AMENDED SPECIFICATION

Reprinted as amended under Section 8 of the Patents and Designs Acts, 1907 to 1939.

PATENT SPECIFICATION

Application Date: May 24, 1937. No. 18741/38. **496,196**

(Divided out of No. 496,245).

Complete Specification Left: June 24, 1938.

Complete Specification Accepted: Nov. 24, 1938.

PROVISIONAL SPECIFICATION

Improvements in Colour Development and Colour Forming Developers

We, KODAK LIMITED, a Company registered under the Laws of Great Britain, of Kodak House, Kingsway, London, W.C.2, do hereby declare the nature of this invention, which has been communicated to me by Eastman Kodak Company, a Company organised under the Laws of the State of New Jersey, United States of America, of 343, State Street, Rochester, New York, United States of America, to be as follows:—

This invention relates to improvements in colour forming developers and in processes of colour development for use in connection with colour photography.

It is known that coloured photographic images may be formed by using a developer which forms a coloured compound on development. The coloured compound thus formed is deposited adjacent to the silver grains of the silver image during the development. It is also known that a coloured image may be formed by adding to certain developer solutions or by incorporating in the gelatino-silver halide emulsion before or after exposure a compound which couples, during development, with the oxidation product of the developing agent and forms a colouring substance which is likewise deposited adjacent to the silver grains of the silver image during development. Such a compound, which is employed in conjunction with a developing agent for the silver and which couples with the oxidation product thereof during development, is referred to herein as a colour coupler.

The present invention concerns new or improved colour forming developers comprising an aromatic amino compound serving as the developing agent and a colour coupler as hereinafter defined and also includes a new or improved colour development process which consists in developing a reducible silver salt image in a photographic element with the aid of an aromatic amino compound in presence of a colour coupler as hereinafter defined as well as the colour photographic elements resulting therefrom. It also includes photographic sensitive elements having such a colour coupler incorporated in one or more emulsion layers.

The silver can be removed from the image after colour development leaving a clear transparent dye image.

The invention also includes a photographic element having at least one layer containing a clear transparent image composed essentially of the product resulting from the coupling *in situ*, during development of a developable silver salt, of a colour coupler as hereinafter defined with the oxidation product of an aromatic amino developer agent and subsequent removal of metallic silver.

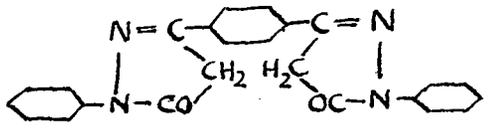
When the silver halide emulsion containing a latent photographic image is developed, the silver halide is reduced to metallic silver and the developing agent is oxidised. The aromatic diamino compounds which have been used as developing agents form, on oxidation, products which will couple with colour couplers during development to form dyes. If such colour couplers are added to the developer solution, or incorporated in the emulsion layer, the dye which is thus formed by coupling during development is deposited in the gelatine or other silver halide carrier adjacent to the metallic silver grain. It is desirable that the dyes thus formed should not readily wander from the place of formation. It is accordingly, desirable that they should be insoluble in water. They are probably not physically attached to the silver grain. The silver may be subsequently bleached out of the carrier layer leaving a pure dye image.

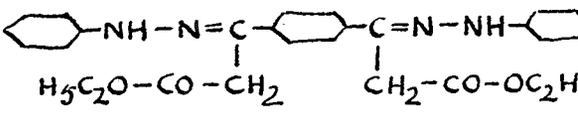
Numerous substances have hitherto been

[*Price* 1/-] Price 4s 6d

employed or proposed as colour couplers among which may be mentioned phenols, naphthols, cresols, nitrophenyl-acetonitriles and acetoacetic esters. It has not, however, always been possible among those hitherto available to select one which exhibits all the desired combination of properties required for any specific case. In colour-developing a gelatino-silver halide emulsion layer it is necessary to select a colour coupler which will give just the desired shade in conjunction with the colours which are produced in other layers. It is moreover, important to employ a colour coupler which gives a coloured compound which is resistant to the normal processing baths employed, although it may often be desirable to have one which gives a colour which can be destroyed and/or removed if desired during some step in the processing. Many of the colour couplers employed according to the present invention are suitable in carrying out the processing described in our prior patents Nos. 427,472, 427,516, 427,518, 427,520, 440,032, 440,089, and 447,092.

According to the present invention the substance employed as a colour coupler is one of the following compounds:—

1. 
1:4-Phenylenedi-3-(1-phenyl-5-pyrazolone).

2. 
1:4-Di-(carbethoxy-acetyl)-benzene-diphenylhydrazone.

These compounds, when present during the development of a silver salt with an aromatic amino developing agent, couple with the oxidation product of such developing agent forming a dye simultaneously with the formation of the silver image.

