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PATENT SPECIFICATION

NO DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improved Photographic Developers and Processes

We, EASTMAN KODAK COMPANY, a Company organised under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester 4, New York, United States of America (Assignees of CHARLETON CORDERY BARD and ALLAN GROSVENOR MILLIKAN) do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to photography and in particular to developers for processing silver halide colour photographic materials. According to the present invention there is provided a method of processing a silver halide colour photographic material to produce a dye image therein by colour development which comprises treating the material with a photographic developer solution which contains a silver halide developing agent and a silver halide solvent consisting of a cyclohexane derivative containing an amino or substituted amino group directly bonded to the carbocyclic ring and a second group which is an amino, substituted amino, hydroxyl or hydroxyalkyl group.

In reversal processes for producing positive dye images from exposed silver halide colour photographic materials, two or more developers are used. The first produces negative silver images in the various silver halide emulsions of the material; the second, and each of any subsequent developers, is a colour developer which reduces the residual silver halide in one or more of said emulsions to silver and concurrently produces proportional quantities of the appropriate dye or dyes which are subsequently revealed by removing the silver. It is advantageous to add development accelerators to some or all of these developers, both to reduce the processing time and to promote complete development

of exposed silver halide and thus obtain low fog and good maximum density in the final image.

The cyclohexane derivatives used as development accelerators in the processes of this invention are water-soluble silver halide solvents. Preferred cyclohexane derivatives are 1 - 4 - bis(methylamino) - cyclohexane, 4 - aminocyclohexanol and 1 - cyclohexylamino - 2 - propanol. The derivatives function satisfactorily even under strongly alkaline conditions, do not tend to react with other developer constituents and are not toxic. They do not, in colour developers, impair the definition of the dye images produced.

The developer compositions of this invention may comprise any of the usual developing agents. For example, the developers intended for negative development may contain one or more compounds selected from the dihydroxybenzenes, 3-pyrazolidones and p-N-methylaminophenol salts. In the latter developers, the second group of the cyclohexane derivative is directly bonded to the carboxylic ring. The developer compositions for colour development contain phenylenediamines such as those described in Specifications 651749 and 653289, and can be used for processing light-sensitive materials which may or may not contain the colour-forming compounds or couplers. The optimum concentration of cyclohexane derivative is generally between 0.5 and 10 grams per litre.

Colour developers according to this invention may be used in conjunction with many different couplers including those listed in Specifications 562,205; 594,314; 649,660; 660,012; 674,161; 680,488 and 898,005.

The developers of this invention may be used in the processing of a wide variety of photographic silver halide emulsions which may contain the usual addenda e.g., sensitizers and stabilizers.

[Price 4s. 6d.]

The use of developers according to this invention is illustrated by the following examples:

EXAMPLE 1

5 A portion of a gelatino-silver-bromide emulsion which had been sensitized with a sulphur compound and a gold salt, was coated on a cellulose acetate support and dried. Two strips were cut from the coating and exposed for 1/25 second to a 500-watt, 3000° K. light source on an Eastman Type 1b sensitometer. One of the exposed strips was developed for 3 minutes in a developer having the following composition:

15 Sodium hexametaphosphate - 0.4 g.
Sodium sulphite (anhydrous) - 40.0 g.
N-methyl-*p*-aminophenol-sulphate - - - - 5.0 g.
Hydroquinone - - - - 2.0 g.
20 Sodium carbonate (monohydrate) - - - - 25.0 g.
Potassium bromide - - - - 1.0 g.
Potassium iodide (0.1% solution) - - - - 2 ccs.
25 Water to make one litre (pH was 10.1 at 70° F.)

The strip was washed for 2 minutes in water and then given a reversal exposure for 10 seconds with a No. 2 Photoflood set at a distance of 60 inches. The strip was next developed for 5 minutes in a developer having the following formula:

35 Sodium hexametaphosphate - 1.0 g.
Sodium sulphite (anhydrous) - 30 g.
Sodium sulphate (anhydrous) - 30 g.
Sodium bromide - - - - 0.5 g.
Potassium iodide (0.1% solution) - - - - 5 ccs.
40 1,4-bis(methylamino)cyclohexane - - - - 5 g.
Coupler* - - - - 0.85 g.
Sodium hydroxide - - - - 3 g.
Colour developer** - - - - 3 g.
Hydroxylamine sulphate - - - 0.35 g.
45 Water to make 1 litre (pH at 80° F. was 12.40)

* 1 - (2', 4', 6' - trichlorophenyl)₃ - [α - (4 - nitrophenoxy) - acetamido] - 5 - pyrazolone

50 ** 4 - amino - N, N, - diethyl - 3 - methylaniline hydrochloride

The strip was washed for 10 minutes in water and treated for 2 minutes in a silver bleach bath having the following composition:

55 Potassium ferricyanide - - 100 g.
Potassium bromide - - - 10 g.
Borax - - - - 7.5 g.
Boric acid - - - - 5.0 g.
Water to make one litre

60 The strip was then treated for 2 minutes in a fixing bath having the following composition:

Sodium thiosulphate (pentahydrate) 200 g.
Sodium sulphite (anhydrous) - - 10 g.
65 Water to make one litre

washed in water and dried. The processed strip showed good definition and speed.

