

[54] **IMPROVED PROCESS FOR PREVENTING THE DISCOLORATION OF A COLOR IMAGE AND IMPROVING IMAGE STABILITY**

[75] Inventors: **Kazuo Shirasu; Hiroyuki Amano; Reiichi Ohi**, all of Kanagawa, Japan

[73] Assignee: **Fuji Photo Film Co., Ltd.**, Ashigara-shi, Kanagawa, Japan

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**Related U.S. Application Data**

[62] Division of Ser. No. 110,291, Jan. 27, 1971, abandoned.

[30] **Foreign Application Priority Data**

Jan. 27, 1970 Japan..... 45-7201

[52] **U.S. Cl.**..... **96/56, 96/22**

[51] **Int. Cl.**..... **G03c 7/00, G03c 7/16**

[58] **Field of Search**..... 96/110, 291, 56, 22, 66, 96/50

[56] **References Cited**

**UNITED STATES PATENTS**

|           |         |                     |       |
|-----------|---------|---------------------|-------|
| 2,384,658 | 9/1945  | Vittum.....         | 96/56 |
| 2,442,930 | 6/1948  | Morreall, Jr.....   | 96/56 |
| 2,579,435 | 12/1951 | Mackey .....        | 96/56 |
| 3,095,302 | 6/1953  | Jeffreys et al..... | 96/56 |
| 3,617,283 | 11/1971 | Ohi et al.....      | 96/56 |

*Primary Examiner*—J. Travis Brown

*Assistant Examiner*—M. F. Kelley

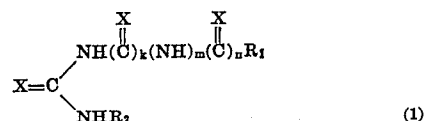
*Attorney, Agent, or Firm*—Sughrue, Rothwell, Mion, Zinn & Macpeak

[57] **ABSTRACT**

In a process for preventing the discoloration of a color image by developing an exposed silver halide color photographic material, removing the silver image thus

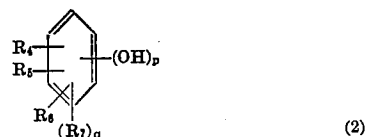
formed together with the residual silver halide and stabilizing the thus formed color image with a stabilizing solution, the improvement which comprises employing a stabilizing solution containing:

a. at least one compound represented by the general formula (1):



wherein  $\text{R}_1$  represents a member selected from the group consisting of a hydrogen atom, an alkyl group, an allyl group, an aryl group and  $\text{NHR}_3$ ;  $\text{R}_2$  and  $\text{R}_3$  represent a member selected from the group consisting of a hydrogen atom, an alkyl group, a carboxyalkyl group, a sulfoalkyl group, an allyl group and an aryl group; said  $\text{R}_1$  and  $\text{R}_2$  may combine with each other to form a 5-membered or 6-membered heterocyclic ring;  $\text{X}$  represents  $=\text{O}$  or  $=\text{NH}$ ; and  $k$ ,  $m$ , and  $n$  are 0 or 1, and

b. at least one compound represented by the general formula (2):



wherein  $\text{R}_4$ ,  $\text{R}_5$ ,  $\text{R}_6$  and  $\text{R}_7$  each represent a member selected from the group consisting of a hydrogen atom, an alkyl group, a halogen atom, a carboxylic acid group, a sulfonic acid group, and  $-\text{CH}=\text{NOH}$ ;  $p$  is 2 or 3,  $q$  is 0 or 1, and  $p + q$  is always 3.

**10 Claims, No Drawings**

# IMPROVED PROCESS FOR PREVENTING THE DISCOLORATION OF A COLOR IMAGE AND IMPROVING IMAGE STABILITY

## CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a Divisional Application of our earlier co-pending application Ser. No. 110,291 filed Jan. 27, 1971 now abandoned, which claims priority from Jan. 27, 1970, based upon Japanese Patent application Ser. No. 7201/70.

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

The present invention relates to an improvement in the stability of images of color photographic materials. More particularly, the present invention relates to an improvement in the stability of images of color photographic materials by processing the color photographic materials in a bath containing a urea compound, a guanidine compound, or a derivative of each of them, together with a di- or tri-hydroxy benzene derivative.

### 2. Description of the Prior Art

In general, it is well known that a color photographic system of forming dyes, such as indophenol, indamine or azomethine produced by reaction of an aromatic amine developing agent and a coupler provides images having poor light fastness. For improving the light fastness of images in such a color photographic system, the following methods have generally been employed:

1. A material absorbing ultraviolet light is incorporated in color photographic materials (see, e.g., specifications of U.S. Pat. Nos. 2,632,701 and 2,747,996). 2. A reducing agent or an antioxidant is incorporated in color photographic materials (see, e.g., specifications of U.S. Pat. Nos. 2,384,658 and 3,095,302).

