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## PROCESS FOR IMPROVING COLOR DEVELOPABILITY OF REVERSAL PHOTOGRAPHIC FILMS

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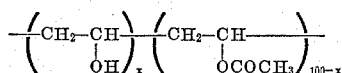
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7 Claims

### ABSTRACT OF THE DISCLOSURE

In a photographic reversal color process employing a photographic element containing three photographic silver halide emulsion layers, comprising first exposing said element to light to produce a latent image therein, developing the exposed element in a photographic black and white developer to produce a black and white negative image, exposing the element to a light of a color to which the first exposed silver halide emulsion layer is sensitive, and developing the resulting element in a color developer for producing a colored image, said color developer containing an aromatic primary amino color developing agent and a photographic color coupler selected from the group consisting of a magenta-forming pyrazolone color coupler, a cyan-forming phenolic color coupler and a yellow-forming open chain ketomethylene color coupler, the improvement which comprises utilizing a binder for said silver halide comprising gelatin and a water-soluble copolymer having a number average molecular weight of from about 5,000 to about 200,000 having repeating units represented by the formula:



wherein  $50 \leq x < 100$  is disclosed.

### BACKGROUND OF THE INVENTION

#### Field of the invention

The present invention relates to color development of a coupler-in-developer type reversal multilayer color photographic sensitive material and especially to a process for increasing the amount of dye produced in reversal color images.

#### Description of the prior art

In multilayer color photographic sensitive materials containing a blue sensitive emulsion layer, a green sensitive emulsion layer and a red sensitive emulsion layer superposed on a support, there are coupler-in-emulsion type color sensitive materials which contain silver halide and color formers (hereinafter referred to as a "coupler") which form dyes by reacting with an oxidation product of an aromatic amino photographic developing agent in the photographic emulsion layers, and coupler-in-developer type color sensitive materials which do not contain couplers in the photographic emulsion layers. The present invention relates to such a coupler-in-developer type color sensitive material.

In the coupler-in-developer type color sensitive material, the following treatments are usually practiced in turn after exposing to light, that is, monochromatic white-black development, exposing to a red light at the support side of the sensitive material, cyan color development by a cyan color developer containing a cyan coupler and an aromatic amino photographic developing agent, exposing to a violet light at the emulsion side, yellow development by a yellow color developer containing a yellow coupler

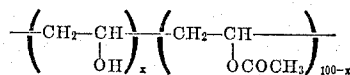
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and an aromatic amino photographic developing agent, and magenta color development by a magenta color developer containing a magenta coupler and an aromatic amino photographic developing agent.

The present invention relates to a new process for improving the density of reversal color images in the cyan color development, yellow color development and magenta color development, and especially to a new process for improving the density of the magenta color image. According to the present invention, a more efficient color reproduction system can be produced by increasing the density produced in the reversal color images. If the same density is kept, thinner emulsion layers can be produced and consequently it is possible to improve sharpness and to decrease the amount of silver halide in the emulsion layers.

### SUMMARY OF THE INVENTION

The new process by this invention for improving the density of the reversal color images comprises treating a silver halide gelatin emulsion containing the following water-soluble polymer as the binder with color developing solutions containing color couplers. The water-soluble polymers used for the above-mentioned, which have been discovered by the present inventors, are those having a repeating unit structure represented by the following formula:



wherein  $50 \leq x < 100$ .

wherein  $x$  is within the range  $50 \leq x < 100$ , preferably

$$60 \leq x \leq 90$$

which represents a ratio of both blocks represented by the above-mentioned rational formula.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferable polymers among these polymers are those having a number average molecular weight in a range of 5,000-200,000, especially 20,000-100,000.

The water-soluble polymer used in the present invention may be added solely to a gelatin emulsion or may be added by substituting a part of the gelatin in the emulsion. Though addition of the water-soluble polymer may take place at any step before coating the emulsion, it is preferable to add it any time from after ripening to coating. The amount of the polymer used in the present invention is preferably in a range of 1%-90%, especially 5%-50%, by weight, based on the combined weight of gelatin and said copolymers.

According to this invention, especially good results are obtainable when the gelatin emulsion contains silver iodide bromide as the silver halide. But it is possible to apply the present invention to many kinds of other silver halide gelatin emulsions. The silver halide emulsion may be sensitized by compounds which contain labile sulfur such as a sodium thiosulfate and allyl thiourea etc., and/or complex salts such as this cyanato aurite, and/or reduction sensitizers such as amino compounds and stannous chloride (refer to "The Theory of the Photographic Process," 3rd edition, Macmillan Company, New York (1966), pages 113-116), and/or polyalkyleneoxide derivatives.

