PATENT SPECIFICATION

Application Date: March 21, 1935. No. 8919/35. 458,665

Complete Specification Left: March 23, 1936.

Complete Specification Accepted: Dec. 21, 1936.

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 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, 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 the silver image during the development. It is also known that a coloured image may be formed by adding to the developer solution a compound which combines with the oxidation product of the developer and forms a colouring substance.

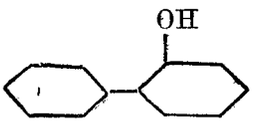
The present invention concerns new or improved colour forming developers comprising an aromatic amino compound and a coupler compound as hereinafter defined and also includes a new or improved colour development process which consists in developing a reducible silver salt image in a photographic element with the aid of an aromatic amino compound in presence of a coupler compound as hereinafter defined.

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 developers form on oxidation products which will react with coupling compounds to form dyes. If such coupling compounds are added to the developer solution, or incorporated in the emulsion layer, a dye is formed by the coupling of this compound with the oxidation product of the aromatic diamino compound and is deposited in the gelatin or other silver halide carrier adjacent to the metallic silver grain. The dyes thus formed do not readily wander from the place of formation. They may be soluble or insoluble in water, but the water-insoluble dyes are preferably used. They are not physically attached to the silver grain so that the silver may be subsequently bleached out of the carrier layer leaving a pure dye image.

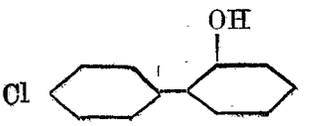
Numerous substances have hitherto been employed or proposed as coupler compounds colour-forming compounds) among which may be mentioned phenols, naphthols, cresols, nitrophenylacetonitriles and acetoacetic esters.

According to the present invention the substances employed as colour couplers are hydroxy diphenyl compounds.

Compounds of this class are meta or ortho-hydroxy diphenyl and their substituted derivatives. Substituent groups include halide, nitro, amino, substituted amino, alkyl, aryl and carboxyl. These groups may be substituted on either ring at any position except in most cases the position para with respect to the hydroxyl group. These compounds form, in general, blue or blue-green dyes by combining with the oxidation product of the aromatic amino developer during development of the image. Specific compounds of this group which may be used are meta- or ortho-hydroxy diphenyl, 2-chloro-ortho-phenyl phenol, 4-chloro-ortho-phenyl phenol, 2-methyl-ortho-phenyl phenol and 4-amino-diethyl-ortho-phenyl phenol. The formula for meta-hydroxy diphenyl may be represented as follows:—

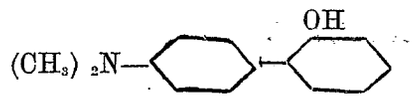


The formula for 4-chloro-ortho-phenyl phenol is,



[Price 1/-]

The formula for 4-amino-diethyl-ortho-phenyl phenol is,



The aromatic amino compounds which may be used as developers in the present invention include the mono-, di-, and tri-amino aryl compounds. The developers usually used are the diamino compounds such as para-phenylenediamine and its substitution products. These developers may be substituted in the amino groups as well as in the ring, forming compounds such as the alkyl-phenylenediamines and alkyl toluylenediamines. These compounds are usually used in the salt form such as hydrochloride or sulphate since these are more stable than the amines themselves. As examples of developers of this class, there may be mentioned diethyl para-phenylenediamine hydrochloride, mono-methyl para-phenylenediamine hydrochloride, diethyl para-phenylenediamine sulphate and diethylaniline hydrochloride.

The following developer solutions may be used to give a coloured image according to the invention:—

FORMULA I.

A.	Dimethyl p. phenylene diamine HCl	2	g.
	Sodium sulphite	5	g.
	Sodium carbonate	30	g.
	Water to	1000	cc.
B.	2-chloro-ortho-phenyl phenol	2	g.
	Acetone	100	cc.

Add B to A

FORMULA II.

A.	Diethyl p. phenylene-diamine HCl	3	g.
	Sodium sulphite	5	g.
	Sodium carbonate	50	g.
	Water to	1000	cc.
B.	m-hydroxy diphenyl	2.5	g.
	Methyl alcohol	100	cc.

Add B to A

Other solvents, particularly alcohols, may be used in bath B.

The present invention may be utilised in the formation of coloured photographic images in plates or papers as well as in films and the dyes will be formed when gelatin or other carrier for the silver halide is used. The emulsion treated may be on one side or both sides of a film support and may be in one layer or a plurality of differently sensitized layers. 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 does not destroy the silver image and a silver image thus treated may be coloured, bleached and recoloured a number of times.

Dated this 19th day of March, 1935.
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 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 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, dur-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 com-

prising 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 developable silver salt, of a colour coupler as hereinafter defined with the oxidation product of an aromatic amino developing agent.