In order to incorporate these compounds in the color photographic material, there is known the method of adding the compounds to photographic emulsion layers and the method of introducing the photographic emulsion layers during processing of the photographic materials depending upon the nature of the compounds employed and the characteristics of the light sensitive materials.

Color photographic light sensitive material is ordinarily subjected to the following processing steps after exposure: For instance, the color photographic material is subjected to the steps of color development, stop-fixing, washing, bleaching, washing, hardener fixing, washing and stabilization as described in "The British Journal of Photography," Sept. 27, 838 (1968) or the steps of pre-bathing, rinsing, color development, rinsing, fixing, washing, bleaching, washing, fixing, washing, and stabilization as described in "Journal of the SMPTE" Vol. 61, No. 12,667 (1963).

It is known to use a processing bath containing a compound having a hydroxyl group, an amino group or a substituted amino group for improving the stability of the images in the above-mentioned known color photographic processing steps (see the specification of U.S. Pat. No. 2,384,658). However, though the light fastness of the magenta dye itself in the color photographic material processed by the bath containing hydroquinone or a derivative thereof described in that patent is improved, it also produces brown stains on the non-image portions of the color photographic material upon light exposure. Also, ascorbic acid described in the

same patent improves the light fastness of magenta dye itself but also is accompanied with brown stains. In addition, the cyan density is greatly reduced during processing.

It is also known that gallic acid improves the stability of the images (see the specification of U.S. Pat. No. 3,069,262). However, gallic acid not only weakly improves the light fastness of the magenta dye as compared with the compounds described in U.S. Pat. No. 2,384,658 mentioned above, but also produces severe brown stains as well. Urea, guanidine or a derivative thereof is also known as a light-fading preventing agent (see the specification of U.S. Pat. No. 3,095,302). However, as described in the specification of U.S. Pat. No. 3,201,244, the effect of urea, guanidine and the derivatives thereof are insufficient in effectively preventing light fading.

Also, it is known that carbohydrazide improves the light fastness of a magenta dye (see the specification of U.S. Pat. No. 3,201,244). However, although the light fastness of the magenta dye is improved by processing a color photographic material with a bath containing this compound, when the color photograph thus processed is preserved at a high temperature, e.g., at 76.7° C, the magenta dye is extremely faded. Furthermore, polyhydroxy compounds (see the specification of U.S. Pat. No. 3,095,302) and cystein (see the specification of U.S. Pat. No. 3,201,243), etc., are also known as light-fading preventing agents whose effects are also insufficient.

## SUMMARY OF THE INVENTION

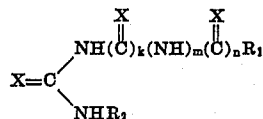
Therefore, an object of this invention is to provide a processing bath which will prevent the fading of color images by light and heat as well as preventing the formation of stains.

Another object of the present invention is to provide color photographic materials, such as color films, transparency, color prints, etc., stable against light and heat by processing the color photographic materials with a specific stabilizing bath.

The above objects of this invention are achieved by processing a color photographic material, which has been subjected to ordinary photographic processes, with an aqueous solution containing at least one urea compound or a guanidine compound, and at least one dihydroxybenzene compound or a trihydroxybenzene compound of the same.

## DETAILED DESCRIPTION OF THE INVENTION

The urea compound and guanidine compound applicable to the present invention include the compounds represented by the general formula (1):



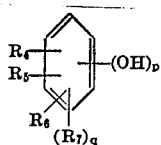
(1)

wherein  $\text{R}_1$  represents a hydrogen atom, an alkyl group, an allyl group, an aryl group or  $\text{NHR}_3$ ;  $\text{R}_2$  and  $\text{R}_3$  represent a hydrogen atom, an alkyl group, a carboxy-alkyl group, a sulfoalkyl group, an allyl group, or an aryl group, said  $\text{R}_1$  and  $\text{R}_2$  may combine with each other to form a 5-membered or 6-membered heterocyc-

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clic ring; X represents =O or =NH; and  $k$ ,  $m$  and  $n$  are 0 or 1.

