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PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements in and relating to Colour Forming Developers and Processes of Colour Development

We, KODAK LIMITED, a British Company, of Kodak House, Kingsway, London, W.C.2, do hereby declare the nature of this invention, which has been
5 communicated to us by Eastman Kodak Company, a body corporate organised according to the laws of the State of New York, United States of America, of 343, State Street, Rochester, New York,
10 United States of America, to be as follows:—

This invention relates to improvements in colour forming developers of the type in which production of a dye occurs
15 along the development of the silver image in silver salt emulsions, and in processes of colour development for use in connection with colour photography.

In the production of colour photographic plates or films, it is frequently desirable to use colour forming developers, such as those containing para-phenylene diamines in which the coloured
20 image is formed by coupling, during development, the oxidation product of the developer with a colour-forming compound. The colour-forming compound may be mixed with the developer, or may be incorporated in the photographic
25 emulsion, before or after exposure. Such developers and particularly the para-phenylene diamine developers often have a low reduction potential and it is, therefore, necessary to employ a relatively
30 long time of development in order to obtain a satisfactory picture.

According to the present invention a colour developer comprises a developer for silver halides, such as an aromatic amino
40 compound, a colour-forming compound and a small quantity of a substance which has a solvent action upon silver salts, especially halides, such as a thiocyanate. In one form the process of colour develop-
45 ment according to the invention consists

in developing a reducible silver salt image by means of an aromatic amino compound in the presence of a colour-forming compound and of a small quantity of a substance which has a solvent action upon
50 silver salts, especially silver halides, such as a thiocyanate.

The employment of a small quantity of a substance having this solvent action, such as a thiocyanate, increases the reduction
55 potential of developers such as the para-phenylene diamines thereby decreasing the time required for development to produce a given gamma, that is to say increases the colour gamma of the
60 colour pictures produced by a given time of development, other conditions such as temperature being constant.

The present invention may be utilised, for example, in colour processing a film
65 base coated with two or more silver halide emulsion layers, each of which has been sensitized to a different region of the spectrum and has been exposed to form
70 a latent colour-separation image in each layer. When the film is developed in a developer in which an aromatic amine such as para-phenylenediamine hydrochloride, is the developing ingredient and
75 which contains a colour-forming compound, the silver halide present in the emulsion is reduced to metallic silver and where this occurs, the paraphenylenediamine is oxidized. The colour-forming
80 compound present in the developer is one which will combine with the oxidation product of the para-phenylenediamine to form a coloured dye compound. Since the
85 oxidation product is formed only where the silver halide is reduced, a dye is formed only at such points. This developer when used alone for developing images produced by exposure in a camera is not entirely satisfactory due to the
90 length of time required for the develop-

- ment. It has now been found that by adding a small amount of a thiocyanate, such as potassium thiocyanate, to the developer, the reduction potential of the developer is increased to such an extent that development takes place in the time which would ordinarily have been required for development by the use of a metol-hydroquinone type of developer.
- 10 The following formulæ illustrate developers which may be used according to the present invention. Formula 1 produces on development a blue-green image and formula 2 produces a magenta image.
- 15 **FORMULA 1.**
- | | | |
|---------------------------------------|-----|----------|
| (a) Diethyl para-phenylenediamine HCl | - - | 3 g. |
| Sodium sulphite | - - | 10 g. |
| Sodium carbonate | - - | 20 g. |
| 20 Potassium thiocyanate | - - | 1 g. |
| Water to make | - - | 1500 cc. |
| (b) Added to (a) | - - | 2 g. |
| 2,3,4-trichloroalphanaphthol acetone | - - | 100 cc. |
- 25 **FORMULA 2.**
- | | | |
|---------------------------------------|-----|----------|
| (a) Diethyl para-phenylenediamine HCl | - - | 1 g. |
| Sodium sulphite | - - | 10 g. |
| Sodium carbonate | - - | 30 g. |
| 30 Ammonium thiocyanate | - - | 1 g. |
| Water to make | - - | 1000 cc. |
| (b) (Added to a) | - - | |
| Brom-thioindoxyl | - - | 1 g. |
| Methanol | - - | 100 cc. |
- 35 Various thiocyanates, such as potassium, sodium and ammonium may be used.
- The present invention is applicable to the formation of coloured images by any method in which a colour is formed by coupling of the oxidation product of an aromatic amine developer with a colour former. The sensitized emulsion may be in one or more layers and may be on one or both sides of a film. The process may also be used with plates as well as
- films and with various types of colour separation processes, for example, in which the colour separation negatives are exposed separately and later superposed to form a complete coloured picture. The colour-forming compound may be present in the developer solution or it may be incorporated in the emulsion layer prior to exposure.
- The amount of thiocyanate used in the developer solution is not critical, but may be varied within relatively wide limits. Amounts varying from one-quarter to 2½ grams per litre of developer solution have been found successful.
- In referring to the aromatic amino developers, it is intended to include the mono-, di-, and tri-amino aromatic compounds, of which the para-phenylenediamines are the compounds generally used. The salt form, such as the hydrochloride or the sulphate, is most desirable, due to its stability in the dry state. These compounds may be substituted in the amino group or in the ring, forming the alkyl phenylenediamines, and the toluenylenediamines.
- A particular advantage of the present invention is the fact that it enables the direct development of colour films to form a coloured image. It is frequently necessary with such films to develop the film in an ordinary metol-hydroquinone developer to a black and white image and later convert this image by colour development to a coloured image. By the aid of the present invention in which thiocyanates are added to the developer, the coloured image may be obtained by direct development.
- The invention is not limited to the specific examples disclosed, but may be used in numerous other forms and modifications.
- Dated this 20th day of March, 1935.
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COMPLETE SPECIFICATION