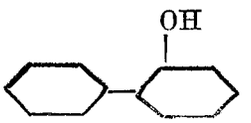
When a silver halide emulsion containing a latent photographic image is developed, the silver halide is reduced to metallic silver and the developing agent is oxidized. The aromatic diamino compounds which have been used as developing agents form, on oxidation, products which will couple with colour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

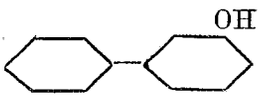
According to the present invention the substances employed as colour couplers are hydroxy diphenyl compounds.

Compounds of this class are meta or ortho-hydroxy diphenyl and their substituted derivatives. Substituent groups include halide, nitro, amino, substituted amino, alkyl, aryl, and carboxyl groups. These groups may be substituted in either ring at any position except in most cases the position para with respect to the hydroxyl group. These compounds form, in general, blue or blue-green dyes by combining with the oxidation product of the aromatic amino-developing agent during development of the image. Specific compounds of this group which may be used are, by way of example,

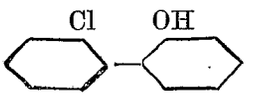
1. *o*-hydroxydiphenyl



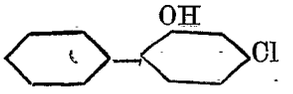
2. *m*-hydroxydiphenyl



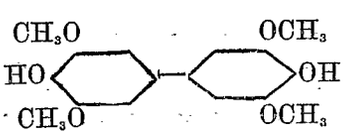
3. 2-chloro-*o*-phenylphenol



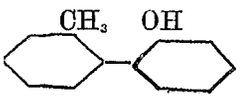
4. 4-chloro-*o*-phenylphenol is,



5. Hydrocoerulignone



6. 2-methyl-*o*-phenylphenol



7. 4-(diethylamino)-*o*-phenylphenol

Hydrocoerulignone is exceptional in that when used in conjunction with *p*-amino-diethylaniline, for example, it gives a red-brown colour.

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, 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 groups or in the ring or in both, forming compounds such as the alkyl - phenylenediamines, toluylenediamines, alkyl-toluylenediamines 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-phenylenediamine, mono-methyl para-phenylenediamine, dimethyl para - phenylenediamine 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.

The following developer solutions may be used to give a coloured image according to the invention:—

FORMULA I.

A.	Dimethyl-*p*-phenylenediamine hydrochloride - - -	2	g.
	Sodium sulphite - -	5	g.
	Sodium carbonate -	30	g.
	Water to - - -	1000	cc.
B.	2-chloro-ortho-phenyl-phenol - - - -	2	g.
	Acetone - - - -	100	cc.

For use, add solution B to solution A.

FORMULA II.

A.	Diethyl-*p*-phenylenediamine hydrochloride - - -	3	g.
	Sodium sulphite - -	5	g.
	Sodium carbonate -	50	g.
	Water to - - -	1000	cc.
B.	*m*-hydroxy-diphenyl -	2.5	g.
	Methyl alcohol - -	100	cc.

For use, add solution B to solution A.

Other solvents for the hydroxy diphenyl, particularly alcohols, may be used in bath B.

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 emulsions treated may be in one layer or a plurality of differently sensitized layers 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.

The hydroxy diphenyls possess advantages over other colour couplers heretofore known and used. They are reasonably cheap and give dyes which are fairly insoluble and satisfactorily stable to heat and light. They comprise a class of compounds giving minus red shades suitable for three colour photography.

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 consisting of a hydroxy diphenyl.

2. A colour forming developer comprising an aromatic diamino developing agent and a colour coupler consisting of a hydroxy diphenyl.

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

4. A colour forming developer as claimed in any of the preceding claims in which the hydroxy diphenyl is 2-chlor-ortho-phenyl-phenol.

5. A process of colour development which includes developing a reducible silver salt image with the aid of a colour forming developer as claimed in any of the preceding claims.

6. 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 hydroxy diphenyl with the oxidation product of an aromatic amino developing agent.

7. A sensitive photograph element having a silver halide emulsion layer, in which is incorporated a colour coupler as defined in Claim 1 or Claim 4.

8. The colour forming developers and methods of colour development employing hydroxy diphenyls as colour couplers in conjunction with aromatic amino developing agents substantially as herein described.

Dated this 21st day of March, 1936.

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

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1937.

ERRATUM

SPECIFICATION No. 458,665.

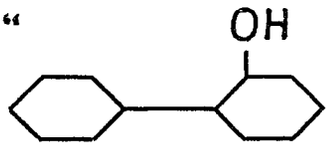
Page 1, line 66, *before* " colour-" *insert* " ("

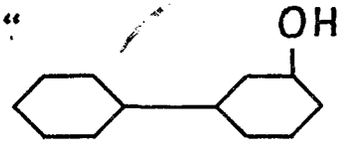
THE PATENT OFFICE,
January 11th, 1938.

CORRECTION OF CLERICAL ERROR

SPECIFICATION No. 458,665

The following correction is in accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the twenty-fifth day of November, 1938:—

Page 1, line 94, *for* "  "

read "  "

PATENT OFFICE,
16*th December*, 1938.

I4450