The dihydroxybenzene compound and the trihydroxybenzene compound applicable to the present invention include the compounds represented by the general formula (2):



(2)

wherein  $R_4$ ,  $R_5$ ,  $R_6$  and  $R_7$  each represent a hydrogen atom, an alkyl group, a halogen atom, a carboxylic acid group, a sulfonic acid group or  $-\text{CH}=\text{NOH}$ ;  $p$  is 2 or 3,  $q$  is 0 or 1, and  $p + q$  is always 3.

As mentioned before, the compound represented by the general formula (1) or the compound represented by the general formula (2) has hitherto been used individually as a light-fading preventing agent. However, the effect thereof is not always sufficient and also is accompanied with undesirable phenomena. On the other hand, when both compounds are used together according to the present invention, totally unexpected results are obtained. That is to say, a combination of the compound represented by the general formula (2) with the compound represented by the general formula (1) inhibits stain formation and also effectively prevents light-fading.

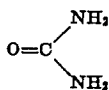
The results obtained by using a processing solution containing the compound represented by the general formula (1) and the compound represented by the general formula (2) according to the present invention are summarized below:

1. The light fastness of magenta dye upon exposure to various types of light is greatly improved.
2. The light fastness of a yellow dye upon exposure to various types of light is greatly improved.
3. When exposed to various types of light, fewer stains are formed.
4. The discoloring and fading of a cyan dye by heating as well as the formation of stains are effectively prevented.

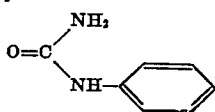
The compound represented by the general formula (1) may be used in the form of an addition salt thereof, such as a carbonate, a hydrochloride, a sulfate, etc., for increasing the water-solubility thereof.

Typical examples of the compounds represented by the general formula (1) to be employed in the present invention are shown below:

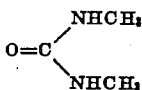
Compound 1:



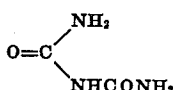
Compound 2:



Compound 3:

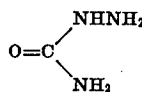


Compound 4:

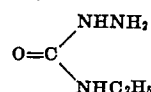


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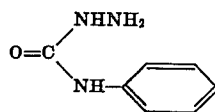
Compound 5:



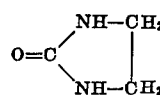
Compound 6:



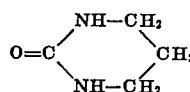
Compound 7:



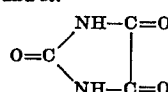
Compound 8:



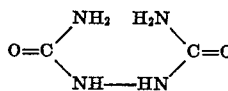
Compound 9:



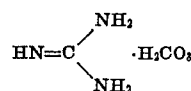
Compound 10:



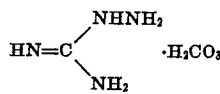
Compound 11:



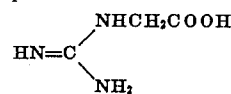
Compound 12:



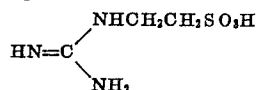
Compound 13:



Compound 14:



Compound 15:

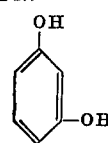


Typical examples of the compounds represented by the general formula (2) used in the present invention are illustrated below:

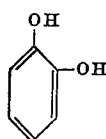
Compound 16:



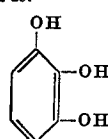
Compound 17:



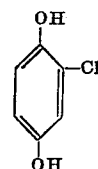
Compound 18:



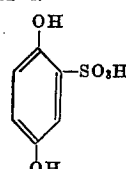
Compound 19:



Compound 20:

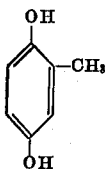


Compound 21:

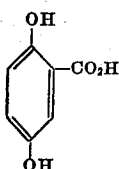


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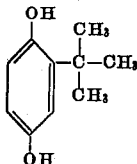
Compound 22:



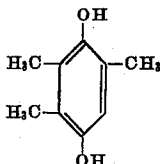
Compound 23:



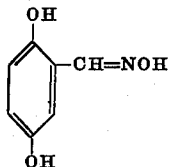
Compound 24:



Compound 25:



Compound 26:



The above-mentioned compounds are well known in the prior art and may be produced by well known methods. Of course, the commercially available compounds may be used as they are.

The amounts of the compounds to be employed represented by the above general formulas (1) and (2) are shown below:

|                     | Amount     | Optimum amount |
|---------------------|------------|----------------|
| General formula (1) | 1-100 g/l  | 15-45 g/l      |
| General formula (2) | 0.1-10 g/l | 1-5 g/l        |

The light sensitive materials to be processed by the processing bath of this invention may be colored photographic light sensitive materials containing acetanilide type yellow couplers as disclosed in the specifications of British Patent No. 1,113,038 and U.S. Pat. No. 3,409,439; the pyrazolone type magenta couplers described in the specifications of British Patent No. 1,142,553 and U.S. Pat. No. 3,337,344; and the phenolic couplers described in the specifications of U.S. Pat. Nos. 2,423,730, 2,474,493, and 2,801,171. However, the present invention is not limited to these light-sensitive materials alone.

