

PATENT SPECIFICATION

Application Date: April 23, 1936. No. 14354/37.

478,991

(Divided out of No. 478,942.)

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One Complete Specification Left: May 24, 1937.

(Under Section 16 of the Patents and Designs Acts, 1907 to 1932).

Specification Accepted: Jan. 24, 1938.



PROVISIONAL SPECIFICATION

No. 14354 A.D. 1937.

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

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, 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 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.

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 colour coupler as hereinafter defined with the oxidation product of an aromatic amino developing agent.

When a silver halide emulsion containing a latent photographic image is developed, the silver halide is reduced to metallic silver and the developing agent is oxidized. 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 not physically attached to the silver grain and therefore 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 Application No. 16012/35.

According to the present invention the substances employed as colour couplers are the phenols and naphthol derivatives hereinafter specified.

Hydroquinone monomethyl ether
 Hydroquinone monobenzyl ether
 Guaiacol
 Eugenol
 1:3-Pyrogallol dimethyl ether
 Saligenin
 4-Nitro-2-hydroxybenzyl alcohol
 o-Benzylphenol
 Quercetin
 5:6:7:8-Tetrahydro- α -naphthol
 2-Aceto-1-naphthol
 1:5-Dihydroxynaphthalene
 Hexylresorcinol
 1-Hydroxy-5-methoxy naphthalene
 Iso-eugenol.

The colours given by the colour couplers named above when used in conjunction with *p*-aminodiethylaniline, for example, as developing agent are blue to blue-green except the following:—

Eugenol (brown) and Quercetin (golden-brown)
 Iso-eugenol (yellow)
 Hexylresorcinol (blue-magenta).

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 aminonaphthols. The developing agents usually used are the diamino compounds such as paraphenylene diamine and its substitution products. These developing agents 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. 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.

The present invention may be utilised in the formation of coloured photographic images on plates or papers as well as on films and the dyes will be formed when gelatine or other carrier for the silver halide is used. 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 21st day of May, 1937.

W. P. THOMPSON & CO.,
 12, Church Street, Liverpool, 1,
 Chartered Patent Agents.

PROVISIONAL SPECIFICATION

No. 14355 A.D. 1937.

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

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, to be as follows:—

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

In particular it relates to colour
10 couplers of the character described in our co-pending application No. 14354/37. In that application we have described the use of a number of named derivatives of phenols and naphthols as colour couplers. We have now found that in general such
15 derivatives of phenol or naphthol are particularly suitable for colour couplers as have in the ortho or para position to the hydroxyl group one of the following groups:— OCH_3 , OCH_2CO —, $\text{CH}:\text{CH}$ —

CO, or a carbon atom forming part of a
20 chain or part of a heterocyclic ring or part of a substituted benzene ring.

Couplers other than those named in the
aforesaid co-pending application which
may be used for the purposes therein
25 described are

Hydroquinone phenacyl ether

Salicylacetone

Disalicylacetone.

These compounds give blue to blue-
30 green colours when developed with *p*-aminodiethylaniline, for example, as developing agent.

Dated this 21st day of May, 1937.

W. P. THOMPSON & CO.,

12, Church Street, Liverpool, 1,
Chartered Patent Agents.

COMPLETE SPECIFICATION

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

We, KODAK LIMITED, a Company
35 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
40 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
45 the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements
50 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
55 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
60 formed by adding to certain developer solutions or by incorporating in the gelatino-silver halide emulsion before or after a compound which couples, during development, with the oxidation product
65 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
70 conjunction with a developing agent for the silver and which couples with the oxidation product thereof during develop-

ment, is referred to herein as a colour coupler.

The present invention concerns new or
75 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
80 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
85 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.
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The silver can be removed from the image after colour development leaving a clear transparent dye image.

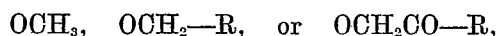
The invention also includes a photo-
95 graphic element having at least one layer containing a clear transparent image composed essentially of the product resulting from the coupling *in situ*, during development of a developable silver salt, of a colour coupler as herein-
100 after defined with the oxidation product of an aromatic amino developer agent.

When the silver halide emulsion containing a latent photographic image is developed, the silver halide is reduced to
105 metallic silver and the developing agent is oxidized. The aromatic diamino compounds which have been used as developing agents form, on oxidation, products which will couple with colour couplers
110 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.

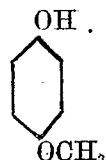
According to the present invention the substances employed as colour couplers are derivatives of phenol or naphthol having ortho or para to the hydroxyl group one of the following groups:—



where R is a hydrocarbon radical (but excluding hydrocoerulignone whose employment in this connection is claimed in Specification No. 458,665).

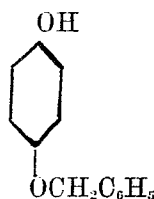
Typical examples of suitable couplers are:—

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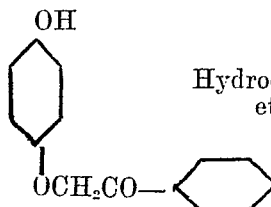
Hydroquinone monomethyl ether

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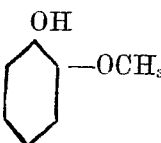
Hydroquinone monobenzyl ether

3



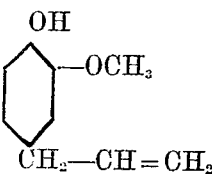
Hydroquinone phenacyl ether

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Guaiacol

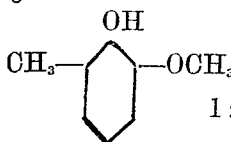
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Eugenol

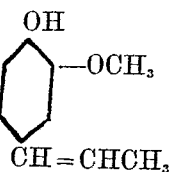
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1:3-Pyrogallol dimethyl ether

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Iso-eugenol.

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.

Hydroquinone monophenacyl ether was prepared by heating a solution of equimolecular proportions of hydroquinone and phenacyl chloride in methyl alcohol to 40—50° C. while passing coal gas therethrough, then adding a slight excess of methyl alcoholic sodium hydroxide at

such a rate that vigorous boiling took place, then refluxing the mixture, cooling it pouring it into dilute aqueous caustic soda saturated with coal gas and finally filtering the resulting solution through active carbon and pouring it upon hydrochloric acid and ice. The precipitate was broken up, washed with water and dried.

10 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 developing agents may be substituted in the amino group or in the ring or in both, forming compounds such as the alkyl phenylene diamines, 25 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. 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 35 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 is the following:—

A

45	diethyl para phenylenediamine	1 gram
	Sodium sulphite - - -	0.5 gram
	Sodium carbonate - - -	20 grams
	Water - - - - -	1 litre

B

50 Colour coupler The molecular equivalent of the developing agent

55 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.

60 Solvents other than acetone, such as alcohols, may also be used.

The colours formed by the compounds named above on coupling with the oxidation product of the developer are blue to 65 blue-green except in the case of compound

No. 5 which gives a brown, and compound No. 7 which gives a brownish yellow colour not of much value. The colours of dyes formed from couplers having further substituents in the ring may vary according to the type of substituent group employed.

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 coloured photographic images on plates or papers as well as on films employing gelatine or other carrier for the silver halide. 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 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 forming developer comprising an aromatic amino developing agent and a colour coupler comprising a derivative of phenol or naphthol having ortho or para to the hydroxyl group one of the following groups:— OCH_3 , OCH_2R or OCH_2COR , where R is a hydrocarbon radical (but excluding hydrocoerulig-none).

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

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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 development employing 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 (but excluding hydrocoerulig-none).

Dated this 21st day of May, 1937.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.