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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

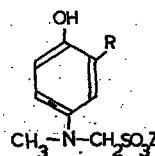
Photographic Colour Development and Colour Developing Solutions therefor

We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America, (Assignees 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 on 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 this invention improved cyan, yellow and magenta colour developers are obtained by using certain tertiary *p*-aminophenols as competing developers in colour developer solutions. The water-soluble competing developing agents of our invention are those represented by the formula:

[Price 4s. 6d.]



wherein R represents the hydrogen atom or an alkyl group having from 1 to 6 carbon atoms, e.g., methyl, ethyl, *n*-propyl, isopropyl, butyl, *n*-amyl, isoamyl or hexyl, and Z represents an alkali metal, e.g., sodium potassium or lithium.

These developing agents may be used to advantage as competing developing agents in colour developer solutions for processing colour photographic materials 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 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



contrast

tertiary aminophenol developing agent of the above formula.

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 - diethylamine 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 example serves to illustrate the invention.

EXAMPLE

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 elements was treated with a black-and-white developer having the composition:

2,4 - Diaminophenol hydrochloride	5 g	75
Sodium sulphite (dessicated)	50 g	
Potassium bromide	5 g	
Water to	1 litre	

to develop a silver negative image, the elements were washed in water, re-exposed 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 g	
Sodium bromide	2.5 g	
Sodium sulphate (dessicated)	60 g	90
Sodium hydroxide	3.8 g	
Potassium iodide	0.01 g	
4 - amino - N - ethyl - N(β - hydroxyethyl) - 3 - methyl aniline	2.0 g	95
1 - hydroxy - 2 - (β - (2 - acetamido) - phenylethyl) naphthamide	2.0 g	
4 - (N - methyl - N - sulphonamethylamino)phenol sodium salt	0.2 g	100
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.

The colour developed elements A and B were treated with a conventional alkali metal ferriocyanide-bromide bleach to convert the silver image to silver halide, followed by a sodium thiosulphate fixing bath to remove silver halide and leave only the cyan dye images.

A comparison of the images in element A and element B showed that aeration of the cyan developer 1 produced no change in the developed cyan dye hue.

Similarly it can be shown that cyan developers containing the other competing developing agents of the formula given above do not produce hue shifts in the developed cyan dye image when the cyan developer solution is aerated.

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.

The competing developing agent used in



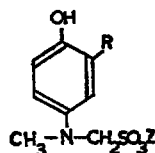
the above Example may be prepared as follows:

To a neutralized solution (i.e., containing NaOH and Na₂O₂) of 86 grams of 4-methylaminophenol sulphate in 500 ml. of water were added 75 grams of sodium formaldehyde sulphite. This mixture was stirred until a complete solution resulted. The resultant solution was cooled to 15°C. whereupon a white solid separated, was collected and dried, yielding 101 grams of product.

WHAT WE CLAIM IS:—

1. A colour developer composition containing

- (1) a primary aromatic amino developing agent
- (2) a colour-forming coupler
- (3) an alkali, and
- (4) a water-soluble competing developing agent having the formula:



wherein R is a hydrogen or an alkyl group containing 1 to 6 carbon atoms, and Z is an alkali metal.

2. Composition of Claim 1 containing an alkali metal sulphite, an alkali metal bromide, and an alkali metal iodide.

3. Composition of Claims 1 or 2 containing a naphtholic coupler.

4. Composition of Claims 1 to 3 containing as developing agent (1) a p - phenylenediamine.

5. Composition of Claims 1 to 4 wherein the competing developing agent (4) is 4 - (N - methyl - N - sulphomethylamino) phenol sodium salt.

6. 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.

7. Process for the colour reversal development of a multilayer, multicolour photographic material characterized in that one employs, in at least one of the colour developers in addition to a primary aromatic amino developing agent, a water-soluble competing developing agent (4) as defined in claim 1.

8. Process of Claim 7 wherein one employs as the competing developing agent (4) 4 - (N - methyl - N - sulphomethylamino) phenol sodium salt in the cyan developer.

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

10. Processes of colour development according to Claim 6, substantially as herein described.

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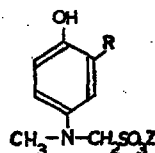
the above Example may be prepared as follows:

To a neutralized solution (i.e., containing NaOH and Na_2O_3) of 86 grams of 4-methylaminophenol sulphate in 500 ml. of water were added 75 grams of sodium formaldehyde sulphite. This mixture was stirred until a complete solution resulted. The resultant solution was cooled to 15°C. whereupon a white solid separated, was collected and dried, yielding 101 grams of product.

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5. Composition of Claims 1 to 4 wherein the competing developing agent (4) is 4-(N-methyl-N-sulphomethylamino) phenol sodium salt. 35

6. 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. 40

7. Process for the colour reversal development of a multilayer, multicolour photographic material characterized in that one employs, in at least one of the colour developers in addition to a primary aromatic amino developing agent, a water-soluble competing developing agent (4) as defined in claim 1. 45

8. Process of Claim 7 wherein one employs as the competing developing agent (4) 4-(N-methyl-N-sulphomethylamino) phenol sodium salt in the cyan developer. 50

9. Colour developer compositions according to Claim 1 and in wet or dry form, substantially as herein described. 55

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