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COMPLETE SPECIFICATION

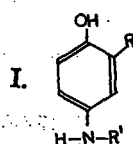
Photographic Colour Development and Colour Developing Solutions therefor

We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America, (Assignees of EDWARD THOMAS PESCH and REMSEN STODDART VAUGHN) of 343, State Street, Rochester 4, New York, United States of America, 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:—

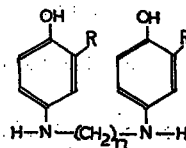
This invention relates to colour photography where at least one photographic colour image is produced by colour development of silver halide such that the oxidation products of the developing agent combine with a colour coupler to produce the image as a dye-image. The invention is specially concerned with the formation of one or more such images by reversal processing of a multi-colour silver halide material.

The colour developers used for such purposes usually consist of aqueous alkaline solutions containing a *p*-phenylenediamine (substituted or not) colour developing agent having at least one primary amino group. The colour forming coupler may also be present in the solution. Sodium sulphite and sodium bromide are often used in these developer solutions. Usually phenolic or naphtholic couplers are used to form the cyan dye image, pyrazolone couplers to form the magenta dye image, and open chain ketomethylene couplers to form the yellow image.

According to the present invention, there is provided a colour developer composition comprising (1) a primary aromatic amino developing agent, (2) a colour-forming coupler, (3) an alkali, and (4) a water-soluble developing agent selected from those having the formula:



and II.



or water-soluble salts thereof wherein R represents a hydrogen atom or an alkyl group; R' represents an alkyl or an aminoalkyl group; and n is an integer of from 1 to 8, such that in compounds having formula I, the total number of carbon atoms in the groups R, and R' taken together is at least 2 and not more than 8, and such that in compounds having formula II, the total number of carbon atoms in the two R groups and in the $-(CH_2)_n-$ group taken together is at least 2 and not more than 8.

Typical examples of the developing agents of Formulae I and II are:—

compound 1. 4 - Methylamino - 2 - methylphenol sulphate.

compound 2. N,N' - Ethylene bis(4-Amino-2 - methylphenol).

compound 3. 4 - (β - Aminoethylamino) phenol sulphate.

These developing agents may be used to advantage as competing developing agents in colour developer solutions for processing colour photographic elements in instances where it is desirable to control colour contrast and colour fog. The competing developing agents of our invention give unexpectedly good results and are valuable for use in colour photographic

[Price 4s. 6d.]

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processing. Our competing developing agents are effective in the control of colour contrast and colour fog especially in that they do not produce colour absorbing impurities which would cause undesirable shifts in hue and/or colour contrast.

Our compounds are useful for preventing the formation of colour fog in adjacent layers, for example, for preventing the formation of cyan fog in the blue-sensitive and in the green-sensitive layers during cyan development or preventing the formation of yellow fog in the magenta layer during yellow development.

Our colour developer compositions, which may be in a wet or a dry form, in their simplest form comprise (1) a primary aromatic amino developing agent, (2) a colour forming coupler, (3) an alkali and (4) a competing secondary aminophenol developing agent of formula I or II.

We have found that it is advantageous to include a compound, such as diethyl hydroxylamine sulphate, or diethyl hydroxylamine hydrochloride in the aqueous solution of the colour developer composition in order to extend the useful life of the developer especially during storage.

Our developer solutions may also contain any of the other addenda commonly used in colour developer solutions, such as an alkali metal sulphite, an alkali metal bromide, an alkali metal carbonate, an alkali metal bisulphite, an alkali metal thiocyanate and/or an alkali metal iodide.

The concentration of the competing developing agents can be varied considerably and will depend upon the particular colour coupler, the particular colour developing agent and the particular competing developing agent to be used. The optimum concentration can be determined by methods well known in the art, that is by making studies of the results given by systematic variations in concentration of these components.