The aromatic amino compounds which may be used as developing agents in the present invention include the mono-, di-, and tri-amino aryl compounds. Among the monoamino compounds may be mentioned the aminophenols and aminocresols and their halogen substituted derivatives as well as the amino-naphthols. The developing agents usually used are the diamino compounds such as para-phenylene diamine and its substitution products. These developers may be substituted in the amino group or in the ring or in both, forming compounds such as the alkyl phenylene diamines, toluylene-diamines, alkyl-toluylene diamines and amino diphenylamines. These compounds are usually kept in the salt form such as hydrochloride or sulphate since these are more stable than the amines themselves. As examples of developing agents of this class, there may be mentioned diethyl para-phenylene diamine, mono-methyl para-phenylene diamine, dimethyl para-phenylene diamine and ortho-amino-diethylaniline.

As would be expected from the behaviour of known colour couplers the shade of the colour obtained by coupling generally varies in accordance with the developing agent selected.

EXAMPLE.

A developing formula which may be used in the following:

A.

Diethyl para phenylene diamine	1 gram
Sodium sulphite	0.5 gram
Sodium carbonate	20 grams
Water	1 litre

B.

Colour coupler	The molecular equivalent of the developing agent.
Water miscible solvent such as acetone	50 cc.

For use, B is added to A.

The developing agent and the proportions of the ingredients used in the above formula may, of course be varied. Solvents other than acetone, such as alcohols may also be used.

The colours formed by the compounds of the present invention on coupling with the oxidization product of the developer are shades of magenta. The shade may of course, be altered by the presence of other substituent groups in the molecule.

Although we have described our invention with particular reference to the use of the colour coupler in the developing

solution itself, our invention is in no way limited to this method. As an alternative method, the colour coupler may be incorporated in the photographic layer before development, and either before or after exposure. It may be absorbed upon the sensitive silver halide grains.

The present invention may be utilized in the formation of colour photographic images on plates or papers as well as on films in which the silver halide is emulsified in gelatine or other carrier. The plates, films or papers may have differently sensitized emulsions of the mixed grain type or superimposed on one side or on both sides of the support. The dyes formed may be decolourized by an oxidizing agent such as chromic acid and colourless soluble compounds thereby formed. The bleaching of the dye in this manner need not destroy the silver image but may convert it into a developable silver salt image which can in turn be coloured, bleached and recoloured a number of times.

Dated this 23rd day of June, 1938.
W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

COMPLETE SPECIFICATION

Improvements in Colour Development and Colour Forming Developers

We, KODAK LIMITED, a Company registered under the Laws of Great Britain, 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 Company organised under the Laws of the State of New Jersey, 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 and in processes of colour development for use in connection with colour photography.

It is known that coloured photographic images may be formed by using a developer which forms a coloured compound on development. The coloured compound thus formed is deposited adjacent to the silver grains of the silver image during the development. It is also known that a coloured image may be formed by adding to certain developer solutions or by incorporating in the gelatino-silver halide emulsion before or after exposure a compound which couples, during development, with the oxidation product of the developing agent and forms a colouring substance which is likewise deposited adjacent to the silver grains of the silver image during development. Such a compound, which is employed in conjunction with a developing agent for the silver and which couples with the oxidation product thereof during development, is referred to herein as a colour coupler.

The present invention concerns new or improved colour forming developers comprising an aromatic amino compound serving as the developing agent and a colour coupler as hereinafter defined and also includes a new or improved colour development process which consists in developing a reducible silver salt image in a photographic element with the aid of an aromatic amino compound in presence of a colour coupler as hereinafter defined as well as the colour photographic elements resulting therefrom. It also includes photographic sensitive elements having such a colour coupler incorporated in one or more emulsion layers.

The silver can be removed from the image after colour development leaving a clear transparent dye image.

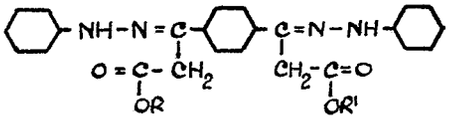
The invention also includes a photographic element having at least one layer containing a clear transparent image composed essentially of the product resulting from the coupling *in situ*, during development of a developable silver salt, of a colour coupler as hereinafter defined with the oxidation product of an aromatic amino developer agent and subsequent removal of metallic silver.

When the silver halide emulsion containing a latent photographic image is developed, the silver halide is reduced to metallic silver and the developing agent is oxidised. The aromatic diamino compounds which have been used as developing agents form, on oxidation, products which will couple with colour couplers during development to form dyes. If such colour couplers are added to the developer solution, or incorporated in the emulsion layer, the dye which is thus formed by coupling during development is deposited in the gelatine or other silver halide carrier adjacent to the metallic silver grain. It is desirable that the dyes

thus formed should not readily wander from the place of formation. It is accordingly, desirable that they should be insoluble in water. They are probably not physically attached to the silver grain. The silver may be subsequently bleached out of the carrier layer leaving a pure dye image.