Furthermore, the processing bath of this invention may be more profitably applied to light-sensitive materials containing ultraviolet absorbers (see, e.g., specifications of U.S. Pat. No. 3,352,681 and British Patent No. 1,026,142). Also, it is effective to add the compound represented by the general formulas (1) and (2) to the stabilizing bath as described in "The British Journal of Photography," Sept. 27, 838 (1968) or "Journal of the SMPTE," Vol. 61, No. 12, 667 (1963).

A better understanding of the present invention will be attained from the following examples, which are

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merely illustrative and not limitative of the present invention.

## Example 1

|    |                                                          |         |
|----|----------------------------------------------------------|---------|
| 5  | Color developing solution (pH 10.6)                      |         |
|    | Sodium metaborate                                        | 25.0 g  |
|    | Sodium sulfite                                           | 2.0 g   |
|    | Hydroxylamine (sulfate)                                  | 2.0 g   |
|    | Potassium bromide                                        | 0.5 g   |
| 10 | 6-Nitrobenzimidazole (nitrate)                           | 0.02 g  |
|    | Sodium hydroxide                                         | 4.0 g   |
|    | Benzyl alcohol                                           | 15.8 ml |
|    | Diethylene glycol                                        | 20.0 ml |
|    | N-Ethyl-N-(methanesulfonamido-ethyl)-p-phenylene diamine | 8.0 g   |
| 15 | Stop fixing solution (pH 4.5)                            | 1 liter |
|    | Ammonium thiosulfate                                     | 120.0 g |
|    | Sodium pyrosulfite                                       | 20.0 g  |
|    | Glacial acetic acid                                      | 10.0 g  |
|    | Water to make                                            | 1 liter |
| 20 | Bleaching solution (pH 7.2)                              |         |
|    | Potassium nitrate                                        | 25.0 g  |
|    | Potassium ferricyanide                                   | 20.0 g  |
|    | Potassium bromide                                        | 8.0 g   |
|    | Boric acid                                               | 5.0 g   |
|    | Borax                                                    | 2.5 g   |
| 25 | Water to make                                            | 1 liter |
|    | Hardener fixing solution (pH 9.5)                        |         |
|    | Ammonium thiosulfate                                     | 120.0 g |
|    | Sodium sulfite                                           | 5.0 g   |
|    | Boric acid                                               | 2.5 g   |
| 30 | Formalin (35-40%)                                        | 40.0 ml |
|    | Water to make                                            | 1 liter |

A color photographic light-sensitive paper produced by coating a baryta-coated paper with a blue-sensitive silver iodobromide emulsion layer containing benzoyl-aceto-2-chloro-5-dodecyloxycarbonyl anilide as a yellow coupler, an intermediate gelatin layer, a green-sensitive silver chlorobromide emulsion layer containing 1-phenyl-3-[3-(N-butylcaprylamidopropionamido)]-5-pyrazolone as a magenta coupler, an intermediate gelatin layer, a red-sensitive silver chlorobromide emulsion layer containing 1-hydroxy-2-[3-(2,4-t-amyphenoxy)propyl]-naphthamide as a cyan coupler, and a protective gelatin layer in the successive order was exposed and subjected successively to the following processings at 30° C using the above-mentioned processing solutions. That is to say, to color development for seven minutes, stop-fixing for two minutes, washing for two minutes, bleaching for two minutes, washing two minutes, hardener fixing for two minutes and then washing for four minutes. Thereafter, the photographic paper thus processed was further processed with each of the following processing baths for two minutes and then dried.

| Processing bath | Addition (amount)                     |
|-----------------|---------------------------------------|
| 1               | Compound 1 (20 g)                     |
| 2               | Compound 1 (40 g)                     |
| 3               | Compound 16 (2 g)                     |
| 4               | Compound 16 (4 g)                     |
| 5               | Compound 1 (20 g) + Compound 16 (2 g) |
| 6               | Compound 1 (20 g) + Compound 16 (4 g) |
| 7               | Compound 1 (40 g) + Compound 16 (2 g) |
| 8               | Compound 1 (40 g) + Compound 16 (4 g) |

Note: In the above table, the addition amount of the additive is the gram number of the additive per 1 liter of the processing bath.