Improvements in and relating to Colour Forming Developers and Processes of Colour Development

We, KODAK LIMITED, a British Company, of Kodak House, Kingsway, London, W.C.2, do hereby declare the nature of this invention, which has been communicated to us by Eastman Kodak Company, a body corporate organised according to the laws of the State of New York, United States of America, of 343, State Street, Rochester, New York, United States of America, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in colour forming developers of the type in which production of a dye occurs along the development of the silver image

in silver salt emulsions, and in processes of colour development for use in connection with colour photography.

In the production of colour photographic plates or films, it is frequently desirable to use colour forming developers, in which the developing agent is an aromatic amino compound such as para-phenylene diamine and in which the coloured image is formed by coupling, during development, the oxidation product of the developing agent with a colour-forming compound. The colour-forming compound (usually termed a colour coupler) may be mixed with the aromatic amino developing agent or may be incorporated in the photographic emulsion, before or after exposure. Such aromatic amino developing agents and particularly the para-phenylene diamines often have a low reduction potential and it is, therefore, necessary to employ a relatively long time of development in order to obtain a satisfactory picture that is to say, with particular regard to the density.

According to the present invention a colour developer comprises an aromatic amino developing agent for silver salts and a colour coupler, whose reduction potential is increased by the presence of a small amount of a soluble thiocyanate. The method of colour development according to the invention consists in subjecting a reducible silver salt image to the action of an aromatic amino developing agent (especially para-phenylene diamine or a substitution product thereof) in the presence of a colour coupler and of a small amount of a soluble thiocyanate serving to increase the reduction potential of the developer.

It is known that silver solvents such as hypo will increase the reduction potential of ordinary black and white developers. In Edin's *Ausführliches handbuch der Photographie* Volume III, Part 2, (1930) at pages 92 and 93 there is discussed the influence of the nature of the developer on the grain size of the reduced silver. It is pointed out that A. and L. Lumière and A. Seyewetz came to the following, among other, conclusions. Two developing substances, not ordinarily employed, namely, para-phenylene diamine and orthoamido-phenol, which in this case are used with sulphite alone, give reduced silver of a colour comparable with that obtained from collodion emulsions and whose grain is finer than that produced by other developer solutions; and they give the following formula for the paraphenylene diamine developer:—Water 1000, para-phenylene diamine 10, anhydrous sul-

phite 60. It is also stated that in a later publication these workers said that practically all developers give a fine-grain image when there is added a solvent for silver bromide and recommend ammonium chloride employed in an amount of 15 to 20 grams per 100 c.c. of developer. Finally, it is mentioned that Lüppe-Cramer, who in a detailed investigation "on dichroic fogging, physical development and pseudosolarisation" employed these developer variations, recommends potassium thiocyanate as a silver bromide solvent, e.g. 5 c.c. of a one-in-five solution to 100 c.c. of hydroquinone-soda developer. We have now found that although silver solvents in general, and hypo in particular, do not increase the reduction potential of aromatic amino developing agents when the latter are used in conjunction with colour couplers, soluble thiocyanates do so. Hypo and cyanides on the contrary retard the colour development.

The increase in the reduction potential of colour developers, containing the para-phenylene diamines as developing agents, brought about by the presence of the small amount of soluble thiocyanate decreases the time required for development to produce a given density, that is to say, increases the colour density of the colour pictures produced by a given time of the development, other conditions such as temperature being constant.

Colour density is determined with the aid of a densitometer using an arbitrary complementary filter on the dye image remaining after the metallic silver has been removed. Thus to compare the colour gamma resulting from development with different colour developers two silver images of equal gamma, say, 1, are taken, converted to the same silver halide, colour developed and treated for removal of silver.