In order to give green-sensitivity and red-sensitivity, the emulsion may include sensitizing dyes which sensitize a wave length range of 500-700 mμ, for example, 1,1'-diethyl-2,2'-cyanine iodide and 3,3'-diethyl - 9 - methyl-

carbocyanine iodide (refer to the above-mentioned literature reference, pages 199-232). The emulsions may include stabilizers such as 4-hydroxy-6-methyl - 1,3,3a,7 - tetra-zaindene (refer to the above-mentioned literature reference, pages 344-346), hardeners such as formaldehyde and mucobromic acid (the same literature reference, pages 54-60) and wetting agents such as saponin and sodium alkylbenzene sulfonate.

Development of the multilayer color photographic material comprising silver halide gelatin emulsions which contain the water-soluble polymer is carried out by a common reversal color processing for the coupler-in-developer type sensitive material. Namely, at least a color developing agent and a diffusible coupler which colors in cyan, magenta or yellow are included in each color developer. As the color developing agent, there are used well-known paraphenylenediamine derivatives such as 4-amino-N,N-diethylaniline, 4 - amino-N,N-diethyl - 3 - methylaniline, 4 - amino - 3 - methyl-N-methyl-N-( $\beta$ -methylsulfonamid-ethyl) aniline and 4 - amino-3-methyl-N-ethyl-N-( $\beta$ -hydroxyethyl) aniline (refer to the above-mentioned literature reference, page 387).

As the diffusible cyan coupler, there are used well-known phenolic couplers such as 2 - chloro - 1-naphthol, 2,4 - dichloro - 1 - naphthol, 2 - (o-acetamide- $\beta$ -phenyl)-1-hydroxy naphthamide, etc. (refer to above-mentioned literature reference, page 387).

As the diffusible magenta coupler, there are used open-chain methylene type couplers such as amylacetoneitrile, 2 - cyanoethyl benzofuran and benzylacetoneitrile and cyclic methylene couplers such as 1 - phenyl - 3 - (4-chloro-benzamido) - 5 - pyrazolone, 1 - phenyl - 3 - (3-nitro-benzoylamino) - 5 - pyrazolone and 1-(2,4,6-trichloro-phenyl) - 3 - (4 - nitroanilino)-5-pyrazolone.

As the diffusible yellow coupler, there are used acyl-acetamide type open-chain methylene couplers such as 2 - acetanilide, 2 - aceto - 2', 4' - dichloroacetanilide, 2 - benzoyl-acetanilide, 2 - benzoyl - 2'-methoxyacetanilide and 2 - methyl - 4 - (methyl sulfonamide-ethyl) ethyl-aniline (refer to the above-mentioned literature reference, page 389 and G. H. Brown et al., "Journal of the American Chemical Society," 79, pages 2917-2927 (1957)).

These well-known color developing agents and couplers are used in combination.

In the following examples, the present invention will be explained in more detail.

### EXAMPLE 1

After melting, by heating, a high sensitive gelatin silver bromoiodide reversal color emulsion which was sulfur-sensitized and gold-sensitized (content of silver iodide: 3.5 mole percent, it was coated on a cellulose triacetate film base (couplers were not included in the emulsion). The binder of the silver bromoiodide in the coated emulsion was gelatin which contained a vinyl acetate-vinyl alcohol copolymer ( $x=88$ , number average molecular weight: approximately 30,000) in many ratios. This emulsion layer was exposed to light by using a NSG II type sensitometer and processed by the following treatments.

Minutes at 27°C.

- (1) Prehardener bath ----- 1
- (2) Water wash ----- 1
- (3) Black and white development ----- 4
- (4) Water wash ----- 3
- (5) Reversal exposure to white light,
- (6) Magenta development ----- 5
- (7) Water wash ----- 2
- (8) Fix ----- 3
- (9) Drying (sample taken for silver analysis).
- (10) Ferricyanide bleach ----- 5
- (11) Fix ----- 3
- (12) Water wash and drying (sample taken for color density measurement),

The various processing solutions have essentially the following composition:

### PREHARDENER BATH

|    |                                 |     |
|----|---------------------------------|-----|
| 5  | Sulfuric acid (conc.) -----cc-- | 1.7 |
|    | Borax -----g--                  | 20  |
|    | Potassium bromide -----g--      | 2.3 |
|    | Sodium sulfate -----g--         | 200 |
|    | 37% formaldehyde -----cc--      | 10  |
| 10 | Sodium bisulfite -----g--       | 1   |
|    | Water to make 1 liter.          |     |