The test of the stability of the images produced was conducted under the conditions shown in the following table.

| Final Processing  | Fluorescent Lamp (10000 Lux)              |         |      |                  | Direct Sunlight                               |         |      |                  |
|-------------------|-------------------------------------------|---------|------|------------------|-----------------------------------------------|---------|------|------------------|
|                   | *Fading ratio after exposure for ten days |         |      |                  | *Fading ratio after exposure for fifteen days |         |      |                  |
|                   | Image                                     |         |      |                  | Image                                         |         |      |                  |
|                   | Yellow                                    | Magenta | Cyan | $\Delta DY^{**}$ | Yellow                                        | Magenta | Cyan | $\Delta DY^{**}$ |
| None              | 25%                                       | 50%     | 10%  | +0.07            | 30%                                           | 50%     | 12%  | +0.07            |
| Processing bath 1 | 23%                                       | 45%     | 10%  | +0.06            | 28%                                           | 46%     | 12%  | +0.07            |
| Processing bath 2 | 21%                                       | 43%     | 10%  | +0.06            | 26%                                           | 44%     | 12%  | +0.06            |
| Processing bath 3 | 25%                                       | 38%     | 10%  | +0.09            | 30%                                           | 37%     | 11%  | +0.09            |
| Processing bath 4 | 25%                                       | 35%     | 11%  | +0.12            | 30%                                           | 35%     | 11%  | +0.11            |
| Processing bath 5 | 15%                                       | 15%     | 11%  | +0.04            | 15%                                           | 16%     | 11%  | +0.04            |
| Processing bath 6 | 14%                                       | 12%     | 10%  | +0.04            | 14%                                           | 12%     | 10%  | +0.04            |
| Processing bath 7 | 12%                                       | 13%     | 10%  | +0.04            | 12%                                           | 13%     | 10%  | +0.04            |
| Processing bath 8 | 12%                                       | 12%     | 10%  | +0.04            | 12%                                           | 12%     | 11%  | +0.04            |

\* The fading ratio is the ratio of the color density reduced during the test of the portion having an initial density of 1.0.

\*\* $\Delta DY$  is the value of the density increase of the non-exposed portion shown by the density of the yellow component.

From the experimental results shown in the above table, the following matters become clear and the effects of the present invention will be easily understood:

1. The known processing baths 1 and 2 gave a slight effect in the prevention of light fastness.

2. The known processing baths 3 and 4 exhibited very little fading prevention of the magenta dye.

3. The processing baths 5-8 of this invention gave remarkable light-fading prevention effect of magenta dye, which has never been obtained by using the known Compound 1 or 16 individually.

4. The processing baths 5-8 of this invention gave excellent light-fading prevention effect of the yellow dye as well as preventing the formation of stains upon light exposure.

The samples processed with the above-mentioned processing baths were preserved for seven days at 76.7° C under low humidity conditions. In this case, the ratios of the color densities reduced during the preservation test of a portion having an initial density of 1.0 and also the stain-increased densities ( $\Delta DY$ ) of the non-exposed portions are shown in the following table:

| Final processing  | Image  |         |      |             |
|-------------------|--------|---------|------|-------------|
|                   | Yellow | Magenta | Cyan | $\Delta DY$ |
| None              | 0      | 1%      | 15%  | +0.06       |
| Processing bath 5 | 0      | 2%      | 5%   | +0.03       |
| Processing bath 8 | 0      | 2%      | 7%   | +0.03       |

As is clear from the above experimental results, the samples processed by the processing baths of this invention exhibited improved stability of the cyan dye to

heat and also formed fewer stains upon heating.

Almost identical results were obtained when color photographic films were used instead of the colored photographic papers.

## EXAMPLE 2

After subjecting the color photographic paper shown in Example 1 to color development, the stop-fixing, washing, bleaching, washing, hardener fixing, and washing as shown in Example 1, the color photographic paper was processed for two minutes in each of the following processing baths and dried:

| Processing bath | Additive (gram per liter)              |
|-----------------|----------------------------------------|
| 9               | Compound 16 (2 g) + Compound 1 (30 g)  |
| 10              | Compound 16 (2 g) + Compound 2 (30 g)  |
| 11              | Compound 16 (2 g) + Compound 4 (30 g)  |
| 12              | Compound 16 (2 g) + Compound 5 (30 g)  |
| 13              | Compound 16 (2 g) + Compound 8 (30 g)  |
| 14              | Compound 16 (2 g) + Compound 10 (30 g) |
| 15              | Compound 16 (2 g) + Compound 12 (30 g) |
| 16              | Compound 16 (2 g) + Compound 14 (30 g) |