The present invention may be utilised, for example, in colour processing a film base coated with two or more silver halide emulsion layers, each of which has been sensitized to a different region of the spectrum, the film having been exposed to form a latent colour-separation image in each layer. When the film is developed in a developer in which an aromatic amine, such as para-phenylene diamine hydrochloride, is the developing agent and which contains a colour coupler, the silver halide present in the emulsion is reduced to metallic silver and where this occurs, the para-phenylene diamine or other aromatic amino compound is oxidized. The colour coupler present in the developer couples with the oxidation product of the aromatic amino compound

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to form a coloured dye compound. Since the oxidation product is formed only where the silver halide is reduced, a dye is formed only at such points. This colour

- 5 developer when used alone for developing images produced by exposure in a camera is not entirely satisfactory due to the length of time required for the development. It has now been found that by
- 10 adding a small amount of a soluble thiocyanate, such as potassium thiocyanate, to the developer, the reduction potential of the developer is increased to such an extent that the rate of colour development
- 15 becomes comparable with the rate of mere development by the well-known metol-hydroquinone type of developer.

The following formulæ illustrate colour developers which may be used according to the present invention. Formula 1 produces on development a blue-green image and formula 2 produces a magenta image.

FORMULA 1.

25	(a) Diethyl para-phenylene diamine HCl	- -	3 g.
	Sodium sulphite	- -	10 g.
	Sodium carbonate	- -	20 g.
	Potassium thiocyanate	- -	1 g.
	Water to make	- -	1500 cc.
30	(b) 2,3,4-thichloroalphanaphthol	- - -	2 g.
	Acetone	- - -	100 cc.
	For use, (b) is added to (a)		

FORMULA 2.

35	(a) Diethyl para-phenylenediamine HCl	- -	1 g.
	Sodium sulphite	- -	10 g.
	Sodium carbonate	- -	30 g.
	Ammonium thiocyanate	- -	1 g.
40	Water to make	- - -	1000 cc.
	(b) Brom-thioindoxyl	- -	1 g.
	Methanol	- - -	100 cc.
	For use, (b) is added to (a)		

Other soluble thiocyanates, such as sodium thiocyanate may be used.

- The present invention is applicable to the formation of coloured images from images in developable silver salts by any method in which a colour is formed by coupling of the oxidation product of an aromatic amine developer with a colour coupler. The sensitized emulsion may be in one layer or a plurality of layers on one side or both sides of a support. The process may also be used with plates as well as films and with various types of colour separation processes, for example, those in which the colour separation negatives are exposed separately and later superposed to form a complete coloured picture. The colour coupler may be present in the developer solution or it may

be incorporated in the emulsion layer prior to exposure.

The amount of soluble thiocyanate used in the developer solution is not critical, but may be varied within relatively wide limits. Amounts varying from one-quarter to 2½ grams per litre of developer solution have been found successful.

In referring to the aromatic amino developing agents, it is intended to include the mono-, di-, and tri-amino aromatic compounds. Among the mono-amino compounds may be mentioned the aminophenols, aminocresols and their halogen substituted derivatives, as well as the aminonaphthols. The developing agents usually used are the diamino compounds such as para-phenylene diamine and its substitution products. These compounds may be substituted in the amino groups or in the ring or in both, forming compounds such as the alkyl-phenylene diamines, toluylene diamines, alkyl-toluylene-diamines and aminodiphenylamines. These compounds are usually kept in the salt form, such as hydrochloride or sulphate, since these are more stable than the amines themselves.

A particular advantage of the present invention is the fact that it enables the direct development of colour films to form a coloured image. It is frequently necessary with such films to develop the film in an ordinary metol-hydroquinone developer to a black and white image and, after bleaching to convert the bleached image by colour development to a coloured image. By the aid of the present invention in which soluble thiocyanates are added to the developer, the coloured image may be obtained by direct colour development.

The invention is not limited to the specific examples disclosed, but may be used in numerous other forms and modifications.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to us by our foreign correspondents, we declare that what we claim is:—

1. A colour developer comprising an aromatic amine developing agent for silver salts and a colour coupler whose reduction potential is increased by the presence of a small amount of a soluble thiocyanate.

2. A colour-forming developer as claimed in claim 1 in which the developing agent is para-phenylene diamine or a substitution product thereof.

3. A method of colour development in which a developable silver salt is subjected to the action of an aromatic amino

- developing agent and a colour coupler in presence of a small amount of a soluble thiocyanate, serving to increase the reduction potential of the developer.
- 5 4. A method of colour development in which a developable silver salt is subjected to the action of para-phenylene diamine or a substitution product thereof, as developing agent, and a colour coupler
- 10 in presence of a small amount of a soluble thiocyanate serving to increase the reduction potential of the developer.
5. In a process of colour development employing a colour developer comprising an aromatic amino developing agent for silver salts and a colour coupler, increasing the reduction potential of the colour developer by adding thereto a small amount of soluble thiocyanate.
- 15 6. Colour developers and methods of colour development substantially as herein described.
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Dated this 21st day of March, 1936.

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