### BLACK AND WHITE DEVELOPER

|    |                                         |      |
|----|-----------------------------------------|------|
|    | N-methyl-p-aminophenol sulfate -----g-- | 5    |
| 15 | Anhydrous sodium sulfite -----g--       | 79   |
|    | Hydroquinone -----g--                   | 2    |
|    | Sodium carbonate (monohydrate) -----g-- | 40   |
|    | Potassium bromide -----g--              | 3.5  |
|    | Potassium thiocyanate -----g--          | 20   |
| 20 | 0.1% potassium iodide -----cc--         | 12.5 |
|    | Sodium hydroxide -----g--               | 1.0  |
|    | Water to make 1 liter.                  |      |

### MAGENTA DEVELOPER

|    |                                                                  |     |
|----|------------------------------------------------------------------|-----|
| 25 | Sodium sulfite -----g--                                          | 5.0 |
|    | 4 - amino - 3-methyl-N,N'-diethylaniline hydrochloride -----g--  | 2.0 |
|    | 1 - phenyl - 3 - (3 - nitrobenzoylamino) - 5-pyrazolone -----g-- | 1.4 |
| 30 | Sodium hydroxide -----g--                                        | 2.5 |
|    | n-Butylamine -----cc--                                           | 5   |
|    | Water to make 1 liter.                                           |     |

### FERRICYANIDE BLEACH

|    |                         |    |
|----|-------------------------|----|
| 35 | Ferricyanide -----      | G. |
|    | Potassium bromide ----- | 60 |
|    | Water to make 1 liter.  | 20 |

### FIX

|    |                          |     |
|----|--------------------------|-----|
| 40 | Sodium thiosulfate ----- | G.  |
|    | Sodium sulfite -----     | 100 |
|    | Water to make 1 liter.   | 15  |

In Example 1, the ratio (by weight) of silver bromoiodide to the binder in the initial emulsion was 6 g. of binder (100% gelatin)/11 g. of silver iodide bromide. The gelatin of this binder was substituted by a vinyl acetate-vinyl alcohol copolymer in many ratios. Results are shown in Table 1.

TABLE 1

| Ratio of polymer in binder of gelatin-polymer mixture (percent by weight) | Magenta. $D_{max}$ . | Silver developed by color developer, mg. Ag./10 cm. <sup>2</sup> | Magenta. $D_{max}$ /silver |
|---------------------------------------------------------------------------|----------------------|------------------------------------------------------------------|----------------------------|
| 0-----                                                                    | 1.9                  | 8.3                                                              | 0.23                       |
| 55 6-----                                                                 | 2.3                  | 9.0                                                              | 0.25                       |
| 12-----                                                                   | 2.8                  | 9.5                                                              | 0.29                       |

It was recognized that  $D_{max}$ /silver increased 20 to 30% when adding the copolymer of the present invention as compared with no addition.

### EXAMPLE 2

The same procedure was carried out as in Example 1 but using a vinyl acetate-vinyl alcohol copolymer ( $x=98$ , number average molecular weight: approximately 22,500) as the polymer.

Results are shown in Table 2.

TABLE 2

| Ratio of polymer in binder of gelatin-polymer mixture (percent by weight) | Magenta. $D_{max}$ . | Silver developed by color developer, mg. Ag./10 cm. <sup>2</sup> | Magenta. $D_{max}$ /silver |
|---------------------------------------------------------------------------|----------------------|------------------------------------------------------------------|----------------------------|
| 0-----                                                                    | 2.3                  | 10.0                                                             | 0.23                       |
| 6-----                                                                    | 2.65                 | 9.5                                                              | 0.28                       |
| 70 12-----                                                                | 2.9                  | 9.7                                                              | 0.30                       |

Similarly, an increase of 2-30% of  $D_{\max}/\text{silver}$  was recognized as compared with the case of no addition of the copolymer of the present invention.

### EXAMPLE 3

The same procedure was carried out as in Example 1 but using a vinyl acetate-vinyl alcohol copolymer ( $x=50$ , number average molecular weight: approximately 50,000) as the polymer.

Results are shown in Table 3.

TABLE 3

| Ratio of polymer in binder of gelatin-polymer mixture (percent by weight) | Magenta. $D_{\max}$ . | Silver developed by color developer, mg./10 cm. <sup>2</sup> | Magenta, $D_{\max}/\text{silver}$ |
|---------------------------------------------------------------------------|-----------------------|--------------------------------------------------------------|-----------------------------------|
| 0-----                                                                    | 2.0                   | 9.0                                                          | 0.22                              |
| 6-----                                                                    | 2.25                  | 9.3                                                          | 0.24                              |
| 12-----                                                                   | 2.40                  | 9.5                                                          | 0.25                              |

As is clear from Table 3, an increase of  $D_{\max}/\text{silver}$  was recognized by addition of the copolymer.

### EXAMPLE 4

Cyan development was carried out (at 27° C. for 5 minutes) instead of the development by the magenta developer in the processing of the emulsion layer in Example 2. Similarly, yellow development was carried out (at 27° C. for 5 minutes) instead of the magenta development. The results of these examples are shown below.