The image of the samples thus processed were tested under the following conditions, the results of which are shown in the following table.

| Final Processing   | Fluorescent Lamp (10,000 Lux)             |         |      |                  | Direct Sunlight                               |         |      |                  |
|--------------------|-------------------------------------------|---------|------|------------------|-----------------------------------------------|---------|------|------------------|
|                    | *Fading ratio after exposure for ten days |         |      |                  | *Fading ratio after exposure for fifteen days |         |      |                  |
|                    | Image                                     |         |      |                  | Image                                         |         |      |                  |
|                    | Yellow                                    | Magenta | Cyan | $\Delta DY^{**}$ | Yellow                                        | Magenta | Cyan | $\Delta DY^{**}$ |
| None               | 25%                                       | 50%     | 10%  | +0.07            | 30%                                           | 50%     | 12%  | +0.07            |
| Processing bath 2  | 21%                                       | 43%     | 10%  | +0.06            | 26%                                           | 44%     | 12%  | +0.06            |
| Processing bath 4  | 25%                                       | 35%     | 11%  | +0.12            | 30%                                           | 35%     | 11%  | +0.11            |
| Processing bath 9  | 12%                                       | 12%     | 10%  | +0.04            | 12%                                           | 12%     | 11%  | +0.04            |
| Processing bath 10 | 15%                                       | 15%     | 10%  | +0.04            | 14%                                           | 14%     | 12%  | +0.04            |
| Processing bath 11 | 13%                                       | 14%     | 11%  | +0.04            | 14%                                           | 14%     | 11%  | +0.04            |
| Processing bath 12 | 14%                                       | 11%     | 10%  | +0.04            | 15%                                           | 12      | 12%  | +0.04            |
| Processing bath 13 | 12%                                       | 12%     | 11%  | +0.04            | 12%                                           | 12%     | 12%  | +0.04            |
| Processing bath 14 | 12%                                       | 12%     | 10%  | +0.04            | 12%                                           | 12%     | 11%  | +0.04            |

| Final Processing   | Fluorescent Lamp (10,000 Lux)             |         |      |             | Direct Sunlight                               |         |      |             |
|--------------------|-------------------------------------------|---------|------|-------------|-----------------------------------------------|---------|------|-------------|
|                    | *Fading ratio after exposure for ten days |         |      |             | *Fading ratio after exposure for fifteen days |         |      |             |
|                    | Yellow                                    | Magenta | Cyan | $\Delta$ DY | Yellow                                        | Magenta | Cyan | $\Delta$ DY |
| Processing bath 15 | 13%                                       | 13%     | 10%  | +0.04       | 14%                                           | 14%     | 11%  | +0.04       |
| Processing bath 16 | 13%                                       | 14%     | 10%  | +0.04       | 14%                                           | 14%     | 12%  | +0.04       |

\* The fading ratio is the ratio of the color density reduced during the test of the portion having an initial density of 1.0.

\*\* $\Delta$ DY is the value of the density increase of the nonexposed portion shown by the density of yellow component.

From the above experimental results, the processing baths of this invention exhibited remarkable light-fading prevention on magenta dyes, light-fading prevention effect on yellow dyes, as well as preventing the formation of stains. Moreover, when the samples processed by the processing baths of this invention were stored at 76.7° C under a low humidity condition, the fading of the cyan dye and the formation of stains were less as illustrated in Example 1.

When color photographic films were used instead of the colored photographic papers, almost the same results were obtained.

### EXAMPLE 3

A color photographic positive film produced by coating an acetate film with a blue-sensitive silver iodobromide emulsion layer containing benzoylaceto-2-chloro-5-dodecyloxycarbonyl anilide as a yellow coupler, an intermediate gelatin layer, a red-sensitive silver chlorobromide emulsion layer containing 1-hydroxy-2-[3-(2,4-t-amylphenoxy)propyl]naphthamide as a cyan coupler, an intermediate gelatin layer, a green-sensitive chlorobromide emulsion layer containing 1-phenyl-3-[3-(N-butyl-caprylamidopropionamide)]-5-pyrazolone as a magenta coupler, and a protective gelatin layer in successive order was exposed and subjected to the following processings at 21° C; i.e. to the steps of pre-bathing for ten seconds, rinsing for fifteen seconds, developing for twelve minutes, rinsing for fifteen seconds, fixing for four minutes, washing for four minutes, bleaching for eight minutes, washing for eight minutes,

fixing for four minutes, and washing for eight minutes.