Our competing developing agents are used

to advantage in colour developer solutions containing any of the well known primary aromatic amino silver halide developing agents, such as the p-phenylenediamines including the N-alkyl phenylenediamines and N-alkyl toluenediamines. These developing agents are usually used in the salt form such as the hydrochloride or sulphate which are more stable than the amine. The p-aminophenols and their substitution products may also be used as colour developing agents when the amine group is unsubstituted. The N-alkyl sulphonamidoalkyl - p - phenylenediamine developing agents are also very useful. All of these developing agents have an unsubstituted amino group which enables the oxidation product of the developer to couple with the colour-forming couplers that form a dye image. Included among the colour developers (1) are, such typical illustrative examples as, 2-amino-5-diethylaminotoluene hydrochloride, N-ethyl-N - β - methanesulphonamidoethyl - 3-methyl - 4 - aminoaniline sulphate, 4 - amino-N,N - diethyl - 3 - methylaniline hydrochloride, 4 - amino - N - ethyl - N - (β - methanesulphonamidoethyl) - m - toluidine sesquisulphate monohydrate, 3 - methyl - p - amino - N,N - diethylaniline sulphate, 4 - amino - N - ethyl - N - (β - hydroxyethyl) aniline sulphate and N,N - dimethyl - p - phenylenediamine hydrochloride.

Any of the well known water-soluble colour coupler compounds can be used to advantage in our colour developer solutions.

The following examples will illustrate the invention.

EXAMPLE 1

Two pieces of a photographic element comprising a support coated with a red-sensitive silver halide emulsion layer were exposed to light through a step wedge (having 0.15 log exposure increments between consecutive steps) in a sensitometer. Each of these photographic elements were treated with a black-and-white developer having the composition:

2,4-Diaminophenol hydrochloride	5 grams
Sodium sulphite (dessicated)	50 "
Potassium bromide	5 "
Water	1 litre

to develop a silver negative image, the elements were washed in water, reexposed to red light and cyan developed in the solution described below to develop a silver positive

and cyan dye positive image. One of these elements identified as (A) was cyan developed with a freshly mixed developer of our invention having the formula:

Cyan Developer 1

Sodium sulphite (dessicated)	10.0	grams
Sodium bromide	2.5	"
Sodium sulphate (dessicated)	60.0	"
Sodium hydroxide	3.8	"
Potassium iodide	0.01	"
4-amino-N-ethyl-N-(β -hydroxyethyl)-3-methyl aniline	2.0	"
1-Hydroxy-2-[β -(2-acetamido-phenyl)-ethyl] naphthamide	2.0	"
4-methylamino-2-methylphenol sulphate	0.2	"
Water to	1	litre

The other element (B) was cyan developed with the same developer after it had been aerated by passing a stream of air through it.

- 5 The colour developed elements A and B, were treated with a conventional ferricyanide-bromide bleach followed by a sodium thio-sulphate fixing bath to remove silver halide and leave the cyan dye images. The optical
- 10 densities of the step wedge dye images to red light and to green light were measured with a densitometer and the results showed that aeration of our cyan developer containing 4-methylamino-2-methylphenol sulphate pro-
- 15 duced substantially no hue shift in the dye images formed on colour development. This valuable characteristic of our developers is unexpected.

Yellow developer solutions and magenta

developer solutions containing our competing developing agents show similar photographic stability (that is, do not produce hue shifts or colour contrast shifts in the developed dye image) upon aeration.

EXAMPLE 2

20 A multilayer, multicolour photographic element containing three silver halide layers, one sensitive to red, one sensitive to green, and one sensitive to blue was given identical exposures to light through a step wedge

25 (having 0.15 log exposure increments between consecutive steps) in a sensitometer. The element was given negative development as in Example 1, water washed, and the red-sensitive layer given selective reexposure to red

30 light. It was then cyan-developed by treating it with a cyan developer having the formula:

35

Cyan Developer 2

Sodium bromide	2.5	grams
6-nitrobenzimidazole nitrate	0.030	"
Potassium iodide	0.008	"
Sodium sulphite (desiccated)	10.0	"
Sodium sulphate	60.0	"
Sodium hydroxide	3.8	"
Sodium thiocyanate	1.0	"
Hydroxylamine sulphate	0.5	"
4-amino-N-ethyl-N-(β -hydroxyethyl)-3-methyl aniline sulphate	2.2	"
2-(<i>o</i> -Acetamido- β -phenylethyl)-1-hydroxy naphthamide	2.0	"
Hexyleneglycol	10.0	ml.
Polyethylene glycol (having a molecular weight of about 1540)	1.0	gram
4-Methylamino-2-methyl phenol sulphate	0.2	"
Water to	1	litre

- 40 The element was then subjected to processing comprising the following steps: water washing, selective reexposure of the blue-

sensitive layer with blue light, yellow development in a developer having the formula;

Sodium sulphite (desiccated)	10.0	grams
Sodium bromide	0.55	"
Potassium iodide	0.026	"
N,N-diethyl- <i>p</i> -phenylenediamine monohydrochloride	3.0	"
6-Nitrobenzimidazole nitrate	0.10	"
Sodium hydroxide	2.8	"
Polyethylene glycol (having a molecular weight of about 4000)	1.0	"
Sodium sulphate	64.0	"
Hexylene glycol	20.0	"
α -Benzoyl- <i>o</i> -methoxyacetanilide	1.5	"
Diethylhydroxylamine sulphate	1.38	"
1-phenyl-3-pyrazolidone	0.50	"
Water to	1	litre

Then the element was water washed, exposed to white light and developed in a magenta developer having the composition:

Trisodium phosphate 12H ₂ O	40.0	grams
Sodium sulphite (desiccated)	5.0	"
Sodium thiocyanate	1.0	"
4-Amino-N-ethyl-N(β -methanesulphonyl-amidoethyl)- <i>m</i> -toluidine sesquisulphate monohydrate	2.9	"
Citrazinic acid	0.72	"
Ethylenediamine	3.0	"
Polyethylene glycol (having a molecular weight of about 4000)	1.0	"
Sodium sulphate	50.0	"
Sodium hydroxide	0.32	"
1-(2,4,6-trichlorophenyl)-3-(4-nitro-anilino)-5-pyrazolone	1.67	"
Hexylene glycol	10.0	ml.
Sodium bromide	0.5	gram
Potassium iodide	0.075	"
Water to	1	litre

- 5 water washed, bleached in a ferricyanide-bromide bleach and fixed with a sodium thio-sulphate fixing bath, washed and dried.

- 10 The element so processed showed that the cyan image had particularly satisfactory sharpness.

EXAMPLE 3

Another piece of a multilayer, multicolour

photographic element was exposed as in Example 2. It was given negative development with the black-and-white developer of Example 1, washed, and processed as described in Example 2 including the cyan development but it was given a different yellow development. It was yellow developed in the following yellow developer composition: 20

Sodium sulphite (desiccated)	10.0	grams
Sodium bromide	0.22	"
Polyethylene glycol (having a M.W. of about 4000)	1.0	"
Potassium iodide	0.01	"
N,N-Diethyl-p-phenylenediamine monohydrochloride	2.0	"
6-Nitrobenzimidazole nitrate	0.040	"
Trisodium phosphate . 12H ₂ O	20.0	"
Sodium sulphate	50.0	"
Hexylene glycol	20.0	ml.
α -Benzoyl-o-methoxyacetanilide	2.0	grams
Diethylhydroxylamine sulphate	2.5	"
1-Phenyl-3-pyrazolidone	0.30	"
4-Methylamino-2-methylphenol sulphate	0.35	"
Water to	1	litre

Other pieces of element were given the same treatment except that the 4-methylamino-2-methylphenol sulphate concentration was varied by several 0.01 gram/litre increments above and below 0.35 gram/litre, and images of similar quality were obtained.

Microscopic examination of cross sections of film samples showed that there was no silver retention in the yellow image layer of the film which was processed in our yellow developer.