The cyan and yellow developers had the following compositions:

#### CYAN DEVELOPER

|                                                          |      |     |
|----------------------------------------------------------|------|-----|
| Potassium bromide -----                                  | g--  | 20  |
| 0.1% potassium iodide -----                              | cc-- | 20  |
| Potassium thiocyanate -----                              | g--  | 3.0 |
| Anhydrous sodium sulfite -----                           | g--  | 10  |
| Sodium carbonate (monohydrate) -----                     | g--  | 30  |
| Sodium hydroxide -----                                   | g--  | 2.0 |
| 5-nitrobenzimidazole nitrate -----                       | g--  | 0.5 |
| 2,4-dichloro-1-naphthol -----                            | g--  | 2.0 |
| 4-amino-3-methyl-N,N'-diethylaniline hydrochloride ----- | g--  | 3.0 |
| Water to make 1 liter.                                   |      |     |

#### YELLOW DEVELOPER

|                                                         |      |      |
|---------------------------------------------------------|------|------|
| Sodium sulfite -----                                    | g--  | 5.0  |
| N,N'-diethyl paraphenylenediamine hydrochloride -----   | g--  | 1.2  |
| Sodium carbonate (monohydrate) -----                    | g--  | 20.0 |
| Potassium bromide -----                                 | g--  | 0.3  |
| 0.1% potassium iodide -----                             | cc-- | 20   |
| 2-benzoyl-(4'-paratoluenesulfonamide) acetanilide ----- | g--  | 1.0  |
| Sodium hydroxide -----                                  | g--  | 4.0  |
| Water to make 1 liter.                                  |      |      |

TABLE 4

| Ratio of polymer in binder of gelatin-polymer mixture (percent by weight) | Cyan $D_{\max}$ . | Silver developed by color developer, mg./10 cm. <sup>2</sup> | Cyan, $D_{\max}/\text{silver}$ |
|---------------------------------------------------------------------------|-------------------|--------------------------------------------------------------|--------------------------------|
| 0-----                                                                    | 1.4               | 9.5                                                          | 0.15                           |
| 6-----                                                                    | 1.8               | 10.0                                                         | 0.18                           |
| 12-----                                                                   | 1.85              | 9.7                                                          | 0.19                           |

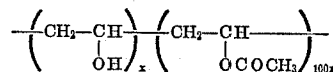
TABLE 5

| Ratio of polymer in binder of gelatin-polymer mixture (percent by weight) | Yellow. $D_{\max}$ . | Silver developed by color developer, mg./10 cm. <sup>2</sup> | Yellow. $D_{\max}/\text{silver}$ |
|---------------------------------------------------------------------------|----------------------|--------------------------------------------------------------|----------------------------------|
| 0-----                                                                    | 1.7                  | 10.0                                                         | 0.17                             |
| 6-----                                                                    | 1.95                 | 10.2                                                         | 0.19                             |
| 12-----                                                                   | 2.1                  | 10.5                                                         | 0.20                             |

10 Increase of  $D_{\max}/\text{silver}$  was similarly recognized at cyan development and magenta development.

What is claimed is:

1. In a photographic reversal color process employing a photographic element containing three photographic silver halide emulsion layers, comprising first exposing said element to light to produce a latent image therein, developing the exposed element in a photographic black and white developer to produce a black and white negative image, exposing the element to a light of a color to which the first exposed silver halide emulsion layer is sensitive, and developing the resulting element in a color developer for producing a colored image, said color developer containing an aromatic primary amino color developing agent and a photographic color coupler selected from the group consisting of a magenta-forming pyrazolone color coupler, a cyan-forming phenolic color coupler and a yellow-forming open chain keto-methylene color coupler, the improvement which comprises utilizing a binder for said silver halide comprising gelatin and a water-soluble copolymer having a number average molecular weight of from about 5,000 to about 200,000 having repeating units represented by the formula:



wherein  $50 \leq x < 100$ .

2. The process of claim 1 wherein the silver halide emulsion to which said copolymer is added is a silver iodobromide emulsion.

3. The process of claim 1 wherein said copolymer has a number average molecular weight of from about 20,000 to about 100,000.

4. The process of claim 1 wherein  $60 \leq x \leq 90$ .

5. The process of claim 1, wherein an amount of said copolymer is present in an amount of from about 1 to about 90 percent by weight, based on the combined weight of gelatin and copolymer.

6. The process of claim 4, wherein an amount of said copolymer is present in an amount of from about 5 to about 50 percent by weight, based on the combined weight of gelatin and copolymer.

7. The process of claim 1, wherein the gelatino silver halide emulsion layer to which said copolymer is added is a magenta color-forming emulsion layer.

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