In the development process indicated above, the developing solution containing the following composition was used:

Developing solution (pH 10.65)

|                                                |         |
|------------------------------------------------|---------|
| Calgon (trade name)                            | 2.0 g   |
| Sodium sulfite                                 | 4.0 g   |
| N,N-Diethyl-p-phenylenediamine (hydrochloride) | 3.0 g   |
| Sodium carbonate (monohydrate)                 | 20.0 g  |
| Potassium bromide                              | 2.0 g   |
| Water to make                                  | 1 liter |

The bath for the pre-bath contained sodium hydroxide, the fixing bath contained sodium thiosulfate, and the bleaching bath contained potassium bichromate. The photographic film thus processed was processed for two minutes with each of the following processing baths:

| Processing bath | Additive (gram per liter)             |
|-----------------|---------------------------------------|
| 17              | Compound 1 (30 g) + Compound 20 (2 g) |
| 18              | Compound 1 (30 g) + Compound 21 (2 g) |
| 19              | Compound 1 (30 g) + Compound 22 (2 g) |
| 20              | Compound 1 (30 g) + Compound 25 (2 g) |
| 21              | Compound 1 (30 g) + Compound 26 (2 g) |

The samples processed in each of the above processing baths were tested for stability of the images thus obtained under the conditions shown in the following table, the results of which are shown in the same table.

| Final Processing   | Fluorescent Lamp (10,000 Lux)             |         |      |             | Direct Sunlight                               |         |       |               |
|--------------------|-------------------------------------------|---------|------|-------------|-----------------------------------------------|---------|-------|---------------|
|                    | *Fading ratio after exposure for ten days |         |      |             | *Fading ratio after exposure for fifteen days |         |       |               |
|                    | Yellow                                    | Magenta | Cyan | $\Delta$ DY | Yellow                                        | Magenta | Cyan  | $\Delta$ DY** |
| None               | 20%                                       | 40%     | 10%  | +0.05       | 24%                                           | 40%     | 13%   | +0.05         |
| Processing bath 2  | 17%                                       | 35%     | 10%  | +0.04       | 17%                                           | 34%     | 13%   | +0.04         |
| Processing bath 4  | 20%                                       | 29%     | 11%  | +0.10       | 20%                                           | 30%     | 13%   | +0.11         |
| Processing bath 9  | 9%                                        | 9%      | 10%  | +0.03       | 9%                                            | 8%      | 14%   | +0.03         |
| Processing bath 17 | 9%                                        | 9%      | 10%  | +0.03       | 9%                                            | 8%      | 14%   | +0.03         |
| Processing bath 18 | 10%                                       | 9%      | 10%  | +0.03       | 9%                                            | 8%      | 13%   | +0.03         |
| Processing bath 19 | 9%                                        | 10%     | 10%  | +0.03       | 10%                                           | 9%      | 13%   | +0.03         |
| Processing bath 20 | 9%                                        | 10%     | 11%  | +0.03       | 10%                                           | 9%      | +0.03 |               |
| Processing bath 21 | 9%                                        | 10%     | 10%  | +0.03       | 9%                                            | 9%      | 14%   | +0.03         |

\*The fading ratio is the ratio of the color density reduced during the test of the portion having an initial density of 1.0.

\*\* $\Delta$ DY is the value of the density increase of the non-exposed portion shown by the density of the yellow component.

From the above experimental results, it is clear that the processing baths of this invention give remarkable light-fading prevention of magenta dyes, light-fading prevention of yellow dyes, and effectively prevent the formation of stains. Also, when the samples processed by the processing baths of this invention were preserved at 76.6°C under conditions of low humidity, the fading of the cyan dye and the formation of stain was less as seen in Example 1.

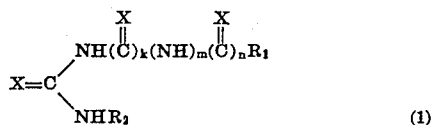
Also, when a color photographic paper was used instead of the color positive film, practically the same results were obtained.

Although the present invention has been adequately described in the aforementioned specification and examples, one readily realizes that various modifications and changes may be made without departing from the scope thereof.