The compounds mentioned above may be prepared as follows:—

COMPOUND 1

To a solution of 955 grams of toluhydroquinone and 45 grams of sodium sulphite in 3 litres of water which was heated to 180°C. in an autoclave, were added 687 grams of 40% methylamine under nitrogen over a period of 3 hours. The autoclave was then cooled to 90°C. and the contents were acidified with sulphuric acid. This solution was cooled to 15°C. whereupon a solid separated, was collected and dried, yielding 575 grams of product, m.p. 242—244°C.

COMPOUND 2

To a solution of 2 grams of lithium aluminium hydride in 400 ml. of anhydrous diethyl ether was added over a period of 15 hours at room temperature, a solution of 5 grams of N,N'-oxalyl bis(4-amino-2-methylphenol) in 500 ml. of anhydrous diethyl ether. After this time, aqueous alcohol was added slowly to the mixture to decompose the excess hydride. The alumina which separ-

ated was dissolved by the addition of sodium potassium tartrate. The ether solution was separated, washed with brine, dried and concentrated in vacuo. The solid residue was recrystallized from acetonitrile yielding 4.2 grams of Compound 2.

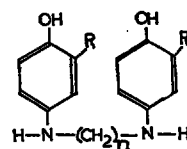
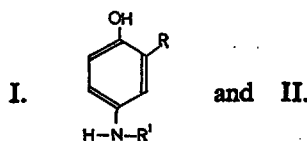
The N,N'-oxalyl bis(4-amino-2-methylphenol) was prepared as follows. To a solution of 12 grams of 4-amino-2-methylphenol and 13 grams of quinoline in 125 ml. of dioxane was added at room temperature with stirring, 6.3 grams of oxalyl chloride. The reaction mixture was stirred for 1 hour at room temperature, after which time the quinoline hydrochloride was filtered off. The filtrate was concentrated in vacuo, and the residue recrystallized from ethyl alcohol yielding 6.8 grams of N,N'-oxalyl bis(4-amino-2-methylphenol).

COMPOUND 3

A mixture of 35 grams of p-bromophenol, 40 grams of 60% ethylenediamine and 2 grams of copper sulphate penta hydrate, in 100 ml. of water was refluxed for 6 hours after which time it was acidified with sulphuric acid. This mixture was concentrated to approximately 1/4 of the original volume and cooled to 15°C. whereupon a solid separated, was collected and dried, yielding 41 grams of product, m.p. 279—280°C.

WHAT WE CLAIM IS:—

1. A colour developer composition comprising (1) a primary aromatic amino developing agent, (2) a colour-forming coupler, (3) an alkali, and (4) a water-soluble developing agent selected from those having the formula:



Sodium sulphite (desiccated)	10.0	grams
Sodium bromide	0.22	"
Polyethylene glycol (having a M.W. of about 4000)	1.0	"
Potassium iodide	0.01	"
N,N-Diethyl-p-phenylenediamine monohydrochloride	2.0	"
6-Nitrobenzimidazole nitrate	0.040	"
Trisodium phosphate . 12H ₂ O	20.0	"
Sodium sulphate	50.0	"
Hexylene glycol	20.0	ml.
α -Benzoyl-o-methoxyacetanilide	2.0	grams
Diethylhydroxylamine sulphate	2.5	"
1-Phenyl-3-pyrazolidone	0.30	"
4-Methylamino-2-methylphenol sulphate	0.35	"
Water to	1	litre

Other pieces of element were given the same treatment except that the 4-methylamino-2-methylphenol sulphate concentration was varied by several 0.01 gram/litre increments above and below 0.35 gram/litre, and images of similar quality were obtained.

