxyethyl) aniline sulfonate	5 g.
Anhydrous potassium carbonate	70 g.
Potassium bromide	1 g.
Anhydrous sodium sulfite	2 g.
Water	1 liter.

a better color separation is obtained with the use of the said separating layer than when using a gelatin layer free from additives.

The 1-methyl-2-naphthol-6-carboxylic acid stearyl-amine may be prepared as follows:

10 g. of 1-methyl-2-naphthol-6-carboxylic acid (whose preparation is described in Example 6)

12 g. of stearylamine

80 cc. of benzene

60 cc. of pyridine

are boiled azeotropically with a water separator until no more water is separated out. 2.5 cc. of phosphorus trichloride in 10 cc. of benzene are added at room temperature. The mixture is heated to boiling and the benzene is slowly distilled off. After 3 hours, the mixture is discharged on to 200 g. of ice and 100 cc. of concentrated hydrochloric acid. It is stirred until the initially viscous precipitate decomposes. It is suction-filtered, dried in vacuo and recrystallized from methanol. M.P. 95-100° C.

What is claimed is:

1. In the process of producing color photographic images in exposed silver halide emulsion layers by developing the emulsion with a color-forming primary amine developer in the presence of a color coupler of the group consisting of phenolic, naphtholic, and activated methylene radical-containing color couplers that reacts with the oxidation products of the developer to form a dye and subsequently treating the developed emulsion layer in a bleaching bath, the improvement according to which the subsequent treatment of the exposed silver halide emulsion layer is carried out in the further presence of a supplemental coupler which reacts with the said oxidation products to form a colorless product and thereby prevent the formation of some of the dye, the said supplemental coupler being a 2-naphthol which is substituted in the 1 position by a radical of the group consisting of alkyl, allyl, cyanoalkyl, carboxyalkyl, and phenylalkyl.

2. A process as defined in claim 1 in which the supplemental coupler is present in the silver halide emulsion layer.

3. A process as defined in claim 1 in which the supplemental coupler is present in a treating bath in which the exposed silver halide emulsion layer is subjected to further treatment.

4. A photographic material having a plurality of adherently united superimposed layers, at least one of which is a silver halide emulsion layer containing a color coupler that reacts with the oxidation products of a primary amine color developer to form a color image when said emulsion is exposed and then developed in such developer, at least one of the layers containing a supplemental coupler which couples with the oxidation products of the primary amine color developer to form a substantially colorless product and thereby prevent the formation of some of the color, the said supplemental coupler being a 2-naphthol which is substituted in the 1 position by a radical of the group consisting of alkyl, allyl, cyanoalkyl, carboxyalkyl, and phenylalkyl.

5. An aqueous alkaline color developer solution containing (a) a primary amine color developer that develops latent images in a silver halide emulsion and thereby forms oxidation products that react with color couplers that are present in the said silver halide emulsion to

form dyes at the developed areas and (b) a supplemental coupler which couples with the said oxidation products to form a substantially colorless product and thereby prevent the formation of some of the color, the said supplemental coupler being a 2-naphthol which is substituted in the 1 position by a radical of the group consisting of alkyl, allyl, cyanoalkyl, carboxyalkyl, and phenylalkyl.

6. An aqueous bleaching bath containing (a) a silver image bleaching agent for bleaching out silver images from color images formed by reaction of a color coupler with the oxidation products of a primary amine color developer and (b) which bath also contains a supplemental coupler which couples with the said oxidation products to form a substantially colorless product and thereby prevent the formation of some of the color, the said supplemental coupler being a 2-naphthol which is substituted in the 1 position by a radical of the group consisting of alkyl, allyl, cyanoalkyl, carboxyalkyl, and phenylalkyl.

7. An aqueous bleach-fixing bath containing (a) a silver image bleaching agent for bleaching out silver images from color images formed by reaction of a color coupler with the oxidation products of a primary amine color developer and (b) a fixing agent for removing silver salts and (c) a supplemental coupler which couples with the said oxidation products to form a substantially colorless product and thereby prevent the formation of some of the color, the said supplemental coupler being a 2-naphthol which is substituted in the 1 position

by a radical of the group consisting of alkyl, allyl, cyanoalkyl, carboxyalkyl, and phenylalkyl.

8. A photographic element comprising a plurality of superimposed silver halide emulsion layers sensitive to different regions of the visible spectrum, at least one of the said layers containing a color coupler that reacts with the oxidation products of a primary amine color developer to form a color image when said element is exposed and then developed in such developer, the said silver halide emulsion layers being separated from each other by a hydrophilic layer containing a supplemental coupler which couples with the said oxidation products to form a substantially colorless product and thereby help to confine the said color image to the layer containing the color coupler, the said supplemental coupler being a 2-naphthol which is substituted in the 1 position by a radical of the group consisting of alkyl, allyl, cyanoalkyl, carboxyalkyl, and phenylalkyl.

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