What is claimed is:

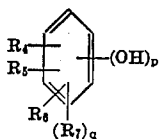
1. In a process for preventing the discoloration of a color image by developing an exposed silver halide color photographic material, removing the silver image thus formed together with residual silver halide and stabilizing the color image thus formed with a stabilizing solution, the improvement which comprises employing a stabilizing solution consisting essentially of:

a. at least one compound represented by the general formula (1):



wherein  $\text{R}_1$  represents a member selected from the group consisting of a hydrogen atom, an alkyl group, an aryl group, an aryl group and  $\text{NHR}_3$ ;  $\text{R}_2$  and  $\text{R}_3$  represent a member selected from the group consisting of a hydrogen atom, an alkyl group, a carboxyalkyl group, a sulfoalkyl group, an allyl group and an aryl group; said  $\text{R}_1$  and  $\text{R}_2$  may combine with each other to form a 5-membered or 6-membered heterocyclic ring;  $\text{X}$  represents  $=\text{O}$  or  $=\text{NH}$ ; and  $k$ ,  $m$ , and  $n$  are 0 or 1, and

b. at least one compound represented by the general formula (2):



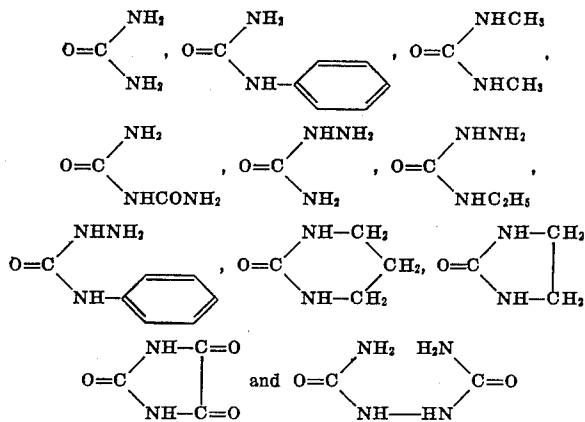
wherein  $\text{R}_4$ ,  $\text{R}_5$ ,  $\text{R}_6$  and  $\text{R}_7$  each represent a member selected from the group consisting of a hydrogen atom, an alkyl group, a halogen atom, a carboxylic acid group, a sulfonic acid group, and  $-\text{CH}=\text{NOH}$ ;  $p$  is 2 or 3,  $q$  is 0 or 1, and  $p + q$  is always 3, said compound represented by the formula (1) being present in an amount of from 1 to 100 grams per liter and said compound represented by formula (2) being present in an amount of 0.1 to 10 grams per liter.

2. The process of claim 1, wherein the amount present of the compound represented by the general for-

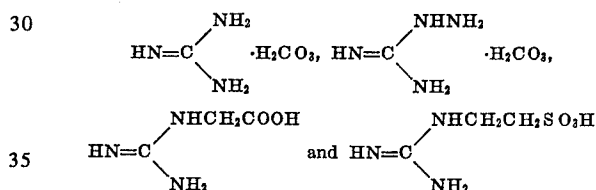
mula (1) in the processing solution is 15-45 g/liter.

3. The process as claimed in claim 1, wherein the amount present of the compound represented by the general formula (2) in the processing solution is 1-5 g/liter.

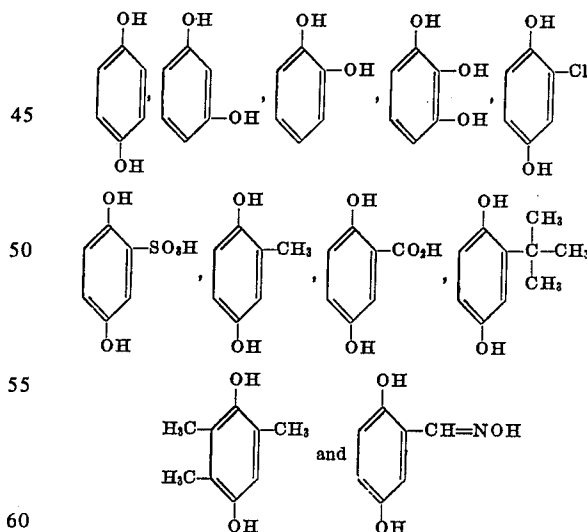
4. The process of claim 1, wherein the compound represented by the general formula (1) is a member selected from the group consisting of



5. The process of claim 1, wherein the compound represented by the general formula (1) is a member selected from the group consisting of



6. The process of claim 1, wherein the compound represented by the general formula (2) is a member selected from the group consisting of



7. The process of claim 1, wherein compound (1) is urea and compound (2) is hydroquinone.

8. The process of claim 1, wherein compound (1) is ethylene urea and compound (2) is hydroquinone.

8. The process of claim 1, wherein compound (1) is parabanic acid and compound (2) is hydroquinone.

10. The process of claim 1, wherein compound (1) is present as an addition salt.

\* \* \* \* \*