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COMPOUND 2

To a solution of 2 grams of lithium aluminium hydride in 400 ml. of anhydrous diethyl ether was added over a period of 15 hours at room temperature, a solution of 5 grams of N,N'-oxalyl bis(4-amino-2-methylphenol) in 500 ml. of anhydrous diethyl ether. After this time, aqueous alcohol was added slowly to the mixture to decompose the excess hydride. The alumina which separ-

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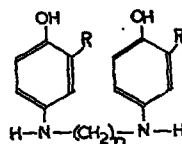
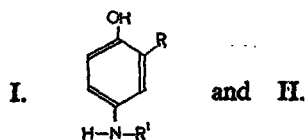
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WHAT WE CLAIM IS:—

1. A colour developer composition comprising (1) a primary aromatic amino developing agent, (2) a colour-forming coupler, (3) an alkali, and (4) a water-soluble developing agent selected from those having the formula:



or water-soluble salts thereof wherein R represents a hydrogen atom or an alkyl group; R' represents an alkyl or an aminoalkyl group; and n is an integer of from 1 to 8, such that in compounds having formula I, the total number of carbon atoms in the groups R, and R' taken together is at least 2 and not more than 8, and such that in compounds having formula II, the total number of carbon atoms in the two R groups and in the $-(CH_2)_n-$ group taken together is at least 2 and not more than 8.

2. A colour developer composition of Claim 1 containing an alkali metal sulphite, an alkali metal bromide, and an alkali metal iodide.

3. A colour developer composition of Claim 1 containing a phenolic coupler, a naphtholic coupler, a pyrazolone coupler, a coumarone coupler, or an open-chain ketomethylene coupler.

4. A colour developer composition of Claim 1 containing as developing agent (1) a 4-aminophenol or a p-phenylenediamine.

5. A colour developer composition in accordance with Claim 1 wherein the water-soluble developing agent (4) is 4-methylamino-2-methylphenol sulphate, N,N'-ethylene bis(4-amino-2-methylphenol), or 4-(β -aminoethylamino)phenol sulphate.

6. Composition of Claim 5 containing, in addition, diethylhydroxylamine sulphate.

7. A colour developer composition comprising (1) 4-amino-N-ethyl-N-(β -hydroxyethyl)-3-methylaniline sulphate, (2) 2-(o-acetamido- β -phenylethyl)-1-hydroxy naphthamide, (3) 4-methylamino-2-methylphenol sulphate, (4) an alkali, and (5) an alkali metal sulphite.

8. A colour developer composition comprising (1) N,N-diethyl-p-phenylenediamine hydrochloride, (2) α -benzoyl-o-methoxyacetanilide, (3) 4-methylamino-2-methylphenol sulphate, (4) an alkali and (5) an alkali metal sulphite.

9. The method of colour developing which comprises treating a silver halide material which has been exposed to a subject with a

colour developer composition according to any of the preceding claims.

10. In the colour reversal development of a multilayer, multicolour photographic material after exposure to light through an original image, said material containing three differently sensitized silver halide emulsion layers, one of said layers being red-sensitive, one of said layers being green-sensitive and one of said layers being blue-sensitive, in which the said exposed element is given a negative black-and-white development, selective reexposure of said red-sensitive layer with red light, treatment of said element with a cyan colour developer, selective reexposure of the said blue-sensitive layer with blue light, treatment of said element with a yellow colour developer, fogging the unexposed silver halide in the green-sensitive layer, treating the said element with a magenta colour developer, treating said developed element in a ferricyanide-bromide bleach and then in a fixing bath, to leave in said element a colour reproduction of said original image, the improvement in the said process comprising the use, in at least one of said colour developers in addition to a primary aromatic amino developing agent, of a water-soluble developing agent (4) as defined in claim 1.

11. The colour reversal development process of Claim 10 characterized in that one employs 4-methylamino-2-methylphenol sulphate as water-soluble developing agent (4) in the cyan developer.

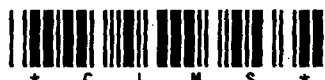
12. The colour reversal development process of Claim 10 characterised in that one employs 4-methylamino-2-methylphenol sulphate as water-soluble developing agent (4) in the yellow developer.

13. Colour developer compositions according to Claim 1 and in wet or dry form, substantially as herein described.

14. Processes of colour development according to Claim 9, substantially as herein described.

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Patent Agent.

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E. Kodak