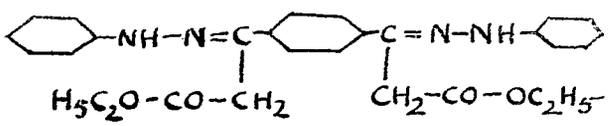
Numerous substances have hitherto been employed or proposed as colour couplers among which may be mentioned phenols, naphthols, cresols, nitrophenyl-acetonitriles and acetoacetic esters. It has not, however, always been possible among those hitherto available to select one which exhibits all the desired combination of properties required for any specific case. In colour-developing a gelatino-silver halide emulsion layer it is necessary to select a colour coupler which will give just the desired shade in conjunction with the colours which are produced in other layers. It is moreover, important to employ a colour coupler which gives a coloured compound which is resistant to the normal processing baths employed, although it may often be desirable to have one which gives a colour which can be destroyed and/or removed if desired during some step in the processing. Many of the colour couplers employed according to the present invention are suitable in carrying out the processing described in our prior patents Nos. 427,472, 427,516, 427,518, 427,520, 440,032, 440,089, and 447,092.

According to the present invention, the substances employed as couplers are compounds containing the grouping:—



Where R and R^1 are alkyl groups.

An example of such a compound is:



1:4 - Di - (carbethoxyacetyl) - benzenediphenylhydrazone.

These compounds, when present during the development of a silver salt with an aromatic amino developing agent, couple with the oxidation product of such developing agent forming a dye simultaneously with the formation of the silver image.

The aromatic amino compounds which may be used as developing agents in the present invention include the mono-, di-, and tri-amino aryl compounds. Among the monoamino compounds may be mentioned the aminophenols and aminocresols and their halogen substituted derivatives as well as the amino-phenols. The developing agents usually used are the diamino compounds such as para-phenylene diamine and its substitution products. These developers may be substituted in the amino group or in the ring or in both, forming compounds such as the alkyl phenylene diamines, toluylene-diamines, alkyl-toluylene diamines and amino diphenylamines. These compounds are usually kept in the salt form such as hydrochloride or sulphate since these are more stable than the amines themselves. As examples of developing agents of this class, there may be mentioned diethyl para-phenylene diamine, mono-methyl para-phenylene diamine, dimethyl para-phenylene diamine and ortho-amino-diethylaniline.

As would be expected from the behaviour of known colour couplers the shade of the colour obtained by coupling generally varies in accordance with the developing agent selected.

EXAMPLE.

A developing formula which may be used in the following:

A.

Diethyl para phenylene diamine	1 gram
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B.

Colour coupler	The molecular equivalent of the developing agent.
Water miscible solvent such as acetone	50 cc.

For use, B is added to A.

The developing agent and the proportions of the ingredients used in the above formula may, of course be varied. Solvents other than acetone, such as alcohols may also be used.

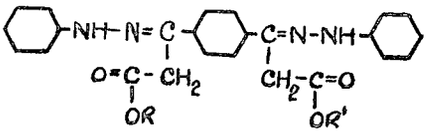
The colours formed by the compounds of the present invention on coupling with the oxidization product of the developer are shades of magenta. The shade may of course, be altered by the presence of other substituent groups in the molecule.

Although we have described our invention with particular reference to the use of the colour coupler in the developing solution itself, our invention is in no way limited to this method. As an alternative method, the colour coupler may be incorporated in the photographic layer before development, and either before or after exposure. It may be absorbed upon the sensitive silver halide grains.

The present invention may be utilized in the formation of colour photographic images on plates or papers as well as on films in which the silver halide is emulsified in gelatine or other carrier. The plates, films or papers may have differently sensitized emulsions of the mixed grain type or superimposed on one side or on both sides of the support. The dyes formed may be decolourized by an oxidizing agent such as chromic acid and colourless soluble compounds thereby formed. The bleaching of the dye in this manner need not destroy the silver image but may convert it into a developable silver salt image which can in turn be coloured, bleached and recoloured a number of times.

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

1. A colour forming developer comprising an aromatic amino developing agent and a colour coupler consisting of a compound containing the grouping:—



Where R and R^1 are aralkyl groups.

2. A colour forming developer as claimed in Claim 1, in which the developing agent is an aromatic diamino compound.

3. A colour forming developer as claimed in Claim 2, in which the aromatic diamino compound is an alkyl substituted phenylene diamine.

4. A process of colour development which includes developing a reducible silver salt image with an aromatic amino developing agent in presence of a colour coupler as defined in Claim 1.

5. A process of colour development which includes developing a reducible silver salt image with a colour forming developer as claimed in any of Claims 1 to 3.

6. A photographic element having a layer containing a clear transparent dye image composed essentially of the product resulting from the coupling *in situ*, during development of a developable silver salt, of a colour coupler as defined in Claim 1, with the oxidation product of an aromatic amino developing agent and subsequent removal of metallic silver.

7. A sensitive photographic element having a colour coupler as defined in Claim 1 incorporated in one or more emulsion layers.

8. The colour forming developers and methods of colour developing the colour couplers hereinbefore particularly described, in conjunction with aromatic amino developing agents.

9. In the production of colour photographic records especially multi-layer records, the employment in conjunction with aromatic amino developing agents of colour couplers of the nature herein defined.

Dated this 23rd day of June, 1938.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool,
Chartered Patent Agents.

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