The other strip was processed as described above but for the omission of the 1, 4 - bis (methylamino) cyclohexane from the colour 70 developer.

Comparison of the two processed strips showed that the 1,4-bis(methylamino) cyclohexane had reduced the maximum density only slightly. 75

EXAMPLE 2

Two identical sets of pictures were taken on reversal colour film of the type described in Specification No. 507,841. The piece of film which had received one set of exposures was processed according to the following procedure. The film was first developed for 3½ minutes at 80° F in a developer of the composition:

Hydroquinone - - - - 2.5 g. 85
N-methyl-*p*-aminophenol sulphate - - - - 4.5 g.
4-Aminocyclohexanol - - - - 6 g.
Sodium sulphite (anhydrous) - 80 g.
Sodium carbonate H₂O - - 30 g. 90
Sodium bromide - - - - 2.5 g.
Sodium hexametaphosphate - 0.5 g.
Potassium iodide (0.1% solution) - - - - 15 ccs.
Water to one litre (pH 10.3) 95

The film was then spray washed with water for 30 seconds and given an 1100 ft. candle-second red light exposure, and developed in a cyan dye producing developer having the following formula: 100

Carbohydrazide - - - - 3.2 g.
Sodium tetrphosphate - - - 0.7 g.
Sodium bromide - - - - 2.50 g.
Potassium iodide (0.1% solution) - - - - 5.0 ml. 105
Sodium sulphite (anhydrous) - 10.0 g.
Sodium sulphate (anhydrous) - 20.0 g.
Sodium hydroxide - - - - 3.30 g.
6-Nitrobenzimidazole (1% solution in 1% sodium hydroxide) 5.0 ml. 110
p-N-benzylaminophenol (as hydrochloride) - - - - 0.70 g.
Coupler* - - - - 1.50 g.
4-Amino-N,N-diethyl-3-methylaniline hydrochloride - 2.60 g. 115

Water to one litre
* 2 - (α - acetamido - β - phenylethyl) - 1 - hydroxynaphthamide

The film was then washed for 30 seconds 120 given a 300 ft. candle second blue light exposure from the emulsion side, and developed in a developer containing 4 - amino - N, N - diethylaniline hydrochloride and the yellow coupler, *p* - (ω - benzoyl - acetamino)benzene 125 sulphon - N - methylamide. The film was next washed, fogged by treatment with a sodium borohydride solution, and developed in a developer containing the colour-developing agent used in Example 1 and the magenta 130

coupler 1 - phenyl - 3 - (diamylbenzoyl) - amino - 5 - pyrazolone. The film was finally bleached, fixed and dried as described in Example 1.

5 The other exposed piece of film was processed in the same way as the first, but for the substitution of 6.5 grams per litre of isopropylamine, a conventional development accelerator, for the 4-aminocyclohexanol in the first developer.

10 The piece of film processed in accordance with this invention had a higher effective speed, a higher maximum density, and lower fog than the piece processed using isopropylamine in the first developer.

EXAMPLE 3

The procedure described in Example 2 was repeated using 6.0 grams per litre of 1-cyclohexylamino-2-propanol, instead of the same concentration of 4 aminocyclohexanol, in the first developer. Again, the film sample processed using the cyclohexane derivative was given a greater effective speed, lower fog and a higher maximum density than the sample processed using isopropylamine.

WHAT WE CLAIM IS:—

1. A method of processing a silver halide colour photographic material to produce a dye image therein by colour development which comprises treating the material with a photographic developer solution which contains a silver halide developing agent and a silver halide solvent consisting of a cyclohexane derivative containing an amino or substituted amino group directly bonded to the carbocyclic ring and a second group which is an amino, substituted amino, hydroxyl or hydroxyalkyl group.

2. A method according to Claim 1 wherein the cyclohexane derivative is 1,4-bis-(methylamino)-cyclohexane, 4-aminocyclohexanol or 1-cyclohexylamino-2-propanol.

3. A method according to Claim 1 or Claim 2 wherein the cyclohexane derivative is present in the developer solution at a concentration of from 0.5 to 10 grams per litre.

4. A method according to any of the preceding claims which is a reversal process wherein the developer solution containing the cyclohexane derivative is the negative developer.

5. A method according to Claim 4 wherein the developing agent in the negative developer is a 3-pyrazolidone, a dihydroxybenzene or a p-N-methylaminophenol salt.

6. A method according to any of Claims 1 to 3 wherein the photographic developer solution is a colour developer wherein the developing agent is a phenylenediamine.

7. A method according to Claim 6 wherein the colour developer contains a colour coupler.

8. A method according to Claim 1 as described herein with reference to either of the Examples.

9. A colour photographic record produced by processing an exposed photographic material by a method according to any of the preceding claims.

10. A photographic colour developer composition which comprises a p-phenylenediamine colour developing agent, an alkaline substance and a silver halide solvent consisting of a cyclohexane derivative containing an amino or substituted amino group directly bonded to the carbocyclic ring and a second group which is an amino, substituted amino, hydroxyl or hydroxyalkyl group.

11. A colour developer composition according to Claim 10 wherein the cyclohexane derivative is 1, 4 - bis - (methylamino) - cyclohexane, 4-amino-cyclohexanol or 1-cyclohexylamino-2-propanol.

12. A colour developer composition according to Claim 10 as described in Example 1 herein.

13. A photographic black and white developer composition which comprises a silver halide developing agent, an alkaline substance and a silver halide solvent consisting of a cyclohexane derivative the cyclohexane ring of which is substituted with two groups one of which is an amino or substituted amino group and the other of which is an amino, substituted amino, hydroxyl or hydroxyalkyl group.

14. A black and white developer composition according to Claim 13 wherein the cyclohexane derivative is 1, 4 - bis - (methylamino) - cyclohexane or 4 - aminocyclohexanol.

15. A black and white developer composition according to Claim 13 or 14 wherein the silver halide developing agent is a 3-pyrazolidone, a dihydroxybenzene or a p-N-methylaminophenol salt.

16. A black and white developer composition according to Claim 15 as described in Example 2 herein.

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coupler 1 - phenyl - 3 - (diamylbenzoyl) - amino - 5 - pyrazolone. The film was finally bleached, fixed and dried as described in Example 1.

- 5 The other exposed piece of film was processed in the same way as the first, but for the substitution of 6.5 grams per litre of isopropylamine, a conventional development accelerator, for the 4-aminocyclohexanol in the first developer.

- 10 The piece of film processed in accordance with this invention had a higher effective speed, a higher maximum density, and lower fog than the piece processed using isopropylamine in the first developer.

EXAMPLE 3

- 20 The procedure described in Example 2 was repeated using 6.0 grams per litre of 1-cyclohexylamino-2-propanol, instead of the same concentration of 4 aminocyclohexanol, in the first developer. Again, the film sample processed using the cyclohexane derivative was given a greater effective speed, lower fog and a higher maximum density than the sample processed using isopropylamine.

WHAT WE CLAIM IS:—

- 30 1. A method of processing a silver halide colour photographic material to produce a dye image therein by colour development which comprises treating the material with a photographic developer solution which contains a silver halide developing agent and a silver halide solvent consisting of a cyclohexane derivative containing an amino or substituted amino group directly bonded to the carbocyclic ring and a second group which is an amino, substituted amino, hydroxyl or hydroxyalkyl group.

- 40 2. A method according to Claim 1 wherein the cyclohexane derivative is 1,4-bis-(methylamino)-cyclohexane, 4-aminocyclohexanol or 1-cyclohexylamino-2-propanol.

- 45 3. A method according to Claim 1 or Claim 2 wherein the cyclohexane derivative is present in the developer solution at a concentration of from 0.5 to 10 grams per litre.

- 50 4. A method according to any of the preceding claims which is a reversal process wherein the developer solution containing the cyclohexane derivative is the negative developer.

- 55 5. A method according to Claim 4 wherein the developing agent in the negative developer is a 3-pyrazolidone, a dihydroxybenzene or a p-N-methylaminophenol salt.

6. A method according to any of Claims 1 to 3 wherein the photographic developer solution is a colour developer wherein the developing agent is a phenylenediamine.

7. A method according to Claim 6 wherein the colour developer contains a colour coupler.

8. A method according to Claim 1 as described herein with reference to either of the Examples.

9. A colour photographic record produced by processing an exposed photographic material by a method according to any of the preceding claims.

10. A photographic colour developer composition which comprises a p-phenylenediamine colour developing agent, an alkaline substance and a silver halide solvent consisting of a cyclohexane derivative containing an amino or substituted amino group directly bonded to the carbocyclic ring and a second group which is an amino, substituted amino, hydroxyl or hydroxyalkyl group.

11. A colour developer composition according to Claim 10 wherein the cyclohexane derivative is 1, 4 - bis - (methylamino) - cyclohexane, 4-amino-cyclohexanol or 1-cyclohexylamino-2-propanol.

12. A colour developer composition according to Claim 10 as described in Example 1 herein.

13. A photographic black and white developer composition which comprises a silver halide developing agent, an alkaline substance and a silver halide solvent consisting of a cyclohexane derivative the cyclohexane ring of which is substituted with two groups one of which is an amino or substituted amino group and the other of which is an amino, substituted amino, hydroxyl or hydroxyalkyl group.

14. A black and white developer composition according to Claim 13 wherein the cyclohexane derivative is 1, 4 - bis - (methylamino) - cyclohexane or 4 - aminocyclohexanol.

15. A black and white developer composition according to Claim 13 or 14 wherein the silver halide developing agent is a 3-pyrazolidone, a dihydroxybenzene or a p-N-methylaminophenol salt.

16. A black and white developer composition according to Claim 15 as described in Example 2 herein.

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